MATERIAIS 2017

ABSTRACTS

9-12 APRIL 2017

EXPLORING MATERIALS...
BRINGING SCIENCE SOLUTIONS
TO THE WORLD

UNIVERSITY OF AVEIRO . PORTUGAL

MATERIAIS 2017

XVIII Congresso da Sociedade Portuguesa dos Materiais
VIII International Symposium on Materials
An International Conference
… Exploring the Latest Progress in Materials Development
… Bringing Science Solutions to the World

9-12 April, 2017
University of Aveiro,
Aveiro, Portugal

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MATERIAIS 2017, XVIII Congresso da Sociedade Portuguesa de Materiais and VIII International Symposium on Materials, will take place in **Aveiro, Portugal, from 9 – 12 April 2017**. **MATERIAIS 2017**, aiming to explore the latest Progress in Materials Development and to bring Science Solutions to the World, provides the ideal forum for scientists, developers, engineers and companies to share their latest breakthroughs, achievements and views in the field of Materials.

MATERIAIS 2017 will be hosted by the University of Aveiro in the beautiful city of Aveiro, and in one of the oldest nations in the world, Portugal. It will cover all areas of Materials from **Functional Materials, Structural Materials and Processing Technologies to Characterization and Modelling**.

MATERIAIS 2017 continues the famous MATERIAIS conferences organized every two years by the Portuguese Materials Society (SPM), and is the eighteenth National and the eighth International Materials Conference, since the inaugural one, held in Lisbon in 1983. **MATERIAIS** returns to Aveiro, after two former editions (1995 and 2005), and follows the last meeting in Porto (MATERIAIS 2015).

During the 3 days, **MATERIAIS 2017** will encompass schools, scientific talks, debate sessions on cutting edge technologies, and a show case event of applications based on scientific development. We will award for the second time the **SPM Career and Recognition Award** (Prémio SPM de Carreira e Reconhecimento) that aims to recognize, encourage and promote the excellency of research and development activities in the area of Materials in Portugal. We will also commemorate the 40th Anniversary of the Department of Materials and Ceramics Engineering (DEMaC) of the University of Aveiro.

Finally we are very pleased to welcome **Materiais 2017 guest society, SOCIEMAT** (Sociedade Espanola de Materiales), **The Spanish Materials Society**. We anticipate that **MATERIAIS 2017** will be a very well attended international meeting, with excellent technical and scientific interaction.

We look forward to seeing you in Aveiro in April 2017.

Paula M. Vilarinho (MATERIAIS 2017 Chair)

Sponsorship

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30
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SPM

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Organization of Materiais 2017

CONFERENCE CHAIR

Paula M. Vilarinho (Department of Materials and Ceramic Engineering, University of Aveiro)

Organizing Committee

Ana Luisa Daniel (Chemistry Department, University of Aveiro)
Ana Maria Rocha Senos (Department of Materials and Ceramic Engineering, University of Aveiro)
João Tedim (Department of Materials and Ceramic Engineering, University of Aveiro)
Maria Elizabete Costa (Department of Materials and Ceramic Engineering, University of Aveiro)
Maria Paula Seabra (Department of Materials and Ceramic Engineering, University of Aveiro,)
Oleksandr Tkach (Department of Materials and Ceramic Engineering, University of Aveiro)
Paula Celeste da Silva Ferreira (Department of Materials and Ceramic Engineering, University of Aveiro)
Rob Pullar (Department of Materials and Ceramic Engineering, University of Aveiro)
Rui Ramos Ferreira e Silva (Department of Materials and Ceramic Engineering, University of Aveiro)
Victor Fernando Santos Neto (Department of Mechanical Engineering, University of Aveiro)

Scientific Committee

Albano Cavaleiro (Department of Mechanical Engineering, University of Coimbra)
Ascensão Lopes (Faculty of Engineering of UP – FEUP, University of Oporto)
Helena Florindo (iMed, University of Lisbon)
João Celestino Rocha (Chemistry Department, University of Aveiro)
Jorge Frade (Department of Materials and Ceramic Engineering, University of Aveiro)
Leonard Francis (The International Iberian Nanotechnology Laboratory – INL)
Luis Gil (Direção Geral de Energia e Geologia, DGEG)
Manuel Vieira (Faculty of Engineering of UP – FEUP, University of Oporto)
Maria Helena Fernandes (Department of Materials and Ceramic Engineering, University of Aveiro)
Paloma Fernandes (Universidad Complutense de Madrid and SOCIEMAT)
Paulo Ferreira (Materials Science and Engineering Program, University of Texas at Austin, USA)
Pedro Granja (Faculty of Engineering of UP – FEUP, University of Oporto)
Sandra Carvalho (Centre of Physics, University of Minho)

The scientific and technical program of the meeting includes the following topics:

Symposium A - Functional Materials

A1 - Bio-inspired materials and materials for healthcare applications

A2 - Magnetic, electric, multiferroic, and plasmonic functional materials

A3 - Materials for energy (talks are separated into Energy Satellite Event), environment and sustainable materials

A4 - Carbon based materials

Symposium B - Structural Materials

B1 - Advances in ceramics, concrete, building materials

B2 - Advances in metals and alloys

B3 - Advances in polymers

B4 - Advances in composites and hybrid materials

Symposium C - Processing Technologies

C1 - Processing using laser/plasma/electric field technologies

C2 - Additive manufacturing

C3 - Coatings and interfaces

C4 – Recycling

Symposium D - Characterization and Modelling

D1 - Physical, chemical and structural characterization

D2 - Mechanical characterization (including at nanoscale)

D3 - Advanced characterization using microscopy techniques

D4 - Materials modelling (advanced atomistic algorithms, computer simulations)

Time	Sunday, April 9		Monday, April 10					Tuesday, April 11			Wednesday, April 12		
08:30	SABio Registration	SAEM Registration	Conference Registration										
08:45		SAEM Opening		Materiais 2017 Opening									
09:00	Bus from UA	Lecture 2.1						Keynote 1	Keynote 2	Keynote 3	Invited Talk 5	Invited Talk 6	Invited Talk 7
09:15				Plenary 1									
09:30	SABio Opening										A2 Talk 8	C3 Talk 1	A4 Talk 1
09:45	Lecture 1.1							A2 Talk 1	A1 Talk 24	A3 Talk 1	A2 Talk 9	C3 Talk 2	A4 Talk 2
10:00								A2 Talk 2	A1 Talk 25	A3 Talk 2	A2 Talk 10	C3 Talk 3	A4 Talk 3
10:15				Coffee Break				Coffee Break			Coffee Break		
10:30	Lecture 1.2	Discussions and Coffee Break											
10:45				Energy Invited 1	A1 Talk 1	Invited Talk 1	Invited Talk 2	Invited Talk 4	C2 Talk 1	A3 Talk 3	A2 Talk 11	C3 Talk 4	A4 Talk 4
11:00		Lecture 2.2			A1 Talk 2				C2 Talk 2	A3 Talk 4	A2 Talk 12	C3 Talk 5	A4 Talk 5
11:15	Lecture 1.3			En. Talk 1	A1 Talk 3	D3 Talk 1	B4 Talk 1	A2 Talk 3	C2 Talk 3	A3 Talk 5	A2 Talk 13	C3 Talk 6	D4 Talk 8
11:30				En. Talk 2	A1 Talk 4	D3 Talk 2	B4 Talk 2	A2 Talk 4	C2 Talk 4	C4 Talk 1	A2 Talk 14	C3 Talk 7	B1 Talk 1
11:45				En. Talk 3	A1 Talk 5	D3 Talk 3	B4 Talk 3	A2 Talk 5	C2 Talk 5	C4 Talk 2	A2 Talk 15	C3 Talk 8	B1 Talk 2
12:00	Lecture 1.4			En. Talk 4	A1 Talk 6	D1 Talk 1	B4 Talk 4	A2 Talk 6	C2 Talk 6	C4 Talk 3	A2 Talk 16	C3 Talk 9	B1 Talk 3
12:15				En. Talk 5	A1 Talk 7	D1 Talk 2	B4 Talk 5	A2 Talk 7	C2 Talk 7	C4 Talk 4	A2 Talk 17	C3 Talk 10	B1 Talk 4
12:30		Lunch		En. Talk 6	A1 Talk 8	Lunch	B4 Talk 6	Lunch			D4 Talk 7	C3 Talk 11	B1 Talk 5
12:45				En. Talk 7							Lunch		
13:00													
13:15													
13:30													
13:45													
14:00	Lecture 1.5	Lecture 2.3						Plenary 2			Rector of UA Talk		
14:15					A1 Talk 9	Invited Talk 3	B4 Talk 7				Plenary 3		
14:30				En. Talk 8	A1 Talk 10		B4 Talk 8						
14:45	Lecture 1.6			En. Talk 9	A1 Talk 11	C1 Talk 1	B4 Talk 9						
15:00				En. Talk 10	A1 Talk 12	C1 Talk 2	B4 Talk 10	Debate on Additive Manufacturing			40 Years Anniversary of DEMaC Special Session - Invited Talks		
15:15				En. Talk 11	A1 Talk 13	C1 Talk 3	B2 Talk 1						
15:30	Discussion and Concluding Remarks	Lecture 2.4		En. Talk 12	A1 Talk 14	C1 Talk 4	B2 Talk 2						
15:45				En. Talk 13	A1 Talk 15	C1 Talk 5	B2 Talk 3				Coffee Break		
16:00				En. Talk 14	A1 Talk 16	C1 Talk 6	B2 Talk 4				40 Years Anniversary of DEMaC Round Table		
16:15				En. Talk 15	A1 Talk 17	C1 Talk 7	B2 Talk 5						
16:30				Coffee Break	A1 Talk 18	C1 Talk 8	B2 Talk 6	Coffee Break					
16:45													
17:00	Guided tour to Museu da Vista Alegre	Q & A session and Discussions		Energy Invited 2				Show Case of Technology + Poster Discussion Session					
17:15					A1 Talk 19	D4 Talk 1	D2 Talk 1						
17:30				En. Talk 16	A1 Talk 20	D4 Talk 2	D2 Talk 2						
17:45				Debates	A1 Talk 21	D4 Talk 3	D2 Talk 3				Awards on achievements		
18:00	Bus to UA				A1 Talk 22	D4 Talk 4	D2 Talk 4						
18:15					A1 Talk 23	D4 Talk 5	D2 Talk 5				SPM and Materiais 2017 Awards		
18:30	Materiais 2017 Registration + Welcome Cocktail					D4 Talk 6	D2 Talk 6						
18:45											Materiais 2017 Closing		
19:00													
19:15													
19:30				Music Show				Gala Dinner			40 Years Anniversary of DEMaC Special Dinner		
19:45													
20:00													
20:15													
20:30													

1. Plenary speakers

- Ian Reaney (Plenary 1)
- Paolo Bartolo (Plenary 2)
- Angus Kingon (Plenary 3)

2. Key note speakers

- Chris Bowen (Keynote 1)
- Jonathan Knowles (Keynote 2)
- Lenny Koh (Keynote 3)

3. Invited Spekers

- Patricia Carvalho (Invited 1)
- João Gomes (Invited 2)
- Daniel Marinha (Invited 3)
- Angus Kingon (Invited 4)
- James Raju (Invited 5)
- David Maestre (Invited 6)
- Raul Arenal (Invited 7)

- Brain Korgel (En. Invited 1)
- Ibrahim Gulyurtlu (En. Invited 2

Topics:

Symposium A - Functional Materials	En.	Materials for energy
	A1	Bio-inspired materials and materials for healthcare applications
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	A4	Carbon based materials
Symposium B - Structural Materials	B1	Advances in ceramics, concrete, building materials
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	B3	Advances in polymers
	B4	Advances in composites and hybrid materials
Symposium C - Processing Technologies	C1	Processing using laser/plasma/electric field technologies
	C2	Additive manufacturing
	C3	Coatings and interfaces
	C4	Recycling
Symposium D - Characterization and Modelling	D1	Physical, chemical and structural characterization
	D2	Mechanical characterization (including at nanoscale)
	D3	Advanced characterization using microscopy techniques
	D4	Materials modelling (advanced atomistic algorithms, computer simulations)

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MATERIAIS 2017 Detailed Scientific Program

Sunday, April 9, 2017

SCHOOL 1

School on Advanced Biomaterials (SABio)

Satellite event of MATERIAIS 2017 under the auspices of UT Austin | Portugal International Collaboratory for Emerging Technology, CoLab

Hotel Montebelo, Ílhavo

08:30-09:00	SABio Registration at Department of Communication and Art (DECA), University of Aveiro (UA)
09:00	Bus Departure from DECA, UA, to Hotel Montebelo, Ílhavo
09:30-09:45	Welcome and Opening Remarks (Hotel Montebelo, Ílhavo) Paula M Vilarinho (*UA / UT Austin | Portugal International Collaboratory for Emerging Technology*) Maria Helena Fernandes (UA, School Organizer)
09:45-10:30	**Phosphate Based Glasses for Biomedical Engineering** Jonathan Knowles *Eastman Dental Institute, Faculty of Medical Sciences, University College London, UK*
10:30-11:15	**Identifying molecular signatures of tumor dormancy as a basis for the rational design of precision nanomedicines** Ronit Satchi-Fainaro *Department of Physiology and Pharmacology Sackler School of Medicine, Tel Aviv University, Israel*
11:15-12:00	**Polysaccharides in the development of advanced biomaterials for tissue engineering** João F. Mano *CICECO, Department of Chemistry, University of Aveiro, Portugal*
12:00-12:45	**Developing next generation methodology for an ethical, accelerated clinical translation of innovative materials** François Berger FMUC, *Institut National de la Santé et de la Recherche Médicale, Grenoble, France*

Lunch

14:00-14:45	**Designing instructive biomaterials for bone regeneration** Pamela Habibović *MERLN Institute for Technology-Inspired Regenerative Medicine, Maastricht University, Netherlands*

14:45-15:30	**3D Printing of Advanced Biostructures** Paulo Bártolo *School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, UK*
15:30-16:30	General Discussion and Concluding Remarks
17:00-18:00	Guided tour to Museu da Vista Alegre
18:00	Get together and bus departure to University of Aveiro

SCHOOL 2

School on Advanced Electron Microscopy (SAEM)

Satellite event of MATERIAIS 2017 under the auspices of UT Austin | Portugal International Collaboratory for Emerging Technology, CoLab

University of Aveiro, Department of Communication and Art (DECA), Aveiro

08:30-08:45	SAEM Registration at Department of Communication and Art (DECA), University of Aveiro (UA)
08:45-09:00	Welcome and Introduction to the Course Paula M Vilarinho (*UA / UT Austin | Portugal International Collaboratory for Emerging Technology*) Leonard Francis (INL, School Organizer)
09:00-10:30	**Transmission electron microscopy and electron diffraction** Patricia Carvalho *SINTEF MK, Forskningsveien 1, N-0373 Oslo, Norway*

Discussions and Coffee Break

11:00-12:30	**Fundamentals and Trends of Scanning Transmission Electron Microscopy** Pedro Costa *Physical Science and Engineering Division, King Abdullah University of Science and Technology, Saudi Arabia*

Lunch

14:00-15:30	**EELS in a TEM: principle and applications** Raul Arenal *Laboratorio Microscopias Avanzadas, INA, University of Zaragoza, Spain*
15:30-17:00	**Seeing is Believing: The Beauty of *In Situ* Transmission Electron Microscopy** Paulo Ferreira *Materials Science and Engineering Program, University of Texas at Austin, USA*
17:00-18:00	Questions & Answers Session and Discussions

MATERIAIS 2017

University of Aveiro, Department of Communication and Art (DECA), Aveiro

18:30-20:00	MATERIAIS 2017 Registration and Welcome Cocktail

Monday, April 10, 2017

University of Aveiro, Department of Communication and Art (DECA), Aveiro

08:45-19:30	MATERIAIS 2017 Registration

08:45-09:15	MATERIAIS 2017 Opening (DECA Amphitheatre)

Chair: João Rocha

09:15-10:15	Substitution and Sustainability in Functional Materials and Devices – Plenary Talk (DECA Amphitheatre)	Ian M. Reaney

Coffee Break

Energy Satellite Event

(DECA Amphitheatre)

Solar energy: photonics & thermics

Chairs: Angus Kingon & Brian Korgel

10:45-11:15	The Future of the Photovoltaics Industry - Invited talk	Brian Korgel
11:15-11:30	Flexible solar cells on paper based substrates	Hugo Águas
11:30-11:45	Electroluminescent Metal-Organic Frameworks based in host: guest or hetero ligand approaches	Carlos Baleizão
11:45-12:00	Oxidation kinetics of sintered SiC for solar receivers	Fernando Oliveira
12:00-12:15	Effective anisotropic etching of silicon wafers in temperature gradients – variation of surface topography and reflectivity with a specially designed apparatus	Petr Smolka
12:15-12:30	High-temperature thermoelectric energy harvesting: materials and approaches	Andrei Kovalevsky
12:30-12:45	Development of rigid polyurethane foam incorporating phase change material microencapsulated with calcium carbonate shell for thermal energy storage	Claudia Amaral
12:45-13:00	PCM emulsions for cold storage	Jorge Frade

Lunch

Energy conversion & storage

Chair: Filipe Figueiredo & João Abrantes

14:30-14:45	Manganese oxide nanostructured supercapacitor electrodes: size matters	Ricardo Silva
14:45-15:00	Environmental friendly screen-printed electrodes for printed lithium-ion batteries	Carlos M. Costa
15:00-15:15	Energy Storage Density of Bismuth Sodium Titanium Based Lead Free Relaxor-Ferroelectrics.	Amit Mahajan
15:15-15:30	Electrochemistry of Hydrogen Evolution in RTILs Mixtures	Luis Amaral
15:30-15:45	Electrical Properties of Pyrochlore Pr_2O_3-ZrO_2 System: A Defect Chemistry	João Abrantes

	Approach	
15:45-16:00	Enhanced densification and improved chemical stability of ZnO-added $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte material for proton conducting solid oxide fuel cells	Muhammad Naeem Khan
16:00-16:15	Nanostructured Bacterial Cellulose based composite anion exchange membranes for energy conversion	Nuno Sousa
16:15-16:30	Ph-m-SPEEKK ionomer and polysiloxane hybrid membranes for direct methanol fuel cells	Alejandro Gutiérrez-Sánchez

Coffee break

Biomass Chair: Luis Gil		
17:00-17:30	Biomass - Invited talk	Ibrahim Gulyurtlu
Opportunities & gaps in renewable energies Chairs: Angus Kingon, Manuel Colares-Pereira, Luis Gil, Jorge Frade		
17:30-17:45	Materials and renewable energy	Luis Gil
17:45-18:15	Debate	

Session 1
(DECA Room 40.1.8)

A1	**Bio-inspired materials and materials for healthcare applications** Chairs: Jonathan Knowles & Paulo Bártolo	
10:45-11:00	Molecularly Imprinted Biodegradable Magnetic Responsive Particles Based on Poly(2-pyrrolidone)	Zlatan Denchev
11:00-11:15	Chitosan/Chitin films with imprinted liquid crystalline architecture	João P. Borges
11:15-11:30	Formation of poly(lactide) stereocomplexes in blends with a cholinium ionic liquid	Paula Barbosa
11:30-11:45	Digital Microfluidics Devices for Nucleic Acid Amplification	Beatriz Coelho
11:45-12:00	A dual-crosslinking strategy to design biofunctional pectin hydrogels for extrusion bioprinting	Ruben Pereira
12:00-12:15	In vitro and in vivo assessment of Pectin Hydrogels for Skin Regeneration and Repair	Aureliana Sousa
12:15-12:30	Effect of poling state of piezoelectric poly(vinylidene fluoride) films on C2C12 myoblast differentiation for skeletal muscle tissue engineering	Sylvie Ribeiro
12:30-12:45	Extracellular electrical recordings using poly (L-lactic) acid coated electrodes	Ana Mestre

Lunch

A1	**Bio-inspired materials and materials for healthcare applications (cont.)** Chairs: Sandra Carvalho & Maria Ascensão Lopes

14:15-14:30	$Ti_{1-x}Ag_x$ and Ag-TiN_x coatings deposited on PVDF substrates for sensors applications	Sandra Mariana Marques
14:30-14:45	Thin Film Nickel Resistance as Temperature Sensor for Application in Neuronal Electrodes	José Marinho Palha
14:45-15:00	Antibiofilm properties of ZnO-based coatings in resorbable metallic biomaterials	Marta Alves
15:00-15:15	Deposition of ZnO nanoparticles by magnetron sputtering onto tantalum nanostructures	Joana Oliveira
15:15-15:30	Efficient upconversion in $Yb:Er:NaT(XO_4)_2$ thermal nanoprobes intended for biomedical applications	Carlos Zaldo
15:30-15:45	Anisotropic calcium carbonate particles in vaterite phase: synthesis and applications	Bogdan Parakhonskiy
15:45-16:00	The effect of porosity on osteogenic differentiation of hMSC in biphasic calcium phosphate scaffolds fabricated by robocasting	Catarina F. Marques
16:00-16:15	Design and FE simulation of a novel implant-supported dental bridge using hybrid materials – Ti6Al4V and PEEK	Duarte Domingues
16:15-16:30	Tribological characterization of Ti6Al4V+HAp and Ti6Al4V+β-TCP biocomposites to assess the primary stability of implants	Telma Dantas
16:30-16:45	New approach on creation multifunctional microcapsules for drug delivery systems	Ekaterina Lengert

Coffee Break

A1	**Bio-inspired materials and materials for healthcare applications (cont.)** Chairs: Ana Luisa Daniel & Paula Ferreira	
17:15-17:30	Development of antimicrobial leather modified with Ag-TiO_2 nanoparticles for footwear industry	Sandra Carvalho
17:30-17:45	NanoShoe: Use of nanoparticles to develop materials with antimicrobial properties for footwear application	Maria José Ferreira
17:45-18:00	Emulsion electrospun fiber mats of PCL/PVA/Chitosan with antibacterial properties as potential wound dressing material	Cláudia Mouro
18:00-18:15	The potential of positive alginate as an antimicrobial agent for wound dressings	Frederico Nogueira
18:15-18:30	Functional material based on $CaCO_3$ mineralized fibrous polymeric matrix for tissue engineering applications	Mariia S. Saveleva

Session 2
(DECA Room 40.2.15)

D3	**Advanced characterization using microscopy techniques** Chairs: Pedro Costa & Joaquim Vieira	
10:45-11:15	Atomic-scale changes induced by hydrogen and boron in crystalline materials – Invited Talk	Patricia Almeida Carvalho
11:15-11:30	Exploring stresses in $K_{0.5}Na_{0.5}NbO_3$ thin films by in-situ TEM sintering	Manuela Fernandes

11:30-11:45	Locally inducing and mapping of structural transformations in Ni-Mn-Ga thin films by scanning thermal microscopy	Maria Pereira
11:45-12:00	Testing Systems for Miniaturized Samples	Matthias Prinz

D1	**Physical, chemical and structural characterization** Chairs: Joaquim Vieira & Pedro Costa	
12:00-12:15	Raman and infrared reflectivity studies of $LaTaTiO_6$ polymorphs	Roberto Luiz Moreira
12:15-12:30	Thermal ageing of an epoxy observed with positron lifetime and mechanical tests	Marco Duarte Naia

Lunch

C1	**Processing using laser/plasma/electric field technologies** Chairs: Ana Senos & Daniel Marinha	
14:15-14:45	Flash Sintering Ceramics – Invited Talk	Daniel Marinha
14:45-15:00	Presentation of two different approaches to elaborate transparent ceramics for LASER and ballistic protection applications	Judith Boehmler
15:00-15:15	Alternative sintering of lead free potassium sodium niobate (KNN): Spark plasma texturing	Rui Pinho
15:15-15:30	Structural and dielectric properties of laser annealed multiferroic nanostructures	João Rodolfo Alves
15:30-15:45	Upconversion luminescence of Ho3+ doped zirconia nanoparticles produced by pulsed laser ablation in water	Rosa Soares
15:45-16:00	Influence of liquid medium and laser fluence on production of silver nanoparticles by pulsed laser ablation	Caroline G. Moura
16:00-16:15	Macro and microstructure properties of microwave fired porcelain	Tiago Santos
16:15-16:30	Copper thin films obtained by cathodic cage: Analysis of plasma confinement by increasing the thickness of the cage lid and the deposition parameters	Fernanda de Melo Fernandes
16:30-16:45	Performance analysis of High speed steel (HSS) drills subjected to different surface treatments to plasma	Thercio Costa

Coffee Break

D4	**Materials modelling (Advanced atomistic algorithms, computer simulations)** Chairs: Vladimir Bystrov & Sérgio Tavares	
17:15-17:30	Numerical Modelling of Welded T-Joint Configurations using Sysweld	Sérgio Tavares
17:30-17:45	Finite element modeling of the mechanical milling and physical characterization of copper powders	Tomás Seixas
17:45-18:00	First principle computational study of Hydroxyapatite structures, properties and related materials	Vladimir Bystrov
18:00-18:15	Comparative analysis of the diffusion-controlled thermal annealing of radiation defects in simple oxides and piezoelectric PLZT ceramics	Anatoli Popov
18:15-18:30	a-SiC:H photodetector in VLC system with RGB LEDs	Paula Louro

18:30-18:45	Modelling and simulation of thin-film coatings for optical applications	Norberto Jorge Gonçalves

Session 3
(DECA Room 40.2.5)

B4	**Advances in composites and hybrid materials** Chairs: Rob Pullar & João Gomes	
10:45-11:15	Developing smart and functional materials for textile applications: Success Cases from Portugal – Invited Talk	João Gomes
11:15-11:30	Expanded corkboard core sandwich structure: low velocity impact and flexural properties	António Torres Marques
11:30-11:45	New Multi-scale Cementitious Composites Developed Using Carbon Nanotubes and Microcrystalline Cellulose	Shama Parveen
11:45-12:00	Tailor-made carbon nanotubes dispersion in epoxy matrices through self-assembly with block copolymers	Joana Guedes
12:00-12:15	Fracture mechanisms of epoxy nanocomposites: influence of carbon nanoparticles with different geometries	Marcia Bär Schuster
12:15-12:30	Effect of carbon nanotube on the micro hot-embossed aluminium powder	Omid Emadinia
12:30-12:45	Hybrid composites with tailored electromagnetic and dielectric properties based on shell-core polyamide microcapsules	Filipa M. Oliveira

Lunch

B4	**Advances in composites and hybrid materials (cont.)** Chairs: Patricia Almeida Carvalho & João Tedim	
14:15-14:30	Synthesis of CNT-silica aerogels	Alyne Lamy-Mendes
14:30-14:45	New Bio-based Multi-scale Composites Developed Using Carbon Nanotubes	Sohel Rana
14:45-15:00	Development of polymer/metal multilayer composites by “Spark Plasma Sintering”	Sebastian Lemonnier
15:00-15:15	Nickel matrix composites reinforced by carbon nanotubes	Sónia Simões

B2	**Advances in metals and alloys** Chairs: Patricia Almeida Carvalho & João Tedim	
15:15-15:30	Assessing the thermomechanical processing steps of NiTi alloy production for orthodontic application	Patricia Rodrigues
15:30-15:45	Study of the Effect of Corrosion on Nickel-Aluminum Bronze in Natural Waters	Ignacio Cobo
15:45-16:00	Explosive welding of similar and dissimilar copper and aluminium alloys	Gustavo Henrique Senna Carvalho
16:00-16:15	Joining of AA6082-T6 aluminium alloys by Friction Stir Welding Mechanical characterization, modelling and numerical simulation	Maria Inês Costa
16:15-16:30	Influence of ultrasound melt treatment in the corrosion of AZ91D-Eco alloy	Vítor Emanuel Rebelo Lopes

16:30-16:45	Corrosion behaviour of alternatives to the WC-Co hardmetal	Alexandre Ferro Rocha

Coffee Break

D2	**Mechanical characterization (including at nanoscale)** Chairs: Paulo M.S. Tavares de Castro & Victor Neto	
17:15-17:30	Validation of cohesive laws for static strength estimation of adhesively-bonded joints	Raul Campilho
17:30-17:45	Determination of Mechanical Properties of aluminium AA6061 and HSLA420 steel using Inverse Analysis	Sara Miranda
17:45-18:00	Effect of σ and χ phases on micro residual stresses in cast super duplex stainless steel	Ricardo Sousa
18:00-18:15	Local Texture Characterization of Stainless Steel Cladding using Neutron Diffraction	Maria José Marques
18:15-18:30	Fracture behaviour of sheet metal materials for different stress triaxialities	Rui Amaral
18:30-18:45	Assessment of standardized methodologies for fatigue design of shafts: DIN 743, FKM and AGMA 6001	Paulo M.S. Tavares de Castro

19:30	Music Show (Rectory of University of Aveiro)

Tuesday, April 11, 2017

Session 1
(DECA Amphitheatre)

A2	**Magnetic, electric, multiferroic, plasmonic functional materials** Chairs: Angus Kingon & Chris Bowen	
09:00-09:45	Piezoelectric and Pyroelectric Materials and Structures for Energy Harvesting – Keynote Talk	Chris Bowen
09:45-10:00	Unidirectional porous PZT with improved pyroelectric and piezoelectric properties for energy harvesting applications	Yan Zhan
10:00-10:15	Crystal structure and piezoelectric properties of $Bi_{1-x}Sm_xFeO_3$ ceramics	Dmitry Karpinsky

Coffee Break

A2	**Magnetic, electric, multiferroic, plasmonic functional materials (cont.)** Chairs: Chris Bowen & Angus Kingon	
10:45-11:15	Perovskite Photovoltaics: Why the Excitement? And What are the Challenges? – Invited Talk	Angus Kingon
11:15-11:30	Ag-TiO_2 nano-heterostructures exhibiting gas sensing properties, visible-light activated photochromism with simultaneous plasmon-enhanced photocatalysis and antibacterial activity	David Tobaldi
11:30-11:45	Turning biocompatible and biodegradable biopolymers into electric and magnetic flexible bionanocomposites	Ana Barra
11:45-12:00	Synthesis, Structure, Optical and Magnetic Properties of New Multifunctional Lanthanide Complexes	Maria Susano
12:00-12:15	Oxyorthosilicates obtained by Laser Floating Zone: from photonic to electrical applications	Francisco Rey-García
12:15-12:30	New features in indentation and scratch testing	Aurelien Fillon

Session 2
(DECA Room 40.1.8)

A1	**Bio-inspired materials and materials for healthcare applications (cont.)** Chairs: Maria Helena Fernandes & Martinho Oliveira	
09:00-09:45	Bone repair and regeneration: relevant aspects – Keynote Talk	Jonathan Knowles
09:45-10:00	Mechanical and tribocorrosion behavior of Ti6Al4V cellular structures impregnated with biomedical PEEK	Flávio Bartolomeu
10:00-10:15	A Single-Step Method to obtain Additive Manufactured 3D Scaffolds with Tailored Surface Topography	Sara Neves

Coffee Break

C2	**Additive manufacturing** Chairs: Maria Helena Fernandes & Martinho Oliveira

11:00-11:15	A new generation of x-ray computed tomography devices for quality insurance and metrology inspection in the field of additive manufacturing	Patrick Möser
11:15-11:30	Study of PLA properties obtained by 3D printing FDM process with FUZZY-PID temperature control and cooling system	Santiago Villa
11:30-11:45	Mechanical behavior of thermoplastic based composites processed by additive manufacturing	Isaac Ferreira
11:45-12:00	Porcelain powders formulation for indirect selective laser sintering	Pedro Duarte
12:00-12:15	A multimaterial approach for the next generation of high performance moulds	Cyril Santos
12:15-12:30	Improving the performance of injection moulding through the application of additive manufacturing	Nilza Reis
12:30-12:45	Influence of the thickness parts produced by SLM on the transformation characteristics of NiTi	Pedro Carreira

Session 3
(DECA Room 40.2.15)

A3	**Materials for environment and sustainable materials** Chairs: Ian M. Reaney & Luis Gil	
09:00-09:45	The industrial-digital revolution: How would this shape future materials and manufacturing supply chain sustainability and efficiency – Keynote Talk	Lenny Koh
09:45-10:00	Natural and synthetic sorbent materials performance for CO_2 capture: a comparative study	Paula Teixeira
10:00-10:15	Boron Detection and Scavenging Materials	José Paulo Farinha

Coffee Break

A3	**Materials for environment and sustainable materials (cont.)** Chairs: Lenny Koh & Ian M. Reaney	
10:45-11:00	Gold nanoisland-decorated TiO_2 for enhanced photocatalysis	Pedro Martins
11:00-11:15	Bimetallic metal nanoparticles on carbon nanotubes embedded in polymeric membranes as supported hybrid catalysts for environmental applications	Vicente Esquivel-Peña
11:15-11:45	Active and transparent chitosan-genipin films: a promising approach for food packaging materials	Idalina Gonçalves

C4	**Recycling** Chairs: Luis Gil & Lenny Koh	
11:45-12:00	Inorganic polymers reinforced with glass fibre waste for construction materials	Rui Novais
12:00-12:15	Eco Composites based on Slate Residues	Luís Nobre
12:15-12:30	Physical and mechanical properties of eco-reactive powder concrete	Samiha Ramdani
12:30-12:45	Transformation of Textile and Wood Waste in new Products	Jorge Lino Alves

Lunch

Chair: Martinho Oliveira

14:00-15:00	Additive Manufacturing: Future Challenges – Plenary Talk	Paolo Bártolo

	(DECA Amphitheatre)	
15:00-16:30	Debate	

Coffee Break

17:00-18:30	Show Case + Poster Session

19:30	Gala Dinner (Escola Secundária José Estevão)

Wednesday, April 12, 2017

Session 1
(DECA Amphitheatre)

A2	**Magnetic, electric, multiferroic, plasmonic functional materials (cont.)** Chairs: Elisabete Costa & K C James Raju	
09:00-09:30	Tunable microwave dielectric properties of ferroelectric thin films and their applications – Invited Talk	K C James Raju
09:30-09:45	High Temperature Giant Magnetoelectric Coupling in $BaTiO_3$:Fe auto-composites	Carlos Amorim
09:45-10:00	Role of topology in apolar-to-polar phase transition of hexagonal RMO_3 (M=Mn, Fe) improper ferroelectrics	Joaquim Vieira
10:00-10:15	Green cellulose-based hydrogel stickers applied as gate dielectric in paper electrolyte-gated transistors	Inês Cunha

Coffee Break

A2	**Magnetic, electric, multiferroic, plasmonic functional materials (cont.)** Chairs: K C James Raju & Elisabete Costa	
10:45-11:00	Comparative Analysis of Structural and Electromagnetic Properties of Cobalt Ferrite With And Without Addition of Niobium Pentoxide	Francisco Carvalho
11:00-11:15	Fabrication and characterization of a DC magnetic field sensor based on magnetoelectric polymer composites	Sílvia Reis
11:15-11:30	Tuning functionalized periodic mesoporous phenylene-silicas for CO_2/CH_4 separation	Mirtha Louenço
11:30-11:45	Nanotechnology Usability tool for optimization of nano-based products	Bárbara Gabriel
11:45-12:00	Piezo-resistive behaviour at high strain levels of intrinsically conductive polymers printed on a flexible polymeric substrate by a novel surface treatment.	Sílvia Cruz
12:00-12:15	Temperature Phase Transition and Modification of Surface States in Self-Assembled Nanocomposites Based on CdSe/ZnS Quantum Dots and Dyes	Eduard Zenkevich
12:15-12:30	Study of the NLO properties of L- Histidine HCl-$[ErNO_3]5H_2O$ crystals	Erasmo Orrantia Borunda

D4	**Materials modelling (Advanced atomistic algorithms, computer simulations) (cont.)** Chairs: Elisabete Costa & K C James Raju	
12:30-12:45	The possibility of use of ferrocene-substituted conducting polymers in paraquat electrochemical detection	Volodymyr Tkach

Session 2
(DECA Room 40.1.8)

C3	**Coatings and interfaces** Chairs: Albano Cavaleiro & David Maestre	
09:00-09:30	Tailoring morphology and optical properties of Cr doped SnO_2 micro- and nanostructures grown by a vapor-solid method – Invited Talk	David Maestre
09:30-09:45	Protective coatings to avoid zirconia aging behavior	Rafael Pereira
09:45-10:00	Using CO_2 supercritical fluid deposition to prepare functional thin film composites	Paula Ferreira
10:00-10:15	Selective metallization of flexible substrates by inkjet printing with electroless copper plating	Geoffrey Barral

Coffee Break

C3	**Coatings and interfaces (cont.)** Chairs: David Maestre & Albano Cavaleiro	
10:45-11:00	On the role of the energetic species in TiN thin film growth by reactive DOMS in Ar/N2	Ricardo Serra
11:00-11:15	Microstructure and Hardness Enhancement of Multilayer CrN/MoN Films	Bogdan Postolnyi
11:15-11:30	Interface Characterization of Industrial Slide-Contact Bearings Coated with Tin Based Alloys	Fernando Simões
11:30-11:45	Synthesis and structural characterization of fluorine-alloyed WS2-C coatings produced by reactive magnetron sputtering	Simone Rodrigues
11:45-12:00	Effect of high dosage on the short-fibber-carbon-reinforced epoxy composites machining process	Sergio Espel de Oliveira
12:00-12:15	Reinforcement Sputtering Functionalization and influence on the interface reaction of 410L- SiCp stainless steel composites	Oscar Carvalho
12:15-12:30	Structural studies of the hydrogenated silicon thin film deposited by RF magnetron sputtering	Zeudmi Fouzia

Session 3
(DECA Room 40.2.15)

A4	**Carbon based materials** Chairs: Raul Arenal & Jorge Frade	
09:00-09:30	Advanced TEM Studies on Different Atomically Thin 1D and 2D Nanomaterials – Invited Talk	Raul Arenal
09:30-09:45	Production and characterisation of alternative activated carbons – a full factorial design approach	Guilaine Jaria
09:45-10:00	Adherent and hard DLC coatings deposited by HiPIMS in Deep Oscillations Magnetron Sputtering (DOMS) mode.	Fábio Ferreira
10:00-10:15	Conductive biopolymer-clay-graphene composite film doped with carbon nanotubes	Cláudia Nunes

Coffee Break

A4	**Carbon based materials (cont.)** Chairs: Raul Arenal & Carlos Baleizão

10:45-11:00	Bacterial cellulose and graphene nanostructures as promising nanocomposites for the development of new insulating and fire-retardant materials	Susana Pinto
11:00-11:15	A graphene-oxide-collagen scaffold as a versatile three-dimensional biomimetic microenvironment for tissue engineering applications	André F. Girão

D4	**Materials modelling (Advanced atomistic algorithms, computer simulations) (cont.)** Chairs: Raul Arenal & Carlos Baleizão	
11:15-11:30	QSPR Modeling Applied to High Molecular Weight Polymers: Ductility Characterization from Elongation at Break	Ignacio Ponzoni

B1	**Advances in ceramics, concrete, building materials** Chairs: Carlos Baleizão & Jorge Frade	
11:30-11:45	Revifeel PLUS: Ceramic tiles with improved thermal comfort	Ana Sampaio
11:45-12:00	Self-healing concrete with bacteria encapsulated in expanded clay	Sandra Simaria De Oliveira Lucas
12:00-12:15	Impact of coal and wheat husk addition on the properties of fired clay bricks	Safeer Ahmad
12:15-12:30	Mechanical characterization of cement pastes reinforced with pristine and functionalized MWCNTs	Hawreen Ahmed
12:30-12:45	Study of mechanical behaviour and correlations with physical and chemical properties of solid ceramic bricks in Asunción	Roberto Rojas Holden

Lunch

MATERIAIS 2017 and 40 Years Anniversary of DEMaC Event (Rectory Amphitheatre)

Chairs: Joaquim Vieira, Paula M. Vilarinho

14:00-15:00	Ceramics and Materials in Aveiro: Commemoration of the Past, and a Perspective on the Future – Plenary Talk	Angus Kingon, Brown University
15:00-15:20	New Challenges of Materials and Surface Engineering in Industry 4.0 - Invited talk	Ricardo Alexandre, T&M
15:20-15:40	Networking for European Materials Scientists and Engineers - Invited talk	Brett Suddell, FEMs

Coffee Break

16:00-17:45	**40 Years Anniversary of DEMaC Round Table** - Addressing words - Prof. Dr Manuel Assunção (Rector, UA) - Addressing words - Prof. Dr Mário Ferreira (director DEMaC, UA) - Addressing words - Prof. Dr Victor Gil (1st Rector of UA) - Addressing words - Prof. Dr Richard J. Brook (Oxford University Emeritus, ECS) - Addressing words - Prof. Dr Ana M Rocha e Senos (DEMaC, UA) - Addressing words –Dr. João Leão Costa (SPCV/AAEC) - Addressing words – Eng. António Miguel Casal das Neves (GRESTEL) - Addressing words – Eng. Manuel Valente (DURIT) - Addressing words - Prof. Dr Júlio Pedrosa de Jesus (Former Rector of UA and Former Minister of Education of Portugal)

	- Addressing words – Prof. Dr. João Lopes Baptista (1st Director of DECV/DEMaC and Former Vice-rector of UA)
17:45-18:15	**Awards on achievements**
18:15-18:45	**SPM 2017 Carreer and Conference Awards**
18:45-	**MATERIAIS 2017 Closing**

Numbered List of Posters

Symposium A - Functional Materials

Bio-inspired materials and materials for healthcare applications (A1)

A1-01	Synthesis and Characterization of Hydroxyapatite Coating on Titanium by Sol-Gel Method	Vinicius Severo
A1-02	Novel biopolymer-silica hybrid nanoparticles prepared by a non-emulsion method	Sofia Soares
A1-03	Degradation of Modified membranes for periodontal Regeneration	Joana Baltazar
A1-04	Calcium phosphate cements as local drug delivery	Susana Olhero
A1-05	Nanostructured magnetic platforms for the sustained delivery of anticancer drugs	Bárbara Leite Ferreira
A1-06	Electrospun composite polyurethane- ZnO biomembranes for vascular graft applications	Hugo Almeida
A1-07	Influence of fiber orientation on the mechanical response of piezoelectric poly(vinylidene fluoride) electrospun fiber mats	Sylvie Ribeiro
A1-08	Study of NiTi orthodontic wires with actuating forces	Patricia Rodrigues
A1-09	Production of polycaprolactone/boron and calcium-containing silicate hybrid nanofibers via a combination of electrospinning and non-aqueous sol gel process	Nathalie Barroca
A1-10	Mechanical caracterization of bovine cortical bone and the role hydration-dehydration cycles	Marco Duarte Naia
A1-11	Influence of electrical polarization on the bioactivity of chitosan/hydroxyapatite porous scaffolds for tissue engineering	Carmo Lança
A1-12	Synthesis and characterization of hemicellulose hydrogels with incorporated magnetic nanoparticles	Marija Milanović
A1-13	PLA-ZnO nanocomposites with anti-bacterial characteristics	Ana Senos
A1-14	Photocrosslinkable hyaluronan-pectin cell-laden bioink for 3D-bioprinting	Mariana Neves
A1-15	Development of e-skin thin film sensors for blood pressure measurement	Andreia dos Santos
A1-16	New Functional Bio MOF Material for the Treatment of Osteoporosis	Jéssica Barbosa
A1-17	Mechanical Properties of Bioactive Dual Layer Materials	Mafalda Costa
A1-18	New wood composites with application in footwear heels	Maria José Ferreira

A1-19	Polarized films of chitosan and hydroxyapatite for bone regeneration	Carmo Lança
A1-20	Histological alterations induced by gold nanoparticles on seabream Sparus aurata	Maria Lopes
A1-21	Preparation and characterization of chitosan vessels to biomedical applications	Andrea Antunes
A1-22	Effects of ZnO-NPs on Histology of Gilthead Seabream, Sparus aurata	Maria Lopes
A1-23	Plasmonic behaviour of noble nanoparticles (Au, Ag) dispersed in AlN	Marco Rodrigues
A1-24	The influence of pressure on the sintering of Ti6Al4V-ZrO2 materials for biomedical applications	Sara Madeira
A1-25	Mechanical properties of layered zirconia to zirconia-hydroxyapatite or zirconia-β-TCP composites for biomedical applications	Diana Faria

Magnetic, electric, multiferroic, and plasmonic functional materials (A2)

A2-01	Nanoscale modifications in Eu3+ doped sol-gel glasses by means of cw laser irradiation through m-lens	Helena Cristina de Sousa Pereira Meneses e Vasconcelos
A2-02	Broadband FMR in Mn-doped Li ferrite nanoparticles	Pablo Hernandez-Gomez
A2-03	Adhesion of Ge2Sb2Te5 Thin Films for Phase Change Memory Application	Petr Lazarenko
A2-04	Three component reaction: Green synthesis of 3,4-dihydropyrimidin-2-(1H)-ones using copper-based catalysts	Kahina Kouachi
A2-05	Multiferroic Nanofibers by Electrospinning	Pedro Rego
A2-06	Al2O3-Ni composites with a gradient distribution of metallic phase obtained by novel centrifugal gelcasting method	Justyna Zygmuntowicz
A2-07	Modification of magnetic ordering through substrate strain	Fábio Figueiras
A2-08	A detailed study of the physio-chemical properties of Fe doped Pr2O2SO4	Tao Yang
A2-09	Preparation and characterization of lead-free K0.5Na0.5NbO3 piezoceramics obtained from mechanochemically activated powders	Anna Wlodarkiewicz
A2-10	Effect of In nanodroplet size on morphology of liquid metal-assisted electrochemical deposited Ge nanowires	Ilya Gavrilin
A2-11	TiO2 nanotubular layers formation with improved conductivity by specific thermal annealing procedure	Alexey Dronov
A2-12	Observation of Positive and Negative Magnetodielectric Effects in Relaxor PbCo1/3Nb2/3O3 Ceramic	Adityanarayan H. Pandey
A2-13	Ultrasonic irradiation as a tool for enhancing the catalytic performance of ZVI nanoparticles towards nitrate reduction	Mohammadreza Kamali

A2-14	Synthesis and Characterization of Mg/Al- Carbonate Layered Double Hydroxides (Mg/Al-CO3LDH 2:1) with high crystallinity	DIB Mustapha
A2-15	Structural and luminescence characterization of heat-treated porous anodic alumina films formed in selenic acid solution	Yulia Nazarkina
A2-16	High room temperature magnetodielectric response on flexible polymer based nanocomposites	Sílvia Reis
A2-17	Synthesis and characterization of AnO:Al thin-films grown by DC-Sputtering	José Moller
A2-18	CO sensors based on nanostructured SnO2 thick films	Elisabete Costa
A2-19	Relaxor to ferroelectric phase transition in 0.83PbMg1/3Nb2/3O3-0.17PbTiO3 single crystal	Juras Banys
A2-20	Structural and magnetic characterization of nickel ferrite/zinc ferrite nanocomposites	Ivan Stijepovic
A2-21	Microstructure studies of hot pressed (K0.5 Na0.5) NbO3 samples	Nivas Babu Selvaraj
A2-22	Synthesis of Fayalite Fe2SiO4 as a Tar Removal Catalyst for Biomass Gasification	Rui Pinto
A2-23	Printable cellulose-based sensors for paper electronics	Raquel Barras
A2-24	Characterization of PVDF-Cu/Ni nanocomposites obtained via immersion precipitation	Ana Senos
A2-25	Evaluating the surface interaction of nanoplasmonic thin films with Candida albicans	Marco Rodrigues
A2-26	Growth and structure of high Curie temperature ferroelectric crystals	Jingzhong Xiao
A2-27	Magnetic properties of Sodium Ferrite obtained by solid state reaction	S. Soreto Teixeira
A2-28	Highly Efficient Luminescent Lanthanide Complex-based Di-ureasils Derived from In-situ Sol-gel Process	Ming Fan
A2-29	BCZT-ferrite composites, effect of magnetostriction of the magnetic phase on the magnetoelectric effec	Muhammad Naveed-Ul-Haq
A2-30	Luminescencent properties of Alexandrite (BeAl2O4:Cr3+) - brazilian mineral.	Neilo M. Trindade
A2-31	Dielectric Properties of Ba1-xBixTi1-x(Mg2/3Nb1/3)xO3 ceramics	Raz Muhammad
A2-32	Dielectric properties of Ni-Doped Barium Hexagonal Ferrites (BaFe12O19)	Muhammad Asif Rafiq
A2-33	Mesoporous silica nanoparticles diameter and morphology control through template supramolecular assembly	Carlos Baleizão
A2-34	Stimuli-Responsive Hybrid Nanoparticles for Smart Delivery	José Paulo Farinha
A2-35	Effect of subgrain textures on magnetic anisotropy of (Co,Ni)O/soft magnetic alloy bilayers and multilayers	Joaquim Vieira
A2-36	The electrical properties of Au/ZnPc/p-Si/Al and Au/AlPc/p-Si/Al organic heterostructures for solar cell	M. Benhaliliba
A2-37	Synthesis by sol-gel of pure and alumina doped nano crystalline powders of zinc oxide. Structural and optical properties study.	Abdelhamid CHARI

A2-38	Structural effects on the optical properties of zinc blende cubic from hexagonal wurzite prepared by the modified colloidal method.	José Moller
A2-39	Red/ NIR emission of ZnGa2O4:Cr3+ nanoparticles produced by pulsed laser ablation in water for bio applications	Rosa Soares
A2-40	Transparent Molybdenum Oxide Thin Films Obtained by Reactive Magnetron Sputtering	Alice Maciel
A2-41	Laser Floating Zone synthesis and characterization of Erbium and Molybdenum co-doped Ytterbium Aluminum Garnet (YbAG:Er:Mo) for optical thermometry	Roberto Costa
A2-42	Adsorption of tannic acid on aluminum oxide (α-Al2O3) particles	Jaíne Webber
A2-43	The electrical conductivity of BiFeO3 nanocrystalline ceramics	Sadyk Sadykov
A2-44	Study of the degradation of inorganic coatings by commercial detergents	Raquel Neves

Materials for energy, environment and sustainable materials (A3)

A3-01	Gd-doped SrTi0.5Fe0.5O3-δ mixed conducting materials: structural, thermal and electrical properties	D. Medvedev
A3-02	Sintering, microstructure and transport properties of BaCe0.5Zr0.3Ln0.2O3−δ (Ln =Y, Dy, Gd, Sm and Nd) materials	D. Medvedev
A3-03	Study of the degradation of ibuprofen by photocatalysts type MXTi1-XO2 / (M = Fe, W…)	Ahcène Soualah
A3-04	Computational optimization of bio-adsorbents for the removal of pharmaceutical compounds from water	José Manuel Pereira
A3-05	Production of activated carbons from raw and bleached pulp to remove drugs from water	Gonçalo Oliveira
A3-06	Microstructure and electrochemical assessment of Cu-CGO cermet anodes	Daniel Macedo
A3-07	The electrochemical properties of the cathodes based on doped lanthanum nickelate for proton-conducting electrolytes	Alexander Kolchugin
A3-08	Structural, thermal, electrical and electrochemical properties of Ca-substituted Nd2-xCaxNiO4+δ (x=0-0.3) cathode materials	Elena Pikalova
A3-09	Thermophysical and heating properties of a composite rubber membrane with energy harvesting purposes	José Norambuena
A3-10	Ionic Liquid-Poly(lactic) Acid Blends towards Proton Conductive Polymer Electrolyte Membranes for Fuel Cells	Paula Barbosa
A3-11	Hydrogen evolution reaction at rGO-supported PdAu and PdFe alloys	Luís Amaral
A3-12	Luminescent electrochromic devices incorporating ionogels	Marita A. Cardoso
A3-13	Photocatalytic degradation of Rhodamine B dye using SiO2-TiO2nano supported in HY zeolite on the cotton textiles	Salmon Landi
A3-14	Exploiting a Taguchi based strategy for optimizing the surface area and crystallinity of iron nanoparticles	Mohammadreza Kamali

A3-15	Chemical Stability of Perovskites-Type Oxide Electrodes for the ORR and HPRR in Alkaline Media	Nuno Sousa
A3-16	Rare earth doped LiMn1.5-xNi0.5RExO4 based cathodes for high improved lithium-ion batteries	Carlos Costa
A3-17	Activated carbon production from Teak wood wastes by physical activation and their application in the removal of pesticides from the liquid phase	Cristóvão Ramiro Belo
A3-18	Temperature influence on pesticides removals from aqueous solutions on activated carbons prepared from synthetic polymers blends	Cristóvão Ramiro Belo
A3-19	Polyacrylonitrile as Template in Preparation of LiNi0.4Co0.2Mn0.4O2 Nanofiber and the Enhanced High-rate Performance for Lithium Ion Batteries	Gang Yang
A3-20	Guidelines for controlled design of NiAl2O4 cellular monoliths towards potential catalytic applications	Andrei Kovalevsky
A3-21	Modification of thermoelectric properties of Nb doped SrTiO3 ceramics by reduced graphene oxide	Alexander Tkach
A3-22	Anodic stripping voltammetric measurement of trace cadmium at lead-coated titanium electrode	Abdelkader Benchettara
A3-23	Plasma nitriding surface as passivation layer for silicon cathode used in photo-electrochemical water splitting	Bárbara Gabriela
A3-24	Carrageenan hybrid siliceous materials for the uptake of metoprolol from water	Maria António
A3-25	Magnetic biohybrid nanosorbents with tunable surface chemistry for the removal of cationic and anionic herbicides from water	Tiago Fernandes
A3-26	Magnetic nanoparticles for trace mercury preconcentration and quantification in waters	Daniela Tavares
A3-27	Influence of wettability on the anti-scaling performance of heat transfer surfaces	Pedro Moreira
A3-28	Surfaces modified by bio-inspired molecules for molecular oxygen reduction catalysis	Rui Sampaio
A3-29	Sustainable Design: Development of new products from pine resin and flax fiber	Jorge Lino Alves
A3-30	Deposition of silver-doped TiO2 (TiO2:Ag) coatings by PVD for footwear industry	Sandra Mariana Marques
A3-31	Magnetised Mn3O4 nanocomposite for water decontamination	Gabriela Cordeiro
A3-32	Advanced Photocatalytic Heterostructered Materials for the Controlled Release of Active Compounds upon Solar Activation	Marta Adriana Forte
A3-33	Influence of Li2S content in a Solid Glass Li+ Electrolyte	Joana E. Oliveira

Carbon based materials (A4)

A4-01	Local Effects of Graphene and Graphene Oxide on the Ferroelectric Properties of P(VDF-TrFE)	Maxim Silibin
A4-02	Decoration of carbon nanostructures using silver sulfide nanocrystals	Joana L. Lopes

A4-03	Synthesis and characterization of magnetic graphene based nanocomposites for the recovery of rare earth elements	Elisabete Afonso
A4-04	Graphene Biosensor	Glenda Biasotto
A4-05	Effect of annealing temperature and addition of carbon nanotubes on power factor of reduced graphene oxide freestanding paper	Alexander Tkach
A4-06	New high-pressure C70 structures	Leonel Marques Joaquim

Symposium B - Structural Materials

Advances in ceramics, concrete, building materials (B1)

B1-01	Cost-Efficient and Eco-Efficient Mortars based on Fly Ash and Waste Glass	F. Pacheco Torgal
B1-02	Characterization of Concrete with Incorporation of Slag From Blast Furnace	José B. Aguiar
B1-03	Cost and property optimisation of concretes containing fly ash using mathematical and statistical strategies	Franky Bruno Witzke
B1-04	Evaluation of ceramic propping agents applied for global shale gas exploration under extreme conditions	Joanna Szymańska
B1-05	Nanostructured mineral materials for controlled release of corrosion inhibitors in reinforced concrete	Celestino Gomes
B1-06	Intangible assets of iron ore tailings as building material	Wanna Carvalho Fontes
B1-07	Physical and mechanical properties of cement mortars with direct incorporation of phase change materials	Sandra Raquel Leite da Cunha
B1-08	Influence of heating rate on the microstructure and mechanical properties of porous fluorapatite ceramic developed from clay and natural phosphate	Mossaab Mouiya
B1-09	Analysis of self compacting concrete production and addition of recycled poly ethylene terephthalate powder	Jonatha Roberto Pereira

Advances in metals and alloys (B2)

B2-01	Superplastic Forming and Friction Stir Welding Technology for Manufacturing of AA2195 Vessel	Ho-Sung Lee
B2-02	Correlation between the microstructure, thermal and electrical properties of CuxAs50Se50-x chalcogenide glasses by using DSC and AC impedance spectroscopy	Mirjana Siljegovic
B2-03	Correlation of electrical and structural properties of semiconducting glassy chalcogenide alloys Ag?As40S30Se30	Dalibor Sekulic
B2-04	Investigation of the stored energy in Cu-Ni-Si alloy after high-pressure torsion	Hiba Azzeddine
B2-05	A DSC analysis of phase transformations in Mg-Ce alloy after severe plastic deformation	Djazia Elfiad

B2-06	Prediction of gas content in aluminum melt alloys	Tânia Ferreira de Azevedo
B2-07	Optimization via iterative processing of the grain boundary characteristics and its consequences on mechanical properties of nickel base superalloy 718	Clarissa Melo
B2-08	Microstructural analysis of an AA 1070 aluminum alloy deformed by ECAP and cold rolling.	Gabriella Maria Silveira de Sá
B2-09	Intergranular corrosion behavior of ZAMAK 3 alloys in wet environments	Maria Victória Biezma
B2-10	Al-Mn-Ni ternary system: die cast microstructure and corrosion behavior	Maria Victória Biezma

Advances in polymers (B3)

B3-01	Influence of self-organized fluid flows on secondary and tertiary structure of bio-macromolecular system	Antonín Minarik
B3-02	Poly(1,4-cyclohexylene 2,5-furandicarboxylate): using 1,4-cyclohexanediol to enhance the thermal properties of FDCA-based polyesters	Marina Matos

Advances in composites and hybrid materials (B4)

B4-01	Preparation of polyamide laminate composites with tailored electrical properties	Filipa Oliveira
B4-02	Potencial use of glulam beams made with teak wood in architecture	Viviane Teixeira Iwakiri
B4-03	Preparation of ZnS-PMMA nanocomposites thin films, study of its optical properties	Chaieb Abderrahmane
B4-04	Characterisation of Nanostructured Copper-Graphene Composites Processed by Mechanical Milling	Tomás Seixas
B4-05	Nano-sized YSZ-metal composites produced by Mechanosynthesis	Ricardo Serrazina
B4-06	Thermal performance assessment/evaluation of polyurethane foams with phase change materials	Claudia Amaral
B4-07	Comparative analysis on the bond of ribbed carbon fiber reinforced polymer bars (CFRP) and ribbed steel bars under moderate temperatures	Victor Calvet Rodriguez
B4-08	Photocatalytic activity of TiO2/graphene and TiO2/graphene oxide nanocomposites	Pedro Martins

Symposium C - Processing Technologies

Processing using laser/plasma/electric field technologies (C1)

C1-01	Portland cement clinker production by concentrated solar radiation	Fernando Oliveira
C1-02	Microstructure of zirconia/titanium composites prepared by Spark Plasma Sintering	Aleksabdra Miazga

C1-03	Surface characteristics of austenitic stainless and tool steels parts manufactured by selective laser melting (SLM)	Daniel Gatões
C1-04	Cerwave – Microwave/gas oven project to fire industrial porcelain	Tiago Santos
C1-05	Multiferroic Ceramics of the Bi1-xLaxFe0.50Sc0.50O3 Metastable Solid Solutions System Prepared Using High-Power Activation	Ilona Zamaraite

Additive manufacturing (C2)

C2-01	Free form fabrication of porcelain products by robocasting	Andreia Carvalho
C2-02	Cork-Polymer Composites based on Polylatic Acid for Fused Filament Fabrication	Sara Silva
C2-03	Additive Manufacturing of porcelain parts by robocasting	Mónica Faria
C2-04	Fully-Printed Zinc Oxide Transistors on Paper	José Tiago Carvalho
C2-05	Binder selection for 3D printing of porcelain parts	Pedro Duarte

Coatings and interfaces (C3)

C3-01	Preliminary Deposition and Study of Multilayer (Ti,Al)N/(Si,Al)N Fillms	Bogdan Postolnyi
C3-02	Surface Analysis of Materials by Elastic Scattering of MeV Ions	José Pacheco de Carvalho
C3-03	Nuclear Reaction Analysis of Materials using MeV Ion Beams	José Pacheco de Carvalho
C3-04	Formation of black silicon by application of different parameters of Ni-assisted chemical etching	Sergey Gavrilov
C3-05	Atomic layer deposition of high dielectric Ta2O5 films on boron doped diamond	Aneeta Jaggernauth
C3-06	Deposition and characterization of CrNx thin films obtained using the PVD technique	Miguel Ângelo Neto
C3-07	Photoluminescence and photocatalytic of the heterostructure based on α -Ag2WO4/ZnO/Ag	Maria Aparecida Zaghete
C3-08	Post-deposition Hydrogen treatment effect on surface roughness and hydrophobicity of amorphous silicon films	Amina Bra
C3-09	Effect of hydrogenation of amorphous silicon surfaces on protein adsorption	Larbi Filali
C3-10	Adhesion between amorphous thermoplastics (Polycarbonate) and PVC membranes: a case study	Luís Nobre
C3-11	Alloying effects at bicomponent Au-Cu and In-Sn particle arrays formation by vacuum-thermal evaporation	Sergey Dubkov
C3-12	Changing the polystyrene surface topography by phase separation	Erik Wrzecionko
C3-13	Scaling a HFCVD reactor for a semi-industrial operation mode	Sérgio Pratas
C3-14	Influence of processing conditions on the grain structure of sputtered copper thin films	Bruno Oliveira

C3-15	Controlling the Au/Iron Oxide interface to optimise plasmonic resonance for Magneto-Optic Diagnostics	Josh Davies

Recycling (C4)

C4-01	Obtaining and characterization of granitic waste processed by hydrocyclone	Ricardo Peixoto Suassuna Dutra
C4-02	Physic-mechanical behavior of stabilized soil block with lime based-fibers (waste tyre rubber and glass fibers)	Melik Bekhiti
C4-03	Reuse of Gypsum Residue in the Manufacturing of 3D Decorative Wall Covering Panels	Eliedson Rafael de Carvalho
C4-04	End-of-Life Vehicle Residues as Raw Materials for Brake Pads	Xavier Silva
C4-05	Preliminary investigations of geopolymeric mixtures based on phosphate washing waste	Rawia Dabbebi
C4-06	Sustainable development of a plaster-based composite (CaSO4.0,5H2O) reinforced PET bottles fibers (polyethylene terephthalate) recycled	Tomaz Rodrigues
C4-07	Valorisation of dregs by its incorporation in geopolymer mixtures	Rui Novais
C4-08	Shrinkage Performance of Waste Based Geopolymers Reinforced with Short Hybrid Polymer Fibres	F.Pacheco Torgal
C4-09	Valorization of dredging sediment of safi port in port works (safi, morocco)	Ahmed Loudini
C4-10	Application of automotive paint sludge in the production of white ceramic	Priscila B. Praxedes
C4-11	Synthetic stone processing from waste glass	María Milagros Laz Pavón

Symposium D - Characterization and Modelling

Physical, chemical and structural characterization (D1)

D1-01	FTIR-ATR spectroscopy applied to coated paper ageing characterization	Natércia Santos
D1-02	Development of sensors and calibration methods for online measurement of viscosity, volume and solid content of non-newtonian fluids	Andreia Furtado
D1-03	Characterization of mortars from built heritage using XRD, XRF and ATD-TG. The case study of the medieval fortification of Safim, Morocco	João Pedro Veiga
D1-04	Synchrotron Radiation X-ray Absorption Spectroscopy in 19th century Portuguese glazed tiles from Pena National Palace, Sintra, Portugal	João Pedro Veiga
D1-05	Mineral Characterization of Bauxite Tailings from the Juruti-Pará-Brazil Mine by X-ray Diffraction and X-ray Fluorescence	Brenda Carvalho dos Santos
D1-06	Piezoelectric and electrical properties of ferroelectric Ba0.8Sr0.2TiO3 films with different thickness	Dmitry Kiselev

D1-07	Influence of ambient temperature on the performance of PCPDTBT:PC71BM BHJ solar cells	Zubair Ahmad
D1-08	Synergistic Erosion-Corrosion Behavior of API X120 Steel in the Sweet Environment	R. A. Shakoor

Mechanical characterization (including at nanoscale) (D2)

D2-01	Optimization of the elastic modulus of thermoplastic cassava starch nanocomposites with modified clay through factorial planning	Abimaelle Silva Chibério
D2-02	Influence of expansion degree on propagation of deformations delay	Belaziz Azzeddine
D2-03	Thermo-mechanical characterization of shape-memory polymeric nanocomposites	Beatriz Fonseca
D2-04	Influence of the temperature on the dynamic behavior of composite structures offshore pipe: experimental analysis	Hamza Benyahia
D2-05	Micromechanical Analysis of Interaction between Matrix Crack and Debonding area in an AlfaFiber / Epoxy Resin Biocomposite	Mokhtar Khaldi
D2-06	Experimental and numerical analysis of the fracture toughness of adhesively-bonded joints	Raul Campilho

Advanced characterization using microscopy techniques (D3)

D3-01	Detection of nano-heterogeneities in CaCu3Ti4O12 ceramics using scanning probe microscopy	Filipe Amaral
D3-02	Nanostructural Characterization 3D of Phases and Interfaces of Portland Cement Mortar	Matheus de Faria e Oliveira Barreto
D3-03	Nano and Microstructural Characterization of Phases and Interfaces of Portlant Cement Mortar Using High Resolution Microscopy	Matheus de Faria e Oliveira Barreto
D3-04	Microstructural characterization of BFRP bars used as replacement for conventional corrugated steel bars.	M. Bär Schuster
D3-05	Piezoresponse and Kelvin probe force microscopy studies to assess local switching on polycrystalline ferroelectric coatings	Marisa Maltez da Costa
D3-05	Microstructural Characterization of ZrN/CrN Nanoscale Multilayer	Sónia Simões

Materials modelling (Advanced atomistic algorithms; Computer simulations) (D4)

D4-01	Growth and Stability of a Model Catalyst on Oxides	Abdelbaki Chemam
D4-02	Influence of granular material characteristics in the behavior of “Bouregreg Valley” soft ground improved with stone columns	Noura Nehab

D4-03	Analysis of the statistical significance of factors in the tensile strength optimization of thermoplastic cassava starch nanocomposites with modified clay	Abimaelle Silva Chibério
D4-04	The influence of geometric discontinuity on the fatigue behavior of aluminum alloy 7075-T6 and 6082-T6	Abdessamad Brahami
D4-05	Macro Approach to Molecular Modelling of Linear Polymers Applied to Estimation of Tensile Modulus for New Materials Development	Ignacio Ponzoni
D4-06	Numerical study of retaining wall backfilled with sand-tire shred mixture	Hachemi DJADOUNI
D4-07	Smart Vehicle Lighting System using a-SiCH Technology	Manuel Augusto Vieira
D4-08	Materials for Non-Pneumatic Tyres (NPTs): a New Concept	António Torres Marques
D4-09	Ductile tear under monotone loading by XFEM method	Abdessamad Brahami
D4-10	The theoretical evaluation of the saccharin electrochemical detection, based on specifically modified polypyrrole in neutral solution	Volodymyr Tkach
D4-11	Grain growth Kinetic during austenitization of 100Cr6 and X20Cr13: NUMERICAL STUDY	Blaoui Mohamed Mossaab
D4-12	Design and fabrication of phantoms to study electromagnetic effects	Norberto Jorge Gonçalves
D4-13	Ferromagnetism in the half-heusler XBaB Compounds from first-principles calculations (X=K, Rb)	Radjaa Benabboun
D4-14	Ab-silico thermodynamics of (giant) magnetocaloric materials	João Amaral
D4-15	Molecular Dynamics Investigation of the Stern Layer for Water-Silica Interfaces	Sarah Hocine

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Abstracts

Plenary Talks

Substitution and Sustainability in Functional Materials and Devices

Ian M. Reaney
Functional Materials and Devices Group, Materials Science and Engineering, University of Sheffield, Sheffield, S13JD, United Kingdom

The ‘grand challenge’ for functional materials is to develop compositions and devices which make use of elements that are abundant, low cost, environmentally-friendly, require little energy to make into useful products and are free from geopolitical concerns. This rather obvious statement underpins much of modern research into functional materials but whilst it is a laudable goal, few technologies adhere to these rules. This presentation discusses some recent studies at Sheffield where we have attempted to develop functional materials and devices using an holistic approach involving modelling and life cycle assessment to support classic functional materials science.

Additive Manufacturing: Future Challenges

Paulo Bártolo
School of Mechanical, Aerospace and Civil Engineering (MACE), University of Manchester, United Kingdom

It is predicted that Additive manufacturing (AM) will change the way we manufacture products, but also how we designed, assemble and even distribute products.

This new form of manufacturing gained relevance as a tool to design prototypes but from that time up to now it is changing drastically and rapidly and is currently a fabrication tool, covering all the engineering areas, from the fabrication of metallic parts to engines, for example, and in the near future expected to fabricate biocompatible parts for tissue reconstruction.

This talk intends to overview the evolution of AM technology, current advantage and limitations and predicting future applications.

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Ceramics and Materials in Aveiro: A Commemoration of the Past, and a Perspective on the Future

Angus I. Kingon
School of Engineering, Brown University, Providence, Rhode Island, 02912 USA

Professor Joao Baptista has played a critical role in shaping the original ceramics group at the University of Aveiro, and its evolution into the current Materials and Ceramics Department. We commemorate his leadership in broadening the scope of the department, and his part in evolving the university from a traditional national university into a well-known international center of research. He has had a single-minded emphasis on building an international reputation for scholarship, along with the development of young faculty and the application of the science in a national context.
In looking ahead, we recognize that the role of the University must continue to evolve, given the competitive global society in which we live. The investment in the institution, its people, and the research has to pay dividends in the short and long term, via measurable impacts on the quality of life and economic well-being of Portuguese society. In this regard, the Materials and Ceramics Department, with its productivity and engagement with industry, must continue to play a leading role.

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Keynote Talks

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Piezoelectric and Pyroelectric Materials and Structures for Energy Harvesting

Chris Bowen, M.Xie, Y.Zhang and J. Roscow
Materials and Structures (MaSt) Centre, University of Bath, United Kingdom

The continuing need for reduced power requirements for small electronic components, such as wireless sensor networks, has prompted renewed interest in recent years for energy harvesting technologies capable of capturing energy from ambient vibrations and heat. This presentation provides an overview of piezoelectric harvesting system along with the closely related sub-classes of pyroelectrics and ferroelectrics [1,2]. These properties are, in many cases, present in the same material, providing the intriguing prospect of a material that can harvest energy from multiple sources including vibration and thermal fluctuations [3,4]. Examples of modeling and manufacture of porous materials and pyroelectric harvesting are discussed where the harvesting generates power from temperature fluctuations using piezoelectric materials such as lead zirconate titanate (PZT) and polyvinylidenedifluoride (PVDF). The potential of novel sandwich structures are also described.

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[1] C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, Energy and Environmental Science, 7, 25-44 (2014)
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[3] J.I. Roscow, R.W.C. Lewis, J. Taylor, C.R. Bowen, Modelling and fabrication of porous sandwich layer barium titanate with improved piezoelectric energy harvesting figures of merit, In Press, Accepted Manuscript, Acta Materialia, 2017
[4] Y Zhang, Y Bao, D Zhang, CR Bowen, Porous PZT ceramics with aligned pore channels for energy harvesting applications, Journal of the American Ceramic Society 98 (10), 2980-2983 (2015)

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Bone Repair and Regeneration: Relevant Aspects

Jonathan Campbell Knowles
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The bone graft substitute market is expected to reach US$3.2 billion by 2022 and there is an expected high value for products for treating mal- and non-union fractures. Thus, the orthopaedic and dental markets have high value and potentially high return. There is a relatively limited range of materials which have at their core a related technology. Most bone graft materials currently are based on calcium phosphates, either naturally derived or synthetic. Processed into these materials is some sort of architecture to allow and promote rapid tissue ingrowth and integration and hopefully eventually replacement. More recent developments have looked at more complex systems utilising growth factor technologies as well as molecules designed for purpose and these will be discussed and their potential pros and cons.

The industrial-digital revolution: How would this shape future materials and manufacturing supply chain sustainability and efficiency

Lenny Koh
University of Sheffield, Sheffield, United Kingdom

Sustainable materials and efficient manufacturing processes are pivotal in ensuring a resource sustainable supply chain. In the context of the 4th industrial revolution, such concept cannot be achieved without the need to rethink, redesign and reconfigure the ‘old legacy’ approach into a ‘future and new’ approach. This talk will discuss some of the key enablers in this revolution, explore the core methodology and technology central to the transition towards an industrial-digital revolution.

Invited Talks

The Future of the Photovoltaics Industry

Brian A. Korgel
McKetta Department of Chemical Engineering and Texas Materials Institute,
The University of Texas at Austin, Austin, TX, 78712-1062, United States

The photovoltaics industry continues to expand with significant job growth and photovoltaic device deployment in both the residential and utility sectors. This growth has been due to a combination of steady technology improvements, reduced manufacturing and deployment costs and increased public awareness. This talk will describe the current state of the industry and the near-term technology roadmap. Future opportunities for the photovoltaics industry will then be discussed, including an emphasis on research needs that could lead to new applications and markets for the solar cell industry.

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Contribution of materials selection in improving efficiency in energy equipment

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The improvement of the efficiency of thermal energy systems could give rise to the optimization of fuel consumption which could results in a decrease in emissions of pollutants to the environment. The selection of correct materials for the construction of energy systems could significantly contribute to this improvement. This is particularly evident in energy systems using fossil fuels and biomass. Greater temperatures employed generally result in increased efficiency but the materials used for the construction of energy systems should be able to deal with higher temperature. In this way, energy produced per kg of fuel gets larger and this can result in lowering the CO_2 emissions. Higher temperature employed could be in the thermochemical conversion of fuel, in heat exchangers, in heat distribution network, etc. However, increased temperature during thermochemical conversion may bring problems of fuel ash reacting with the construction material. Care should be taken in selecting materials to ensure that it can withstand any attack by ash composition but simultaneously giving rise to more efficient energy system. Construction materials could include equipment body usually built in metals, refractories and insulation materials.

Atomic-scale changes induced by hydrogen and boron in crystalline materials

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Interstitial atoms play central roles in defining relevant properties of crystalline materials. However, their presence is difficult to detect by electron microscopy due to weak scattering power. In this work, aberration-corrected scanning transmission electron microscopy (a-c STEM) is employed to investigate effects of hydrogen (H) in palladium-based (Pd-based) membranes for gas separation and of boron (B) in cubic silicon carbide (3C-SiC) for intermediate-band solar cells. Structural changes induced by these solutes are revealed by high-angle annular dark field (HAADF), annular bright field (BF), X-ray energy dispersive spectroscopy (EDS) and electron diffraction.

Hydrogen diffuses into the subsurface regions of Pd-based membranes during long-term exposure to high H_2 pressure differences at moderate temperatures. When supersaturation is reached, precipitation initiates on appropriate low energy sites, such as grain boundaries. These structures act as unsaturable traps leading to continuous recombination of atomic H, which results in the nucleation of cavities that grow to sizes up to tens of nanometers. The low level of strain in the surrounding metal lattice demonstrates an internal pressure able to balance the constrictive surface tension. The cavities do not contribute to unselective leakage flux but can represent the origin of pinhole formation. Alloying elements, such as Ag and Cu, are able to hinder the unwanted a + b spinodal decomposition of the Pd-H system but seem to promote the formation of larger cavities.

Intermediate-band solar cells are promising candidates for the next generation of photovoltaic devices due to the potential for enhanced conversion efficiency. The development of an intermediate band in 3-C SiC demands relatively high concentration of B in solid solution. Therefore, remaining above the solvus surface is crucial to prevent preipitation which would lead to carrier scattering in the absorber material. The evolution of B solubility with temperature and its precipitation behavior in sublimation-grown 3C-SiC crystals are used to propose the solvus line in the BC-SiC pseudo-binary diagram.

Developing smart and functional materials for textile applications: Success Cases from Portugal

J. Gomes
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In the last 15 years, we have been witnesses of a silent but continuous evolution of the textile industrial sector in Portugal, driven and anchored on continuous incorporation of technological developments and supported and cemented by active pursuit of new competences. The decline of more traditional textile manufacturing business models of the turn of the century has not only been totally reversed, but the sector has completely inverted the trend by presenting record productivity and profitability, and now constitutes one of the main staples of Portuguese national export trade balance, but additionally a hallmark of for industrial reinvention, requalification and valorisation via innovation.

At the basis of this evolution and turn of fates of the Portuguese textile industry is the development and investment in new manufacturing technologies, new industrial management strategies and the integration of new technologies based on development of advanced materials coupled with new competences added to the sector via engagement with other industries. The investment in development of new processes and competences in materials science has yielded a comprehensive array of new high-added value technical products, and the integration of high performance materials even into more traditional and mainstream processes has empowered companies with competitive advantages in the global market.

Our presentation will focus on case-studies and recent examples of the application of materials science development and innovation and integration of R&D projects into industrial processes and manufacturing textile lines, highlighting how new materials and developments on the integration of new materials solutions are enabling the development of new high added-value products. Discussion will focus on the integration of printed and embedded electronic wearables in textile structures in clothing; development of new coating and surface engineering technologies based on the application of nanostructured materials and the engineering of new sustainable dying processes using nanomaterials and biomaterials; development of integrated nanostructured composites for textile fibres and yarns, and also the development of fibre and yarn based integrated electronic devices such as sensor-actuators and active matrixes.

The main key technology challenges will also be addressed, and we will focus on the roadmap of major hurdles to the integration of new nanomaterials and printed electronics into and onto textile structures and fibres, and advanced materials solutions resulting from the development of applied R&D projects.

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Flash Sintering Ceramics

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Flash sintering is a recent technique where an electric field is applied to a conductive ceramic to enhance sintering [1]. To densify ceramics, a typical conventional cycle requires T>1200 °C and can take several hours. In stark contrast, 8YSZ can be flash-sintered in mere seconds at 800 °C. For this reason, flash sintering aroused significant interest for its potential in decreasing production time and cost of ceramics. Furthermore, the conduction behavior during flash sintering is striking different from the normal Arrhenius-type increase with temperature. Such unusual observations led to speculation about the underlying sintering mechanisms under flash conditions, leading to propositions of defect nucleation for additional current [2], and partial grain boundary melting for fast diffusion rates. Such claims lacked empirical support. More recently, R. Todd et al. derived a model accurately describing the electrical behavior during flash sintering [3], followed by an empirical description of the conductivity of YSZ during flash sintering [4].

In this talk, we will summarize the evidence supporting classic densification and conduction mechanisms during flash sintering, concluding that Joule heating produced by ionic current alone is sufficient to justify extreme shrinkage rates observed during flash sintering. We show that microstructural evolution of 8YSZ during flash sintering is identical to conventional sintering, and describe the conductivity variation during flash sintering, accounting for current runaway and apparent non-linearity, under a variety of conditions. We find correctly estimating sample temperature variation during flash sintering converts the apparent non-linearity into well-known Arrhenius behavior. We show that the model is equally valid under constant heating rate and in isothermal conditions.

Despite the classical nature of the mechanisms involved, flash sintering remains a remarkable discovery and an interest technique. We will discuss the potential for application in light of current limitations and advantages.

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[2] Raj, R. et al., J. Am. Ceram. Soc. 94, 1941–1965 (2011)
[3] Todd, R. I. et al., J. Eur. Ceram. Soc. 35, 1865–1877 (2015)
[4] Du, Y. et al. J. Eur. Ceram. Soc. 35, 749–759 (2015)

Perovskite Photovoltaics: Why the Excitement? And What are the Challenges?

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The new photovoltaic devices based on perovskite materials such as methylammonium lead iodide (MAPI) have continued to demonstrate astonishing increases in efficiency. Coupled with their low temperature processing and low cost raw materials, the materials suggest the potential for a significant reduction in the cost of installed solar power. In addition, the properties of the materials have intriguing implications for other electronic devices.

But, predictably, the materials come with challenges. In this paper the unique properties and advances are briefly summarized, and the challenges mentioned. One particular challenge, namely the presence of rapid ion migration, which competes with electronic transport, is discussed in greater detail. We demonstrate careful transport measurements that allow insight into the competitive transport mechanisms. Implications for a variety of applications are discussed.

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Tunable microwave dielectric properties of ferroelectric thin films and their applications

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Ferroelectrics are known to exhibit an electric field dependent dielectric constant. But below their Curie Temperature, their electric field dependent polarization exhibit hysteresis and hence this phase is used for non volatile memories. However this phase with hysteresis is not suitable for varactor applications. Hence in the paraelectric state ferroelectric thin films can be used to make varactors. To achieve high figures of merit, low dielectric loss is also equally important. Often ferroelectrics tend to give higher tunability at the cost of a higher dielectric loss. There are some non-ferroelectric materials that got equivalent sites for some of their ions which can hop between them to give field dependent dielectric constant. Their tunability is relatively low and same is the case with their dielectric loss and as a result they give useful figures of merit. Examples of both category of materials were grown in thin film form by RF sputtering and PLD process. $(Ba_{0\cdot5},Sr_{0.5})TiO_3$ (BST) that was grown is an example of the former while $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (c-BZN) is an example of the latter. The results obtained shows that there is a strong substrate dependence on the tunability with these thin films as is their crystalline texture and crystalline orientation of the films. It is important also to note that when it comes to losses, most of the loss in these films arises from the metal layer used for the measurement itself. Substitution in BST composition is found to result in very attractive changes in tunability and loss. From a varactor point of view, the way the capacitor structure is fabricated is also equally important. A parallel plate structure gives high tunability with low tuning voltages but with multi mask processing whereas a planar capacitor gives small tuning with large tuning voltages but it can be made with a single mask process and hence compatible with many substrates and processes. One of the realized structures viz. high overtone bulk acoustic resonators (HBARs) offer a test structure to characterize the piezoelectric properties of the thin films that are used for making them. It opens up an avenue for extracting a number of thin film material parameters which are generally difficult to elucidate but important for device applications.

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Tailoring morphology and optical properties of Cr doped SnO_2 micro- and nanostructures grown by a vapor-solid method

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Increasing attention has been recently focused in tailoring the dimensions, morphology and composition of SnO_2 micro- and nanostructures synthesized by different methods in order to optimize and broaden its applicability in different fields of research. As some examples, nanostructures with high surface to volume ratio are suitable for gas sensing, while the use of microtubes and microrods allows their performance as optical microcavities. Besides, optical, electrical or magnetic properties, can be tuned by appropriate doping.

In this work a thermal evaporation method has been used to fabricate Cr doped SnO_2 elongated nano- and microstructures which dimensions and morphology depend on the thermal treatments and the employed precursors. Using metallic Sn and Cr_2O_3 as starting materials leads to the growth of nanostructures in forms of wires, belts, zig-zags and boomerangs after treatments carried out at 800 ºC [1], while microstructures in forms of tubes, rods and plates were grown at 1400 ºC when using SnO_2 and Cr_2O_3 as precursors [2]. The presence of Cr, in a concentration around 1 at. %, has demonstrated to increase the number of as-grown structures and to modify their morphology as well. X-ray absorption spectroscopy (XAS) measurements carried out at a synchrotron facility confirm that Cr is preferentially incorporated in the rutile SnO_2 lattice as Cr^{4+}, when lower temperatures are used during the growth, or as Cr^{3+} if high temperatures are employed. The luminescence of SnO_2 can be also modified by Cr doping, which leads to a new emission centered at 1.5 eV. Besides, a quenching of the orange emission (1.94 eV) associated with the presence of oxygen vacancies is promoted when high temperatures are used during the synthesis.

The characteristic dimensions of the Cr doped microstructures allows their use as optical microcavities [1]. Fabry-Pérot (FP) or Whispering-Gallery (WG) modes have been observed in the probed microstructures, which also show waveguiding behavior. According to our results, by selecting the appropriate thickness to width ratio, either FP or the combination of FP and WG modes can be obtained in the one structure, which allows to achieve the tunability typical to FP resonators and the properties of WGM. The possibility to choose among morphologies could be of interest for different applications, as for example tubes could be of interest due to the ability of filling them with other substances and use them as sensors or lab-on-chip devices. The analysis of the resonances allows us to estimate the refractive index of Cr doped SnO_2 with a value of $n = 1.98 \pm 0.25$.

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Advanced TEM Studies on Different Atomically Thin 1D and 2D Nanomaterials

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The recent advances in transmission electron microscopes (TEM) bring access to electron probes of one angstrom within energy resolutions of ~ 100 meV (even few tens of meV) even working at low acceleration voltages (60-80 kV) [1]. These performances offer new possibilities for probing the optical, dielectric and electronic properties of nanomaterials with unprecedented spatial information, as well as for studying the atomic configuration of nanostructures [1-3].

In this contribution, I will present a selection of recent works involving all these matters. These works will concern the study of the atomic structure & configuration of 1D and 2D atomically thin nanostructures (including nanotubes & graphene/graphene-like materials in pristine and hybrid forms) as well as the opto-electronic properties studies carried out via electron energy-loss spectroscopy (EELS) measurements [4-10]. These works will illustrate the excellent capabilities offered by the use of a Cs probe-corrected STEM, combined with the use of a monochromator, to study these properties within a very good spatial resolution.

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Satellite Event on Materials for Energy

Flexible solar cells on paper based substrates

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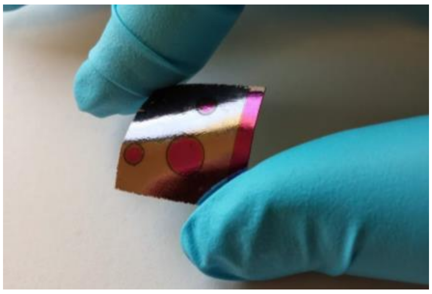
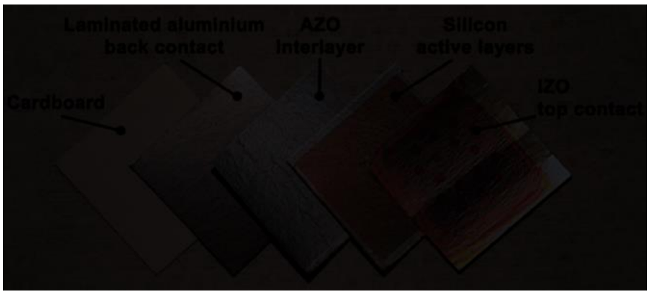
The next-generation of low cost flexible, disposable, portable and potentially wearable electronic systems will require the integration of energy power sources to turn them fully autonomous. For this reason, it is highly demanding to develop thin, lightweight, and flexible energy sources with various sizes and shapes and capable of being integrated with low cost consumer oriented systems.

Cellulose paper has excellent mechanical properties, such as flexibility and foldability, and it is a low cost, recyclable, and environmental friendly material. Due to these properties paper-based photovoltaic (PV) devices are the ideal power source for most of the low cost disposable electronic commodities. However, cellulose fibrous structure makes it quite challenging to fabricate good-performing inorganic PV devices like thin film silicon cells on such substrates. The advances presented here demonstrate the viability of fabricating thin film silicon PV cells on a paper coated with a cast-coating layer of a hydrophilic mesoporous (HM) material which gives it a smooth finishing. Such layer can, not only withstand the cells production temperature (150 °C), but also provides an adequate paper sealing and surface finishing for the deposition of the cell's layers. Using this concept solar cells with a 3.4% cell efficiency (with 41% fill factor, 0.82V open circuit voltage and 10.2mA/cm^2 short-circuit current density) were obtained [1]. Alternatively, thin film silicon solar cells were also demonstrated on paper based packaging material, used in the food and beverage industry, consisting of a multilayer of cellulose, polymer and aluminium. Solar cells with efficiencies of 4% and fill factor of 54% were obtained [2].

This work has opened the door to the use of paper as a reliable low cost substrate to fabricate inorganic PV cells for a plethora of indoors applications with tremendous impact in multisectorial fields such as the food, pharmacy and security.





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Electroluminescent Metal-Organic Frameworks based in host:guest or hetero ligand approaches

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Metal-Organic Frameworks (MOFs) have been recently used with success in photovoltaic devices and other clean energy applications, due to their semi-conductor behavior. These are promising results for the use of MOFs as light-harvesters and semi-conductors in solar and electroluminescence cells. Moreover, MOFs allow the introduction of light harvesting dyes with high electron-accepting behavior in their structure to leverage the performance.

In this communication we will report two cases where MOFs have been applied as active material in electroluminescence devices.

In the first case, we report the entrapment of perylene dianhydride molecules into MOF5 pores with strong interaction between host and guest, and with a remarkable electrolumincescence response. Optical microscopy, SEM, PXRD and fluorescence spectra clearly show the stabilization of isolated PDA molecules inside the MOF5 pore structure, after careful host activation. Laser flash photolysis reveals a strong interaction between perylene dianhydride molecules and MOF5 through changes in the charge separation state characteristic of MOF5. A electroluminescence cell was prepared using PDA@MOF5 as active material [1].

In the second case we report the preparation of a MOF containing an anthracene moiety. The reaction of 9,10-di(4-pyridyl)antracene and biphenyl.-4,4'-dicarboxilic acid and zinc nitrate under solvothermal conditions yields a microcrystalline powder. The obtained DPyA-MOF was characterised by single crystal X-ray diffraction, and its photophysical and electrochemical properties were studied [2].

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Oxidation kinetics of sintered SiC for solar receivers

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Concentrating solar power (CSP) is amongst the most promising clean energy for supplying the needs of electricity of our modern society. With respect to electricity generation, the major renewables (wind and solar) are both intermittent and diffuse. These are drawbacks that must be solved somehow. Indeed, to achieve a full development of CSP technologies, significant research efforts are still needed. In particular, solar receivers are one of the most critical system components of CSP technology.

Solar receivers must absorb the concentrated solar flux and transfer it to a given heat transfer fluid in an efficient way. For this purpose, they must operate under extreme working conditions, namely high temperatures in excess of 1000 ºC and steep temperature gradients. Under such conditions, the main degradation mechanisms imposed on the materials are thermal fatigue, corrosion and erosion (caused by mineral dust). From this perspective, materials used to construct such receivers need to be carefully selected in order to fulfil the requirements of such demanding application.

The most promising material is silicon carbide (SiC) owing to its dark colour, which makes it a good absorber, coupled with its high thermal conductivity. As yet, little data is available on the long-term ageing performance of such materials under extreme solar irradiation fluxes. In this respect, knowledge of the oxidation kinetics of candidate SiC materials is of crucial importance. Hence, the oxidation of a pressureless sintered silicon carbide in dry oxygen, at temperatures in the range of 900-1400 ºC, was investigated. Oxidation follows a parabolic rate law with an activation energy of 165 kJ mol^{-1} in the range 1100 to 1300° C, suggesting that the interstitial diffusion of oxygen molecules through amorphous SiO_2 is the rate-controlling mechanism. With increasing exposure time, the oxide film consists predominantly of cristobalite and a glassy phase which offers protection to the unexposed SiC substrate.

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Effective anisotropic etching of silicon wafers in temperature gradients – variation of surface topography and reflectivity with a specially designed apparatus

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The minimization of energy losses on silicon wafers intended for solar panel assembly is one of the fundamental tasks in production of efficient power units. Decreasing the reflection of electromagnetic radiation from silicon surfaces can be achieved by thin layer antireflective coating and/or surface texturing. Anisotropic surface texturing process of monocrystalline (100, 110 and 111) or polycrystalline silicon often utilizes acidic or alkaline solutions with various additives. Also quite complicated machinery with many moving parts is used. The aim of the study was to develop a special apparatus, allowing avoiding possible contamination of wafers during the etching process by using etching solution containing only potassium hydroxide and isopropyl alcohol and employing the so-called Bénard-Marangoni thermocapillar instability, where the main driving force for spontaneous self-organized liquid movement is the temperature difference between the bottom layer of the liquid and its open surface. Opposed to the situation where the etching medium and reaction by-product move randomly in the surface vicinity, the self-organized flow initiated by the temperature difference makes the etching solution to quickly change over the surface and no accumulation of reaction product at the surface occurs, thus not slowing the etching rate. Also, as the apparatus does not contain any moving parts, so the sources of possible contamination are greatly reduced, this is among the key aspects monitored in the silicon wafer processing industry. It was further proved, that the silicon wafer surfaces (orientation 100) etched in the apparatus exhibit significantly lower reflectivity in the visible spectrum compared to the original samples. The apparatus thus may allow for more rapid, efficient and ecological process of silicon wafer surface topography modification.

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High-temperature thermoelectric energy harvesting: materials and approaches

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Sustainable energy supply to the population based on environmentally-friendly and efficient technologies represents one of the major societal challenges in 21st century. One of the promising solutions is thermoelectric conversion of waste heat or solar heat into electricity, using sustainable and scalable devices, with self-sufficiency to enable mobile or remote applications. Theoretically, thermoelectric generation provides one of the most reliable ways for conversion, irrespectively of the source size and without using turbines, moving parts or producing CO_2, with potential applications in power plants, various industrial processes, incinerators, geothermal sources and for automotive waste heat recovery. Driven by a need to develop low-cost and thermochemically stable materials, oxide – based electroceramics are considered as a promising alternative to traditional thermoelectrics. Yet, ZT values obtained for the best-known oxide thermoelectrics are lower than those required by the most of potential applications. This work aims to demonstrate some new structural engineering and nanostructuring approaches for triggering high thermoelectric performance in donor-substituted strontium titanate- and zinc oxide- based materials. Particular emphasis is given to controlling the defect chemistry mechanisms and nanocomposite concept, as tools to decouple the electrical and transport properties and to promote higher conversion efficiency. The obtained results provide useful guidelines for both optimization of the electrical and thermal transport in known materials and identification of structural features, which allow flexible design of performing oxide thermoelectrics.

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Development of rigid polyurethane foam incorporating phase change material microencapsulated with calcium carbonate shell for thermal energy storage

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The use of phase change materials (PCMs) and rigid polyurethane foams (RPU) in building solutions and components to improve the thermal performance and to enhance the energy efficiency of the building is an up-to-date challenge. These two materials are widely used in buildings for thermal insulation and thermal storage purposes, respectively. Taking the joint advantages of the excellent thermal insulation performance of RPU foams and the thermal energy storage of the thermal storage capacity of PCMs, the development to RPU composite foams can be designed to function as a latent heat thermal energy storage (LHTES) system. The major aim of the present study is to improve the thermal characteristics of RPU foams that have been almost exclusively used for thermal insulation purposes but can also have find application as potential thermal energy storage component.

To overcome the low thermal conductivity of the RPU foam matrix, a method to prepare PCM microcapsules (mPCMs) based on paraffin core and calcium carbonate shell ($CaCO_3$) has been developed to enhance the thermal conductivity and thus achieve a more effective charging and discharging process. The mPCMs were synthesized using a self-assembly method and their chemical composition was confirmed by FTIR (Fourier transform infrared spectroscopy). Scanning electron microscopy (SEM) images demonstrated that the microcapsule samples exhibit a quasi-spherical morphology and that these microcapsules are constituted by nanoparticles agglomerates. The mPCMs exhibited a successful encapsulation ratio determined by the core/shell mass ratio, good phase-change performance with significant thermal storage capacity evaluated by dynamic scan calorimeter (DSC) testing. Thermogravimetric analysis (TGA) showed the thermal stability of paraffin inside the $CaCO_3$ shell.

The mPCMs were then incorporated in RPU formulations to yield composite foams containing 1.8 wt% of mPCMs. SEM images of the RPU composite foams allowed to assess whether the stirring process destroys the mPCMs and how those particles are dispersed into the RPU matrix. The influence of mPCMs incorporation into the RPU foams on the thermal and energy storage properties was evaluated by DSC.

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PCM emulsions for cold storage

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Water or aqueous solutions are the basis of low cost phase change materials (PCM) for cold storage in air conditioning, refrigeration or other application in cryogenics. However, these still show shortcomings or gaps between their actual properties and required selection ranges. Critical limitations include insufficient thermal conductivity to sustain high charge/discharge power and undue expansion/contraction on freezing, with negative impact on risks of mechanical failure of the storage system. The thermal response may also be affected by discontinuities at interfaces between encapsulating materials and the PCM. Thus, this work reports the preparation and characterization of emulsified PCMs, which were designed to minimize volume changes and to enhance thermal conductivity. Volume changes upon freezing and remelting are minimized by the opposite effects of contraction on sodidifying the organic phase and expansion on freezing the aqueous phase. The thermal response is also enhanced by additions of graphite platelets and promoting their self-organisation at the inorganic/organic interface. Surfactants and gelling additives are used to stabilize the emulsified PCMs and to retain the distribution of the conducting phase during repeated phase changes, without undue microstructural ageing.

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Manganese oxide nanostructured supercapacitor electrodes: size matters

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In the view of the development of novel functional materials, the suitable desired of one material, acting as support, can be combined with complementary convenient properties of a second material. In this context, atomic layer deposition (ALD) emerges as a highly suitable technique to elaborate 3D hybrid nanostructures which represent a promising direction for building binder-free supercapacitor electrodes. As a matter of fact, ALD is a unique technique for the deposition of conformal and homogenous thin films, even on 3D structures with large aspect ratio. ALD is based on a reaction between precursor materials, which are separated into successive surface reactions. In this manner, the reactants are kept separated and react with surface species in a self-limiting process, i.e. without the presence of a gas phase reactions. The conformal growth provided by ALD is a direct consequence of self-saturated surface reaction control. Inherent to the process, is the possibility to accurately control the thickness of the deposited film at almost atomic level simply by counting the number of deposition cycles.

Here, we will present an ALD approach for the deposition of manganese oxide for coating 3D arrays of carbon nanotubes without damaging the substrate geometry. As a result, these binder-free nanocomposite electrodes, with the incorporation of unique merits of each component, can provide a larger electrochemically active surface area and better electron transport, thus leading to noticeably improved cycling and rate performance. Several nanocomposite electrodes, with different manganese oxide thicknesses (i.e. different number of deposition cycles), were prepared and their electrochemical properties evaluated. It is anticipated that such 3D hybrid nanostructures have enhanced performance in supercapacitors application.

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Environmental friendly screen-printed electrodes for printed lithium-ion batteries

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Energy storage systems are increasingly needed, among others, to suitably manage the energy generated by environmental friendly energy sources, such as photovoltaic, wind and geothermal. Thus, efficient electrical energy storage systems are one of the main issues to resolve energetic challenges. The most widely used energy storage system are the lithium-ion batteries, with a market share of 75%.

Considering the high demand for small and light portable electronic devices (smart cards, RFID tags and remote sensors), printed batteries are an excellent alternative to conventional batteries because they are light, flexible and can be produced at large scale with low cost.

Very important issues in these batteries are safety, health and environment criteria. In this sense, the N-methyl-2-pyrrolidone, NMP, solvent, typically used for the fabrication of many of those batteries, should be substituted by a environmentally friendlier one.

In this work, new processable inks based on carbon coated lithium iron phosphate (C-LiFePO4, LFP) and graphite for cathode and anode, respectively, were developed with the help of a “green solvent” denominated by N,N’-dimethylpropyleneurea (DMPU). The properties of the electrodes were compared with films prepared with conventional NMP.

After 45 charge-discharge cycles, the inks with 2.25 mL of DMPU solvent and processed by screen-printing present 52 $mAh.g^{-1}$ at 2C for the cathode and 349 $mAh.g^{-1}$ at C/5 for the anode. The new inks presented in this work are extremely useful for the development of printed batteries with environmental friendly electrodes.

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Energy Storage Density of Bismuth Sodium Titanium Based Lead Free Relaxor-Ferroelectrics

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Relaxor-based ferroelectrics are potential materials for pulsed power capacitors with high energy density due to their high spontaneous polarization and low remanent polarization. Until now, the maximum energy density was reported for the lead-based relaxor $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ in the form of a thin film (~ 11 J/cm^3). Unfortunately, the numbers for bulk ceramics are much lower (2.73 J/cm^3). Moreover, lead is toxic, and there is need for lead-free alternatives. One of the alternatives is $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) – based compounds due to their high spontaneous polarization (> 30 µC/cm^2) and reversible weak ferroelectric and ferroelectric transition. The transition temperature for BNT lies > 100 °C and can be shifted close to room temperature by A-site the substitution without compromising the spontaneous polarization.

In this context, we have investigated the BNT – $NaNbO_3$ compounds with A-site substitution with different mol. % of Li ions to achieve high energy storage density. The ceramics were fabricated using the solid state mixing route. The ceramics show relaxor ferroelectric loops at room temperature with energy density up to ~ 0.7 J/cm^3, which can be attributed to the phase transitions produced by the chemical pressure that was induced by co-substitution on the A-site in BNT-based ceramics. The phase and microstructure of the ceramics were characterized using X – Ray diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively. Piezo Force Microscope (PFM) was used to investigate the localized domains in the ceramics. The present studies emphasis that the BNT based compounds are an attractive candidate for lead-free high power energy storage applications.

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Electrochemistry of Hydrogen Evolution in RTILs Mixtures

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As energy demands are growing, the efficient production of hydrogen (H_2) is of fundamental importance in addressing global energy issues, as well as in minimizing environmental effects of fossil fuels. Water electrolysis is an advantageous method because it is not dependent on fossil hydrocarbon sources and originates no carbon emissions. Additionally, the H_2 produced by this method is very pure, and can rely exclusively on renewable primary energy sources.

Industrial water electrolysis cells usually use metal-based electrodes and a potassium or sodium hydroxide solution as electrolyte. The relatively limited overall energy efficiency of electrolysis is in part related to the hydrogen evolution reaction (HER) and to the ohmic resistivity of the electrolytic bath. The low stability of the electrode materials and the low conductivity of the alkaline aqueous solutions are among the main technical problems with these cells. Additionally, gas bubbles must be effectively eliminated from the solution.

The use of room temperature ionic liquids (RTILs) in replacement of aqueous electrolytes or in mixture with conventional aqueous electrolytes has great potential to enhance water electrolysis efficiency because of their ability to modify the electrode-electrolyte interfaces by affecting the intermolecular interactions. RTILs are semi-organic salts composed entirely of organic cations and organic or inorganic anions at (or near) room temperature. Besides their wide range of fluidity, other interesting properties are high ionic conductivity, excellent thermal and chemical stability, high heat capacity and cohesive energy density.

In this work, small amounts of 1-ethyl-3-methylimidazolium-based RTILs were tested as additives to alkaline solutions for hydrogen evolution. HER kinetics was investigated by voltammetry and chronoamperometry experiments and the impedance of the system was assessed by electrochemical impedance spectroscopy (EIS). Electrochemical measurements were performed using a platinum foil electrode in 8 M KOH electrolytes containing 0, 1, or 2 vol.% of each of the tested ionic liquids. Polarization curves were obtained for all different electrolytes, and then Tafel analysis was performed and the main kinetic parameters were determined. Higher currents were obtained and the impedance measurements revealed a significant decrease of the overall impedance in the RTIL-added electrolytes. The promising results of this work show the beneficial effects of using small amounts of RTILs as electrolyte additives for hydrogen production.

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Electrical Properties of Pyrochlore Pr_2O_3-ZrO_2 System: A Defect Chemistry Approach

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Praseodymium zirconium solid solutions have been studied as an oxygen storage material, a potential cathode material for medium-temperature solid oxide fuel cells (SOFCs). Coprecipitation method was used to prepare $(Pr_{1.85}Zr_{0.15}Zr_2O_{7\pm\delta}$, $Pr_2Zr_2O_7$, and $Pr_2(Zr_{1.9}Pr_{0.1})O_{7\pm\delta}$. Electrochemical impedance spectroscopy was used to obtain electrical conductivity measurements as a function of temperature and oxygen partial pressure. Compared to the stoichiometric pyrochlore $Pr_2Zr_2O_7$, it was observed an increase of the ionic conductivity for both Pr- and Zr-rich pyrochlore compositions. These increases of conductivity were interpreted as oxygen vacancies and oxygen interstitial formation, respectively, for Pr-rich and Zr-rich compositions.

Assuming oxygen vacancies and interstitials concentrations fixed by the non-stoichiometry, the mobilities of these charge carriers were evaluated. All defect chemistry equilibrium constants were calculated by fitting (using the Levenberg–Marquardt numerical method) experimental data of the dependence of the conductivity as a function of the oxygen partial pressure obtained at isothermal conditions (1000, 900, 800 and 700°C).

Calculated thermodynamic data were used to propose a complete defect chemistry model for the pyrochlore Pr_2O_3-ZrO_2 system.

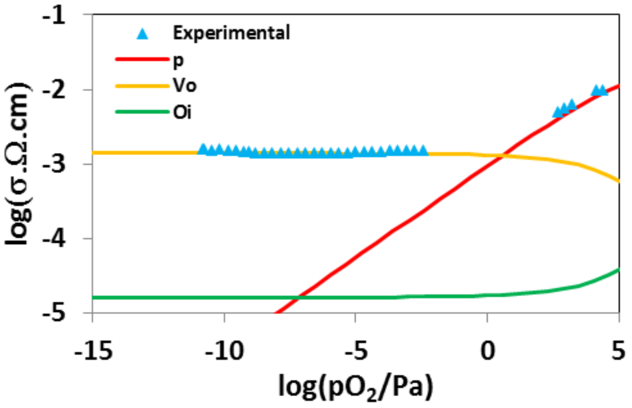

Figure 1. Oxygen partial pressure dependence for $Pr_2(Zr_{1.9}Pr_{0.1})O_{7\pm\delta}$.

Enhanced densification and improved chemical stability of ZnO-added $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte material for proton conducting solid oxide fuel cells

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$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) proton conducting electrolyte material was processed via solid state reaction method and ZnO was added in various wt. %. 1 wt. % of ZnO was found as the optimum amount for obtaining the maximum densification and a quite significant shrinkage of 24.23% was achieved. An increase in the grain size was observed with increase in the sintering temperature from 1300 – 1400 ºC with a maximum relative density of 99.1% at the sintering temperature of 1350 ºC. A maximum value of ionic conductivity of 13.25 x 10^{-3} S cm^{-1} at 600 ºC was achieved in humidified 5 vol% H_2/Ar atmosphere. The average value of the thermal expansion co-efficient (α) was measured to be 8.53 x 10^{-6} K^{-1} in the temperature range of 50 – 1100 ºC, which is close to the α value for Pr-based cathode materials. The chemical stability of ZnO-added BZCYYb sample in pure CO_2 up to 1200 ºC was found about 3 times higher than the blank BZCYYb (without ZnO), however still some small peaks corresponding to $BaCO_3$ and CeO_2 were observed in XRD pattern after chemical stability test. Hence, ZnO-added BZCYYb is a promising electrolyte material for fuel cell applications.

Nanostructured Bacterial Cellulose based composite anion exchange membranes for energy conversion

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Bacterial cellulose (BC) is produced by bacteria directly with a three-dimensional, cross-linked nano- and micro-fibrillar structure delivering excellent mechanical properties [1]. The effects of the exposition to alkaline and acid conditions typically found in Solid Alkaline Fuel Cells and Proton Exchange Membrane Fuel Cells were found to not impair the mechanical stability of BC. So, the use of the naturally formed mats of BC to produce nanocomposites, combining the enhanced thermo-mechanical behavior of BC with other polymers bearing functional groups capable of conducting ions, was recently proposed [2]. These composites membranes were synthesized through free radical polymerization of a polyelectrolyte inside the BC mats. Here, we propose a similar method to produce BC-based anion conductive "green" membranes that combine the thermo-mechanic characteristics of BC and the anionic conductivity of various quaternary ammonium containing polymers. The first anion conductor to be used, poly[2-(acryloyloxy)ethyl]trimethylammonium chloride (PAETACl), suffered a degradation through an alkaline hydrolysis mechanism as result of the electrophilic nature of the ester in this polymer. Stability was achieved by replacing the ester by an amide with reduced electrophilicity in poly(3-acrylamidopropyl) trimethylammonium chloride (PAPTACl). The nanocomposite membranes based on PAPTACl, free of defect and variable thickness within 80 µm - 400 µm, were thermally stable up to 200 °C, close to what is observed for pure BC. The storage modulus was close to 1 GPa, revealing that the viscoelastic behavior of BC is maintained. The in-plane anionic conductivity achieved 7.61×10^{-2} S.cm^{-1} at 94 °C / 98% RH, a value lower than the usually observed for typical proton conductive membranes, but a top figure for anion exchange membranes.

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Ph-m-SPEEKK ionomer and polysiloxane hybrid membranes for direct methanol fuel cells

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In the proton exchange membranes (PEM) area, a perfluorinated polymer with sulphonic acid groups named Nafion is the reference today. The advantages of Nafion are a high proton conductivity and good thermal and mechanical stabilities [1]. However, Nafion experiments dehydration at about 100 °C diminishing the membrane conductivity, the diffusion coefficient to MeOH (D) is relatively high and it also has an elevated cost [2]. A promising alternative are sulphonated aromatic hydrocarbons such as the poly(aryl ether ketone) family [3].

In this work, a sulphonated poly(aryl ether ether ketone ketone) (Ph-m-SPEEKK) was synthesized and characterized by FTIR, NMR and elemental analysis. In attempt to improve its properties such as, higher proton conductivity and lower D to MeOH, an inorganic-organic phase based on polysiloxanes was added. The polysiloxane phase (PSP) was prepared using a sol-gel process, with PDMS as oligomer and phenyltrimethoxysilane (PTMS) or tetraethoxysilane (TEOS) as crosslinkers. Hybrid membranes (HMs) were obtained by the solvent casting method adding the PSP in 10, 15 and 20 w/w% to Ph-m-SPEEKK dissolved in DMSO.

The ion exchange capacity (IEC), water uptake (WU), proton conductivity (30 and 80 °C with 50-95% RH) and D to MeOH (25 and 60 °C) of the membranes were determined. Results showed that the HMs prepared present notorious differences in the transport properties. HMs with TEOS showed diminished transport properties, proton conductivity (83.4 mS/cm at 80 °C and 95% RH) and D to MeOH (27 x10^{-7} cm^2/s at 60 °C), while the HMs with PTMS showed enhanced transport properties, proton conductivity (158.6 mS/cm) and D to MeOH (35 x 10^{-7} cm^2/s) as compared to those of membranes prepared with the pristine sulphonated polymer (94.2 mS/cm at 80 °C and 95% RH, 35.2 x 10^{-7} cm^2/s at 60 °C) These effects are probably due to a change in the nanostructure of the membrane. HMs with higher proton conductivity and lower transport of MeOH than Nafion 117 (87.6 mS/cm at 80 °C and 95% RH, D= 50 x 10^{-7} cm^2/s) were obtained.

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Materials and renewable energy

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An overview on the subject of materials and renewable energy, mainly from the research point of view will be carried out. Energy and materials are nowadays driving science and technology. There is a search for a cleaner, cheaper and more efficient energy production and this is obviously related with the development of new and innovative materials. As energy is a top priority materials research can enable Europe to meet its future energy and climate goals. The importance of raw materials for the energy sector and the future of advanced materials for low carbon energy are addressed. Materials based solutions to the energy problem and guidance on research in this field are also the aim of this work.

Different environmental and supply concerns related with fossil fuels have driven scientists to explore new technological solutions looking for alternative means for energy production and storage. New and innovative materials are in the core of the new findings in this field

Without continuous innovation in advanced materials the performance improvement, cost reduction and extended life time of energy technologies would not be possible

Solar modules, wind turbine blades, batteries, wave power components, amongst others, all rely upon advanced materials and, e.g. the efficiency of solar modules needs to increase, the weight of turbine blades must be reduced, batteries need longer life cycles and, in general, corrosion resistance must be improved.

The Materials Information System (MIS), established in 2014, provides information on materials used in the SEP-Plan technologies. Sixty metals were identified as vital for the different energy technologies covered by the SET-Plan.

A wide range of advanced materials in sufficient quantities will be needed to modernize energy installations. Even though several years of Research and Innovation (R&I) can be taken before the development and market uptake of these materials as every-day components.

A technical roadmap was published by the European Commission to establish what materials are needed in order to drive the next generation power sources or to make buildings more efficient.

A study published in 2011, called Critical Metals in Strategic Energy Technologies revealed potential bottlenecks to the deployment of LCEs (nuclear fission, photovoltaics (PV), wind, bioenergy, carbon capture, storage and grids) related with shortages of certain metals. So a European Innovation Partnership on Raw Materials was set up in 2012.

Also included in the field of materials and energy is the production and test of materials using energy, as, e.g. the use of high temperatures obtained with Concentrated Solar Energy.

The development of new materials is intimately related with the development and evolution of low carbon energy technologies. Several research lines are being followed and new ones must be started.

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Symposium A - Functional Materials

Bio-inspired materials and materials for healthcare applications (A1)

Molecularly Imprinted Biodegradable Magnetic Responsive Particles Based on Poly(2-pyrrolidone)

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Molecular imprinting of synthetic polymers is a process where a monomer is polymerized in the presence of the target analyte (the imprint molecule, IM), which acts as a molecular template. The monomer initially forms a complex with IM. After polymerization and subsequent removal of the latter, binding sites upon the polymer surface is revealed that are complementary in size and shape to the analyte molecules. In that way, a molecular memory is introduced into the polymer, which is now capable of rebinding the analyte with a very high specificity. Thus, the process of molecular imprinting can be used to create the central part of the modern biosensor, *i.e.*, their recognition element that identifies a specific analyte [1].

In this work as synthetic polymer poly(2-pyrrolidone) (PPD) was used and as a IM – bovine serum albumin (BSA). BSA is frequently used peptide molecule to model the enzymes. PPD was selected because of the following reasons: (i) it is a robust semicrystalline polymer possessing all typical for polyamides stability to extreme environments, such as the presence of acids or bases, organic solvents, or high temperatures; (ii) PPD is biocompatible an biodegradable; (iii) PPD contains N-H and C=O functional groups capable of non-covalent interaction (self-assembly) with the peptide BSA molecule.

The main idea of this work was to combine the molecular imprinting with microencapsulation aiming at the preparation of smart biodegradable microparticles susceptible to external magnetic fields and bearing recognition sites sensitive to BSA as target analyte. For this reason, activated anionic polymerization of 2-pyrrolidone was performed in the presence of Fe nanoparticles and BSA. The use of a special catalytic system permitted the process to be carried out at 40ºC so as to avoid denaturation of IM. The conversion of the polymerization process reached 60%. Subsequently, the BSA was removed to produce the molecularly imprinted particles (MIP). MIP were characterized by various microscopy, spectral, X-ray and thermal techniques. The selectivity of MIP toward BSA was found to be increased by 56% as compared to PPD particles without molecular imprinting by means of specially designed UV/VIS spectroscopy method. The presence of magnetic cores in MIP allows their easy and fast removal from the analytic system. The general conclusion is that the MIP obtained by the new combined method have potential for future biomedical applications.

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Chitosan/Chitin films with imprinted liquid crystalline architecture

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Nature has always delighted us with its ability to evolve highly specialized biological systems based on straightforward bottom-up self-assembly processes [1,2]. The specific design of nanostructures and their assembly into hierarchical larger macrostructures allows the unique combination of features that are only virtually available in natural tissues and are far more developed than those currently achieved by man-designed materials [3]. Inspired by chitin based hierarchical structures observed in arthropods exoskeleton, this work reports the capturing of chitin nanowhiskers' chiral nematic order into a chitosan matrix in the form of films (Fig.1).

Highly crystalline chitin nanowhiskers (CTNW) with spindle-like morphology and average aspect ratio of 24.9 were produced by acid hydrolysis of chitin. CTNW were uniformly dispersed at different concentrations in aqueous suspensions. The suspensions liquid crystalline phase domain was determined by rheological measurements and polarized optical microscopy (POM). Chitosan (CS) was added to the CTNW isotropic, biphasic and anisotropic suspensions and the solvent was evaporated to allow the formation of films [4]. Films' morphology and mechanical properties were explored and a strong correlation between experimental results and theoretical model was established. By playing on the ratio chitin/chitosan two different layered structures, one formed by chitosan layers induced by the presence of chitin and another formed by chitin nanowhiskers layers could be obtained, allowing the tunning of materials' mechanical properties.

Transferring natural system principles into a synthetic application is a hard process requiring precise organization of biomaterials from the nano to the macro level. In this work the results testify that the hybrid films exhibit the imprint of the liquid crystalline state of matter achieved by the CTNW self-assembly, mimicking chitin's natural arrangement found in living tissues.

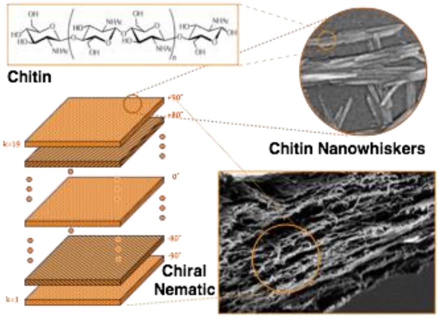

Fig.1 – Chitin film exhibiting a Bouligand like architecture.

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Formation of poly(lactide) stereocomplexes in blends with a cholinium ionic liquid

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Aliphatic polyesters represent a large part of biodegradable polymers and among these, poly(lactic acid) (PLA) appear to be one of the most attractive because of its availability and biodegradability [1]. A great variety of techniques and additives have been evaluated to improve the physicochemical properties of PLA and enlarge its range of application fields [2]. In this study we report a novel method to produce poly(lactic acid) (PLA) stereocomplex (SC) crystallites from high molecular weight PLA by incorporation of choline dihydrogen phosphate ([Ch][DHP]) ionic liquid into the PLA matrix at room temperature. The morphology of membranes with 5 wt.% and 10 wt.% [Ch][DHP] consists of PLA microspheres with enhanced crystallinity and *ca*. 50-60 μm in diameter, formed due to the PLA/[Ch][DHP] immiscibility. Combined results of X-ray diffraction, Fourier transform infrared spectroscopy and differential scanning calorimetry confirm the formation of the PLA SC crystals. The electrical conductivity of these membranes measured by impedance spectroscopy is in the range $6x10^{-7}$– $4x10^{-6}$ Scm^{-1}, with the highest values being obtained for samples with 10% choline and at 98% high relative humidity. On the other hand, piezoresponse force microscopy and atomic force microscopy revealed a new phase with enhanced piezoelectric properties at the microsphere interfaces, which is directly related with the formation of SC crystalline domains. These novel biomembranes provide a novel, cost-effective and faster synthetic method to produce PLA SC and reinforce the potential of this new morphology to produce soft piezoelectric mats.

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Digital Microfluidics Devices for Nucleic Acid Amplification

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Diagnostic tools have met a rising interest in the scientific community, particularly regarding the transition of laboratory diagnostics to point-of-care (POC). Particularly, Digital Microfluidics (DMF) has recently emerged as an innovative technology with enormous potential for POC applications, since it allows individual maneuvering of micro- to picolitre droplets over an electrode array, thus enabling micro-scale reactions.

In this work, we demonstrate the successful design of DMF devices for nucleic acid amplification, allowing rapid detection of common proto-oncogene DNA sequences. The DMF chip is fully transparent and presents several unconventional features regarding other DMF devices. As can be seen on Figure 1, the T-shaped DMF chips include zig-zag electrodes, which facilitate droplet movement. All samples are inserted in the chip through drilled ports on the top plate, by using a mere pipette, and reaction products are withdrawn in the same way, allowing the production of closed devices. A specially designed temperature control system assures temperature control and stability within the chip.

We will present evidence of low concentration target DNA detection in less than 1 hour, for □L reaction volumes, with higher amplification efficiency than the bench-top counterpart.

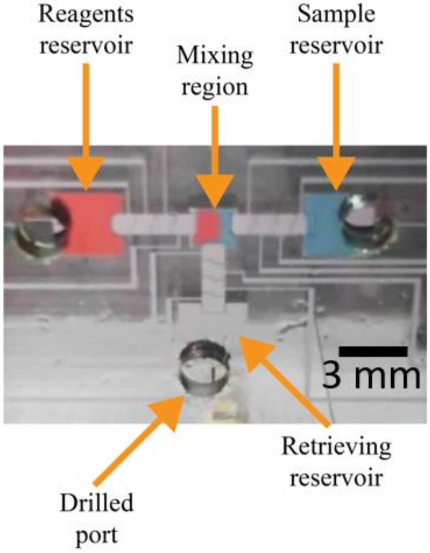

Figure 1: DMF device layout, with identification of the main elements that comprise the chip.

A dual-crosslinking strategy to design biofunctional pectin hydrogels for extrusion bioprinting

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Pectin is a structural polysaccharide extracted from the primary cell wall of plants that has received increased attention for tissue engineering, due to its biocompatibility, biodegradability and mild ionic gelation. In this study, we explored the ionic gelation ability of pectin to design biofunctional and dual-crosslinked pectin methacrylate macromers for extrusion bioprinting.

Citrus pectin was modified by the introduction of methacrylate groups, yielding photo- and ionic-crosslinkable derivatives. The viscoelastic and rheological properties of solid hydrogels and prepolymer solutions, respectively, were evaluated using a strain-controlled rheometer. The polymer was functionalized with a cell-adhesive peptide through thiol-Michael chemistry to allow cell anchorage. Bioprinting was performed in a Regemat3D system using pectin derivatives loaded with dermal fibroblasts, photocrosslinked by the exposure to UV light, and cultured for 14 days.

Pectin derivatives formed photocrosslinked solid hydrogels under cytocompatible conditions, allowing the direct incorporation of fibroblasts. Cells remained viable and metabolically active within the hydrogels in a matrix-stiffness dependent manner. The biofunctionalization of pectin with cell-adhesive peptide supported cell spreading. The ionic gelation ability of pectin was explored to tailor the viscosity for bioprinting, allowing the printing of cellular 3D structures with high levels of shape fidelity. After printing, the hydrogel constructs were photocrosslinked for shape maintenance, supporting cell viability and the deposition of extracellular matrix components. Biofunctionalized pectin hydrogels represent a promising system in the development of bioinks for the bioprinting of cell-laden hydrogels.

This work was financed by European Regional Development Fund (ERDF) through the COMPETE 2020 - Operational Programme for Competitiveness and Internationalization (POCI), Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, and Portuguese funds through Portuguese Foundation for Science and Technology (FCT) in the framework of the project Ref. PTDC/BBB-ECT/2145/2014. Ruben F. Pereira, Aureliana Sousa and Cristina C. Barrias are grateful to FCT for the doctoral grant SFRH/BD/91151/2012, postdoctoral grant SFRH/BPD/90047/2012 and research position FCT Investigator (IF2013), respectively.

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In vitro and *in vivo* assessment of Pectin Hydrogels for Skin Regeneration and Repair

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Hydrogels are being used as a tissue engineering tool for many years [1], studies describe their potential as wound healing adjuvant [2]. Hydrogels comprise a mixture of hydrated polymers: water makes up to 90% of their weight. They appear to have the capacity to effect selective, non-surgical debridement. Different formulations result in a varying ability to donate water and absorb fluid from the wound [3] however pectin hydrogels remain largely unexplored. We are investigating the properties and the potential of Pectin hydrogels [4] as a basis for a full system combining properties of wound healing dressing and skin cells carrier. The interaction between these hydrogels and cells namely the production of ECM components is also being addressed as well as the in vivo performance as full-thickness wound dressing. The main goal of this work is the investigation of the properties and potential of Pectin hydrogels as a basis for a full system combining properties both as of wound healing dressing and as skin cells carrier.

An internal gelation strategy was adapted from alginate to prepare pectin hydrogel matrices by internal gelation. The $CaCO_3$/GDL molar ratio was set at 0.5 (ret=0.5), and the gelation time allowed for 30 min. to occur to maintain fibroblast viability. In vitro generated pectin matrices with the different cell types were assessed by confocal microscopy. Full-thickness skin dorsal wounds were performed using a cylindrical biopsy punch and pectin hydrogel was applied to the wounds of male Wistar rats. Standard histological protocols were used along the different timepoints to evaluate wound closure and regenerated skin characteristics.

We have performed comparative studies on the interaction between these hydrogels and cells, cell-cell crosstalk and production of ECM components. Our results show that these hydrogels are a suitable 3D microenvironment for primary Human Neonatal Dermal Fibroblasts (HNDF), which are able to survive and proliferate for long *in vitro* culture periods embedded in hydrogels of the various pectins formulations. Fibroblasts are also able to assemble an intricate ECM mesh since the initial steps of 3D culture with several ECM components (fibronectin, elastin, laminin, collagen IV, collagen I).

The high in vivo biodegradability of pectin matrices presents pectin as a promising material for skin regeneration applications. We performed in vivo wound healing assays in Wistar rats showing no adverse host reaction and full pectin biointegration. Furthermore, complete regeneration of full-thickness wounds was also achieved.

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Effect of poling state of piezoelectric poly(vinylidene fluoride) films on C2C12 myoblast differentiation for skeletal muscle tissue engineering

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Skeletal muscles, comprising between 40-45% of an adult human body mass, are responsible for generating voluntary movement, postural support, breathing and locomotion. Severe injuries resulting in a muscle mass loss can lead to extensive and irreversible loss of muscle function [1]. In this sense, tissue engineering (TE) and regenerative medicine are growing fields of interest due to promising results in regenerating tissue functions [1]. Adhesion, proliferation and differentiation of specific cells can be promoted and/or improved by the use of active materials. In particular, piezoelectric materials allow incorporating electrical and mechanical stimuli to the cells. This is a recent paradigm with large potential in TE applications [2]. Further, many body tissues are subjected to varying mechanical loads, such as muscle [3], and the charge surface can stimulate cell response. In this sense, the use of polymer based electroactive materials capable to mimic mechanical and electrical biological cues emerged as a novel approach for TE applications.

Poly(vinylidene fluoride) (PVDF) is the biocompatible polymer with the largest piezoelectric response. Thus, piezoelectric polymers proved to be able to induce surface transient charge and induced a higher cell growth and differentiation compared with the non-piezoelectric controls [4]. This work reports the influence of the substrate polarization of electroactive β-PVDF on C2C12 myoblast cells differentiation under static conditions. C2C12 were cultured on different β-PVDF film surfaces(non-poled, “poled -” and “poled +”) and C2C12 differentiation was determined using a qualitative indirect immunofluorescence detection of the myosin molecule. It is demonstrated that charged surfaces improve myoblast cell differentiation and the maturation index of myotubes(five or more nuclei) is higher in the charged samples with differentiation medium. Therefore, the potential application of electroactive materials for muscle regeneration is demonstrated.

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Extracellular electrical recordings using poly (L-lactic) acid coated electrodes

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Poly (L-lactic) acid (PLLA), a semi-crystalline synthetic polymer, is a promising material for bone tissue engineering due to its particular properties combination namely biodegradability, biocompatibility and piezoelectricity.

In this contribution gold microelectrode arrays coated with thin layer of PLLA fibres were used to record electrophysiological signals from autonomous cardiac contractile cells present in embryoid bodies (EBs) and from zebrafish hearts. The goal is to make use of the PLLA piezoelectric properties to detect ultra-small mechanical forces generated by the cell contractile activity.

Fig. 1 shows a set of periodic electrical current pulses recorded using a PLLA coated electrode. The spikes corresponds the beating frequency of a zebrafish heart placed on top of the PLLA based electrode. Periodic burst of small electrical oscillations were also detected using PLLA films. We propose these oscillations are caused by mechanical forces generated during the cardiac beating. These findings seem to confirm the piezoelectric behaviour of PLLA fibres.

The signals generated in the piezoelectric film were record by measuring the displacement current across the interfacial double-layer (Helmholtz layer) established at the PLLA/cell culture medium interface. This method is extremely sensitive and allows the detection of ultra-week electrical signals (few pico-amperes) with a signal-to-noise ratio that can reach values higher than 30.

PLLA coated electrodes were also evaluated as piezoelectric stimulators for zebrafish bone-derived cell lines. Preliminary results are reported.

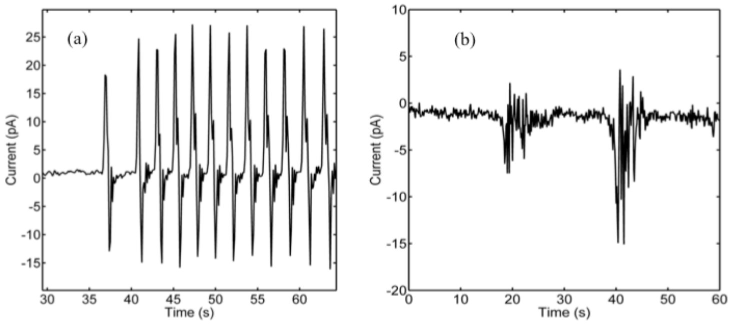

Fig. 1 (a) Periodic cardic beat of a zebrafish heart recorded *in vitro* using gold electrodes coated with a thin PLLA film, (b) burst of electrical oscillations.

$Ti_{1-x}Ag_x$ and Ag-TiN_x coatings deposited on PVDF substrates for sensors applications

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Electroactive polymers are the most interesting class of polymers used as smart materials in various applications, such as the development of sensors and actuators for biomedical applications in areas as smart prosthesis, implantable biosensors and biomechanical signal monitoring, among others.

The aim of this work was the development of multifunctional coatings on a polymeric base substrate for biosensor applications. The coatings were deposited by magnetron sputtering on polymers based sensors and the different processing conditions allowed to obtain two different systems: $Ti_{1-x}Ag_x$ with different Ag/Ti atomic ratio and different Ag-TiN_x samples with increasing N content. These electrodes were deposited at room temperature on poly(vinylidene fluoride), PVDF. Only on Ag-TiN_x electrodes it was possible to found Ag clusters.

Sheet resistivity values showed a typical behavior of a binary alloy system for the $Ti_{1-x}Ag_x$ series and for the Ag-TiN_x series, increasing nitrogen flow lead to lower sheet resistivity values than in the sample without nitrogen. Piezoelectricity of the different samples of $Ti_{1-x}Ag_x$ series presented similar values, but for the Ag-TiN_x series, the increase of nitrogen flow leads also to a decrease of the piezoelectric response. Despite this behavior, it was possible to conclude that the deposition conditions do not significantly affect the piezoelectric response of the polymer which maintain its suitable characteristics for sensor applications.

The mechanical and piezoresistive performance of the two series was assessed by uniaxial stretch tests and electrical resistance variation measurements during mechanical stimulus, respectively. It was possible to conclude that all electrodes show piezoresistive properties.

The antimicrobial activity of samples from both series was assessed by agar diffusion method (Halo test). Only the Ag-TiN_x series presented antibacterial activity, promoted by the Ag clusters.

Osteogenesis was also evaluated using MC3T3 osteoblastic cells. The results indicated lower cells attachment on the Ag-TiN_x electrodes compared with the $Ti_{1-x}Ag_x$ electrodes. The same behavior was observed for proliferation and differentiation tests.

So, as main conclusion, a multifunctional electrode was achieved with antibacterial activity, which at an early stage does not promote animal cells adhesion and it still has proper electrical and mechanical properties. Further, it preserves the piezoelectric response of the polymer when deposited on PVDF and shows itself suitable and useful piezoresistive response for sensor applications.

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Thin Film Nickel Resistance as Temperature Sensor for Application in Neuronal Electrodes

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Neuronal electrodes have been probing a variety of neural circuits so the scientific community can improve its knowledge about several brain diseases and disorders. Recording and stimulation of brain networks have already reached widespread clinical application. Indeed, deep brain stimulation has proved to show beneficial effects in a variety of neurological conditions, such as depression, obsessive compulsive disorder, chronic pain, Parkinson's disease, epilepsy, essential tremor, dystonia, Tourette syndrome, blindness, deafness and spinal cord injuries. More recently, optogenetics has shown potential in selectively controlling dysfunctional circuits throughout optical neuromodulation, and therefore also has been proposed to assist several diseases and neuropsychiatric disorders. Optogenetics serves of neuronal electrodes with optical stimulation capability, usually called optrodes. Optrodes with optical stimulation achieved through light emitting diodes (LED's) are in development in several groups. LED's presents a possible hazard to neuronal tissue because the heat produced, which could damage the neuronal tissue.

This work pretends to monitor the neuronal tissue temperature in order to avoid neuronal tissue damage. A thin-film nickel (Ni) resistance temperature detector (RTD) was fabricated for integration in an optrode. The RTD is composed by two main parts, the pads in aluminum (Al), and the resistor filament in Ni. A silicon wafer with a thin layer of silicon oxide (to ensure electrical isolation) was used as substrate. Both Al and Ni materials were deposited by electron beam technique. The characterization of the sensor was made in a controlled environment capable of increasing its inner temperature. A range between 0 ºC to 100 ºC with increments of 5 ºC were used to characterize the sensor and determine the temperature coefficient of resistance (TCR), so we could trace a direct association between the resistance and the correspondent temperature. A 4-wire configuration was used to measure the resistance, since long cables were used to connect the sensor and the data acquisition board (outside of the controlled environment). An extra Ni sample was deposited at the same time of the sensor to measure the thin-film resistivity. Ni thin-film resistivity was also measured at different temperatures to determine the resistivity evolution with the temperature. The resistivity measurements was determined by Van der Pauw method.

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Antibiofilm properties of ZnO-based coatings in resorbable metallic biomaterials

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In a growing older society, where immune compromised patients are increasing, there is an urgent need to find new solutions to overcome medical device-related infections. In this quest, prevention is the key point. Antibiofilm surfaces can prevent the formation of microbial biofilms and consequently avoid infection spreading.

Zinc oxide, known for a long time for its antimicrobial properties, is a promising candidate for the functionalization of biomaterials surfaces towards antibiofilm properties. So far, the majority of the antimicrobial studies have addressed the effect of free ZnO on planktonic microbial cells (free cells), with limited studies addressing such effect on microbial biofilms, a much more resistance form of microbial infections than their planktonic counterparts.

In this sense, nano and micro sized ZnO-derived coatings were developed on Zn surfaces and their antibiofilm properties addressed against important pathogenic bacterial and fungal species: *Staphylococcus aureus*, *Candida albicans* and *Candida parapsilosis*.

The results showed a reduced biofilm formation of these three pathogenic species on the nano sized ZnO-derived coating while only *C. parapsilosis* had a reduced biofilm formation on the micro sized ZnO-coating. Morphological alterations on the microbial cells were evidenced by the presence of buds on their surfaces. These buds, correlated with the formation of ZnP-derived compounds, seem to result from the degradation of these resorbable biomaterials. An increased degradation rate observed for ZnO coated Zn, when compared with bare Zn, yielded a biomimetic layer rich in hydroxyapatite, an important CaP-derived bone analogue that may contribute for a decreased bone implant rejection. The mechanical disruption caused by pathogenic microbes on both the nano and micro sized ZnO-based coatings, and the differential degradation observed on these ZnO coated Zn surfaces suggests that a complex antibiofilm mechanism is laying behind ZnO coatings. This intricate antibiofilm effect goes far behind the simplistic antimicrobial of free ZnO particles.

By shading some light on the ZnO antibiofilm properties, novel and efficient ZnO-based coatings can be design for an improve resilience of resorbable metallic biomaterials to important implant-related infections.

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Deposition of ZnO nanoparticles by magnetron sputtering onto tantalum nanostructures

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Dental implants are prone to failure as a result of biological complications, such as peri-implantitis disease, which is characterized by the inflammation of the soft and hard tissues adjacent to the implant surface [1]. This disease is caused by the bacterial adhesion and consequent biofilm formation onto the implant surface, which delays the osseointegration of the implant [2]. In this sense, to reduce the appearance of bacterial infections, this study proposes the incorporation of antibactericidal zinc oxide nanoparticles on tantalum nanostructured surface.

Tantalum oxide nanostructures (Ta_2O_5) were obtained by anodizing a Ta sheet in 14.6 M H_2SO_4:0.73 M HF, during 90 seconds, at room temperature with applied potencial varying between 25V and 50V in order to obtain different pore sizes. Thereafter, ZnO NP's were deposited onto silicon wafers and the Ta_2O_5 nanostructures by DC-pulsed magnetron sputtering, at non reactive mode, with a highly pure (99.99 %) zinc target. The discharge pressure, deposition time and the substrate bias voltage were carefully controlled to attain the desired distribution and shape of the ZnO NP's.

Eletron microscopy was used to characterize the NP's morphology, physical and chemical properties. On the other hand, zinc ions release and surface antibacterial activity was determined by inductively coupled plasma and halo test (zone of inibition - ZOI), respectively. The deposition results reveal a Volmer-weber growth of ZnO NP's on silicon substrates at 6 Pa, during 60 seconds without application of substrate bias voltage. However, at the same deposition conditions a Stranski-Krastanov growth of ZnO NP's onto Ta nanostructures was detected. This fact can be explained by the different surface topography and surface properties between the silicon and the Ta nanostructured substrates [3]. Furthermore, redistribution of the ZnO nanoparticles was obtained by applying a bias voltage due to a back-sputtering process, which was evidenced in the nanostructured Ta.

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Efficient upconversion in Yb:Er:NaT(XO_4)$_2$ thermal nanoprobes intended for biomedical applications

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Yb and Er codoped NaT(XO_4)$_2$ (hereafter Yb:Er:NaTX; T = W, Mo and X = Y, La, Gd or Lu) nanoparticles (NPs) prepared either by coprecipitation (ultrasmall diamond shaped 5-7×10-12 nm^2) or by solgel (near to nanospheres with diameter 50-80 nm) have been synthesized for the purpose of upconversion (UC) ratiometric nanothermometry, based on the thermal change of the intensity ratio of $^2H_{11/2}$ and $^4S_{3/2}$ UC Er emissions. The Yb and Er compositions to optimize the UC output have been determined as 20-25 at% and ≈5 at%, respectively. On the basis of bulk materials, the green UC yield of these compounds is comparable to that of the widely used Yb:Er:β-NaYF$_4$ one, despite the much larger cutoff phonon energy of the formers. In fact, the UC yield of Yb:Er:NTX materials increases with temperature up to 400 K while the UC yield of Yb:Er:β-NaYF$_4$ decreases monotonously above room temperature, thus the application of Yb:Er:NaTX optical probes is particularly suitable for the temperature window of interest for biomedical applications (≈ 293-317 K/ 20-44 ºC). Such different spectroscopic behavior is attributed to a phonon assisted $^4F_{9/2}\rightarrow{}^4G_{11/2}$ Er^{3+} excitation which quenches the red UC ($^4F_{9/2}\rightarrow{}^4I_{15/2}$), feeding the green one. It has been determined that at 317 K the thermal sensitivity (S) of Yb:Er:NTX compounds is in the $S = 88\text{-}124 \times 10^{-4}$ K^{-1} range, i.e. it is up to 3.5 times larger than that of Yb:Er:β-NaYF$_4$ ($S = 34 \times 10^{-4}$ K^{-1}), being so far the record value for this type of optical thermometers.

Mesenchymal stem cells (MSCs) have been cultured in medium containing water dispersions of TWEEN80 modified ultrasmall NaGd(WO_4)$_2$ NPs. It has been evidenced that the NPs are incorporated into the cells without deterioration of their metabolic activity after 72 h of incubation with up to 10 mg of NPs per ml of culture medium. Thanks to the ability of MSC to engraft to tumoral tissue, the aim of these cultures is to use MSCs as NP vehicles to deposit the nanothermal sensors into tumors without the need of NP surface functionalization. Due to the huge surface to volume ratio of ultrasmall UCNPs their fluorescence quantum yield decreases by three orders of magnitude with regards to bulk, hampering their optical detection. This UC quenching is reduced in the larger solgel prepared NPs, however the size increase may compromise their distribution in the body. In order to learn about the size limits for efficient NP body distribution, we have perfused 25at%Yb:5atE%r:NaLu(MoO_4)$_2$ NPs in a mouse and we have imaged them with fluorescence lifetime and multiphoton microscopies. It is shown that NPs with size in the 50-80 nm range and likely their aggregates reach all mouse organs, although only the smallest ones are able to reach the brain.

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Anisotropic calcium carbonate particles in vaterite phase: synthesis and applications

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Development of theranostic micro- and nano objects, which allow to do a quick diagnostics and can and provide a appropriate treatment of diseases, will be an important step to the personalized medicine. However, there are just limited number of structures which can combine a drug delivery and sensing function. One of the perspective molecules detection method is the surface enhanced raman spectroscopy, provided by plasmonic resonance nanoparticles.

For this reason the synthesis of nanoparticles in the matrix of perspective drug carrier will give a nice opportunity to add the additional sensor properties.

In our work we use as matrix inorganic calcium carbonate porous particles. The novel sythesis method of such particles allow to formate the porouse structure with various size and shapes like spherical ellipsoidal, star-like with the size range from 400 nm till microns. The biocompatibility, easy production and cheapest made these structure perspective drug delivery systems. We developed in situ synthesis of the silver nanoparticles in the matrix using the silver reaction: reduction of the silver from tollens reagent. The limited volume of the matrix as well as the reaction time and reagent concentration) has strong influence to the silver nanoparticles size and shape.

We demonstrated the possibility to control size of the silver. Such methods of the particles synthesis allow to provide cheap nanoparticles in large amount, which will be stabilised by external matrix of containers.

For demonstration a wide range of such containers applications as drug system the enzyme alkaline phosphatase (ALP) was encapsulated to study payload release dynamics. Furthermore, it is responsible for mineralization of bone tissue in vivo. Hence, ALP-loaded vaterite could be applied for bone regeneration. In addition, ALP has been applied as an anti-inflammation drug to combat certain diseases.

We believe that such decorated with silver nanoparticles microspheres can be used for optical based detection of molecules, as well as a reservoir for the loading of a payload. The dual functionality calcium carbonate microspheres can be used for theranostics.

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The effect of porosity on osteogenic differentiation of hMSC in biphasic calcium phosphate scaffolds fabricated by robocasting

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The strategies to regenerate bone include the use of scaffolds with suitable 3-D porous structures to act as temporary templates. Porosity is necessary for bone tissue formation since it allows migration and proliferation of osteoblasts and mesenchymal stem cells, matrix deposition in the empty spaces, as well as vascularization. Therefore, pore size and pore size distribution as well as pore interconnectivity play critical roles in bone formation *in vitro* and *in vivo*. Manufacturing biocompatible scaffolds with suitable architecture (e.g. geometry, size, and pores' spatial distribution) and providing an appropriate microenvironment for bone cells have been the major obstacles in Tissue Engineering and constitute some of the greatest challenges in this area. Robocasting is a direct-write assembly (DWA) technique that allows the production of scaffolds with customized shape and predefined, reproducible internal morphology, according to a computer design, without the need for subsequent machining.

In the present study, diverse macroporous scaffolds have been prepared by robocasting, using biphasic calcium phosphate [hydroxyapatite (HA)/β-tricalcium phosphate (β-TCP)] doped with strontium and zinc as raw materials. Concentrated fluid suspensions were obtained by dispersing the powders in aqueous media using a suitable dispersant and a binder. The addition of flocculating agent drastically changed the rheological properties of the system to obtain inks with suitable viscoelastic behavior for robocasting process. Scaffolds with different pore sizes and rod diameter of 410 μm were fabricated and sintered at 1100°C. The size and morphology of the starting powder particles, as well as the concentration of the processing additives, were shown to play the major roles in the robocasting process. All scaffold types tested presented compressive strength values comparable to or even higher than that of cancellous bone. A systematic study was also conducted to evaluate the *in vitro* osteogenic potential of mesenchymal stem cells (MSCs) cultured on the scaffolds and correlate their performance with scaffolds macroporosity, assessing different cell parameters as morphology, viability, proliferation and osteogenic gene expression.

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Design and FE simulation of a novel implant-supported dental bridge using hybrid materials – Ti6Al4V and PEEK

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The treatment of a partial or full edentulous mandible by means of implant-supported and retained prostheses have become a routine therapy, supported by positive clinical outcomes. Despite achieving satisfactory success, prostheses complications such as implant fracture, pre-implant bone loss due to the excessive transferred load were often observed. Furthermore, bone resorption underneath the framework in the absence of teeth and implants was reported.

The present study, therefore, aims to propose a novel framework design of implant-supported prosthesis using hybrid structures consisting of Ti6Al4V and PEEK, Fig. 1, which are both common materials of choice for dental and orthopedic implants. Three cellular Ti6Al4V structures with different open-cell sizes (300-500 µm) are designed and manufactured by selective laser melting (SLM). The cellular structures are then filled and coated by PEEK owing to its superior wear and chemical resistance as well as biocompatibility when compared to titanium. Mechanical characteristics of aforementioned structures are obtained both experimentally and numerically, presenting a young modulus similar to the mandibular bone. A finite-element modelling of the implant-supported prostheses is performed considering stress/strain distribution within the bone and the prosthesis due to occlusal loads. Regarding clinical reports, the range of acceptable strains to prevent the bone resorption is 300-1500 µE (microstrain). The best design of the framework is thus explored such that resulting strains satisfy the criterion associated with the clinical accepted strain range. Design variables can be listed as bridge length and diameter, the number of implants and material properties of the bridge, which are taken into account by the present study.

The results demonstrate that the framework deforms due to occlusal loads and transfers loads to the bone and implants smoothly. In addition, strains observed within the bone domain place within the acceptable strain range reported clinically. It can be concluded that the novel implant-supported overdenture developed throughout the current study may resolve the bone-resorption issue. Considerable decreases of stresses along implants are also observed, which can reduce the occurrence of implant fracture due to excessive loads reported clinically with previous designs.

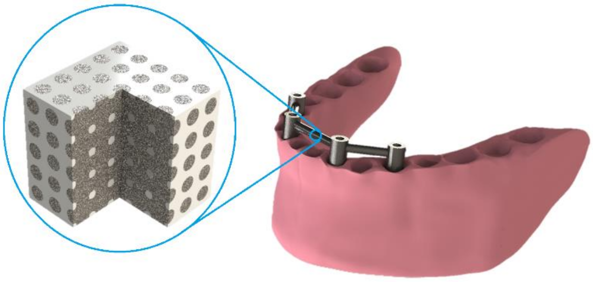

Fig. 1. A representation of the implant-supported prosthesis with a hybrid framework made of cellular Ti6Al4V structure filled and coated with Peek

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Tribological characterization of Ti6Al4V+HAp and Ti6Al4V+β-TCP biocomposites to assess the primary stability of implants

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Due to their mechanical properties, good biocompatibility and high load bearing capacity, Titanium and its alloys have been extensively used in several engineering fields, namely in biomedical applications such as prosthesis and articular implants. However, the osseointegration time of these metallic components needs to be reduced to promote a faster healing process. To achieve such decrease in the implant fixation time, the addition of a bioactive phase to the Ti matrix seems to be a good alternative. HAp and β-TCP are two of the most used calcium phosphates in biomedical applications due to their similarity in composition with bone and bioactivity.

Samples of Ti6Al4V, Ti6Al4V+HAp and Ti6Al4V+β-TCP were processed by the hot pressing technique. Tribological tests against Al_2O_3, lubricated in PBS at 37 °C were carried out on a ball-on-flat reciprocating sliding geometry, under normal loads in the range of 3N to 30 N. Furthermore, samples with two different surface finishing conditions (polished and sandblasted) were tribologically tested, in a reciprocating flat-on-flat geometry, against samples of rectified bovine femoral cortical bone tissue, to assess the primary stability of implants. Experiments against bovine bone were carried out at room temperature, with an applied normal load of 50 N, lubricated in phosphate buffered solution and a sliding distance of 100 mm.

As far as the tribological tests against Al_2O_3 are concerned, it was observed an increase in the values of both the coefficient of friction and the wear rate with the addition of a bioactive phase to the Ti alloy. Regarding the tribological tests using bovine femoral cortical bone tissue, static and kinetic friction were characterized. Results revealed that an increase in the surface roughness leads to an increase in the static friction coefficient values, whereas the kinetic friction for the biocomposites follows an inverse trend - an increase in the surface roughness leads to a decrease in the kinetic friction coefficient values. These results may be attributed to an increased adhesion component of friction associated with the bioactive phase. Given the aforementioned results this study will demonstrate that an implant design solution based on Ti6Al4V+HAp or Ti6Al4V+β-TCP with polished surfaces results in an improvement of the primary stability of implants, when compared to traditional rough surfaces, due the adhesion between bone and the bioactive particles. It is also expected that an earlier secondary stability will occur.

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New approach on creation multifunctional microcapsules for drug delivery systems

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Creation of new tools for theranostic can make personalized medicine. We focused our work on creation of multifunctional alginate hollow microcapsules with embedded plasmonic silver nanoparticles that could be used in the medical field. Realization of theranostic conception demands of two functions: loading of the drug in obtained microcapsules and its release in the area of interest. The template method of synthesis of the alginate particles allows encapsulation of the large amount of the drug. The possible mechanism of encapsulated substance release from alginate containers by ultrasound impact was demonstrated.

Such microcapsule shell contained the silver nanoparticles is sensitive to electromagnetic radiation in the near IR region (785 nm). Due to this fact such type of particles can provide the sensor function via the surface enhanced Raman scattering mechanism. Rhodamine B as model substance can be detected in the concentration range from 10-8 to 10-4 M. The nontoxic behaviour of the obtained silver alginate microspheres was demonstrated by the Alamar Blue test.

Since the micro- and nano-sized containers that protect the contents from external influences and release it only in response to specific environmental conditions to the desired destination are non-toxic, biocompatible and have promising applications in the medicine.

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Development of antimicrobial leather modified with Ag-TiO_2 nanoparticles for footwear industry

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The proposed work aims to functionalize leathers for footwear industry with antimicrobial properties based on Ag-TiO_2 nanoparticles. The synthesis of nanoparticles was carried out through an innovative and optimized method. This hydrothermal method is simple and inexpensive and prepares well crystalline materials. The structural characteristics were evaluated by X-ray powder diffraction and the results showed that the TiO_2 nanoparticles are in the anatase phase, with dimensions below 10 nm. Leather samples were functionalized with TiO_2 and Ag-TiO_2 nanoparticles, and it was possible to prove that these nanoparticles do not change the surface chemical composition of the leathers. These results were achieved by Fourier transform infrared spectroscopy which showed the maintenance of characteristic chemical bands of leathers (-CH_3 stretching vibration).

The antimicrobial activity was evaluated by agar diffusion tests tested against two bacteria species – a Gram negative and a Gram positive, Pseudomonas aeruginosa and Staphylococcus aureus, respectively and a fungus specie – Candida albicans. The results revealed that the leathers covered with Ag-TiO_2 nanoparticles are antimicrobial. The cytotoxicity of nanoparticles was also assessed by MTS test using fibroblast 3T3 which shows the cell's viability. This test has done since that these nanoparticles easily penetrated inside the human body. The results showed that the nanoparticles are non-cytotoxic.

The functionality of leathers covered with Ag-TiO_2 nanoparticles was achieved obtaining leathers to the footwear industry.

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NanoShoe: Use of nanoparticles to develop materials with antimicrobial properties for footwear application

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Footwear industry pursues the development of added value fashion and comfortable shoes. Presently, consumers require that footwear integrates fashion, emotional desires and multifunctional performances. Consumers are searching for differentiated products which promote their life style and wellbeing. To keep competitive, the footwear companies need to put their efforts in the creation of advanced products to meet the needs of the actual market. In this way the footwear and allied trade sectors have been investing in the development of new materials namely leather with antimicrobial properties. The control of bacteria and fungus growth is important to prevent and minimize the generation of malodors and some foot skin problems. The footwear industry has been exploring the potential of nanoparticles on the development of new products with high performance.

This route was initiated at CTCP in collaboration with FCUP with a more fundamental study to prepare stable Ag NPs with antimicrobial properties. Ag NPs antimicrobial properties were confirmed against E. coli, S. epidermis and B. subtilis (figure 1). Ag NPs were also used on leather surface modifications to confer antimicrobial properties. Cu, CuO and ZnO nanoparticles were also studied as alternatives to Ag NPs. Furthermore, the nanoparticles were characterized by TEM/SEM images and UV-Vis and their stability and antimicrobial properties were accessed. Although Cu NPs revealed good antimicrobial properties their low stability render them difficult to be used in industrial applications. By contrast ZnO showed good stability and also displayed antimicrobial properties. The following step is the use of commercial NPs to develop advanced and innovative nanotechnology based solutions for leathers and footwear products, aiming a new sustainable and customer-driven production of consumer goods; where the health, environment, high quality of components, fair marketing communication and competitive sales price are combined to promote the competitiveness of the companies.

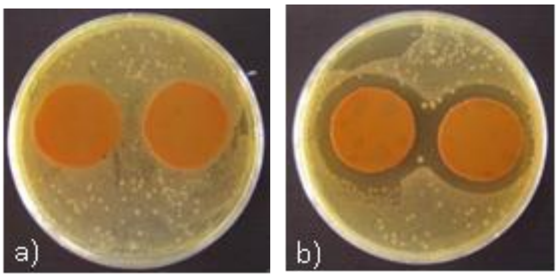

Figure 1. Antimicrobial of unmodified leather (a) and leather modified with Ag NPs (b)

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Emulsion electrospun fiber mats of PCL/PVA/Chitosan with antibacterial properties as potential wound dressing material

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Last decades a wide range of modern wound dressings have been developed.[1] Modern wound dressings goes beyond the traditional function of covering and absorb wound exudate providing a moist environment to facilitate a quick wound healing process and a protective barrier against the entry of pathogenic bacteria [1]. Damaged skin is particularly sensitive to microbial invasion and infections by pathogenic microorganisms as for example *Staphylococcus aureus* including Methicillin-resistant *Staphylococcus aureus* (MRSA), being the major cause of the inability of wounds to heal properly [2]. In fact, the emergence of strains resistant to antibiotics together with the risk of toxicity associated with systemic therapy used for wound treatment, conveyed interest in developing new biocide methods for the prevention of wound infections.

One of the most promising strategies is based on the development of wound dressings containing antimicrobial agents which are released locally to suppress bacterial growth in a controlled manner. However, the cost associated with this type of dressings represents a challenge for this market and the risk of bacteria resistance persists [1-3]. To overcome these limitations, the purpose of this study is to develop an new electrospun wound dressing. The electrospinning is a simple and low-cost method which allows to produce nanofiber mats with promising characteristics for application in the wound treatment [4,5]. Furthermore, it is associated with different strategies and allows the incorporation of medicinal plant extracts and its derivatives, such as essential oils, widely known for their traditional therapeutic properties [4,5]. Although the medicinal plant extracts are interesting natural agents, its stability can be affected by chemical and enzymatic degradation, losses by volatilization or thermal decomposition [6]. Thus, its incorporation by electrospinning emulsion seems a viable strategy to maintain structural integrity and the bioactivity of these compounds to be used in the prevention and treatment of wound infections. In this context, ternary blend of PCL/PVA/Chitosan was used to prepare electrospun wound dressings and proved to be a promising material for wound dressing applications.

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The potential of positive alginate as an antimicrobial agent for wound dressings

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Pseudomonas spp. and Staphylococcus spp. infections are sometimes resistant to therapy under hospital environment and the commonly used drugs are associated with a high microbial resistance. Thus, it is crucial to find new bioactive agents to treat nosocomial dermatitis, like the modified polymer alginate, which is naturally occurring and it is compatible with cellular functions.

The aim of the present work was to evaluate the anti-*P. aeruginosa* and anti-*S. aureus* activity of positively charged alginate wound dressing, in order to replace antibiotics currently used in the healthcare industry. The positively charged alginate wound dressing presented a microbial reduction of log 6 against *P. aeruginosa* and *S. aureus*, comparatively with the non-functionalized wound dressing after 24h of incubation. A new strategy for modifying alginate was developed, dramatically increasing its mechanical properties and giving it antimicrobial properties.

Functional material based on $CaCO_3$ mineralized fibrous polymeric matrix for tissue engineering applications

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Designing of functional materials for regenerative medicine and tissue engineering is a crucial task of the material science nowadays. Composite nanostructured materials based on a biocompatible polymer and an inorganic constituent are developed and explored intensively due to their potential for biomedical applications. In this study we designed the nanostructured composite consisting of nonwoven polycaprolactone (PCL) fibers coated with porous calcium carbonate $CaCO_3$. Such modification of fibers allows the functional properties of nanofibrous material to be achieved. In regard to bone tissue formation, the $CaCO_3$ is bioactive material due to its ability to form strong biomaterial-bone interface. The presence of calcium carbonate provides osteoconductive properties of PCL/$CaCO_3$ scaffold which are beneficial for bone reconstruction materials designing. Moreover, the porous structure of vaterite is suitable for loading of various substances (medicaments, growth factors, dyes, nanoparticles). Vaterite coatings on PCL electrospun fibers provide capabilities of functional substance storage and release in scaffold interior and environment. In such way PCL/$CaCO_3$ materials can be promising candidate for designing scaffolds provided with the function of cell growth control by incapsulated agent.

In this research we present the simple but efficient technique of polymeric fibrous matrix mineralization by porous $CaCO_3$ and an ability to control the coating homogeneity, $CaCO_3$ mass and polymorph during mineralization process. In vitro cytotoxicity tests and in vivo biocompatibility tests showed that PCL/$CaCO_3$ scaffold did not release toxic substances and are suitable for cell cultivation and implantation.

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Mechanical and tribocorrosion behavior of Ti6Al4V cellular structures impregnated with biomedical PEEK

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When designing an implant several aspects must be taken in consideration: biocompatibility, adequate mechanical properties (strength and Young's Modulus); surface roughness; material structure and also the tribological behavior. Ti6Al4V is a titanium alloy commonly used in biomedical applications like implants, principally due to its mechanical properties, biocompatibility, chemical stability and high corrosion resistance. Poly-Ether-Ether-Ketone (PEEK) is a biocompatible polymer with attractive properties essentially regarding wear and fatigue resistance. This work presents a materials design that combines Ti6Al4V cellular structures produced by Selective Laser Melting and PEEK, that was impregnated into the open-cells of the cellular structures. The first part of this work was the Ti6Al4V cellular structures production by using an Additive Manufacturing (AM) technique named Selective Laser Melting (SLM). AM techniques are exciting methods to produce personalized cellular structured components with advantageous biomechanical properties, difficult to achieve using conventional processes like casting and forging (typical processing routes for implants). This technology is a cyclic process that fabricates a component layer-by-layer by using laser energy to melt powders. The second part of this work consisted on the PEEK impregnation into the open cells of the Ti6Al4V cellular structures parts by using a pressure assisted technique (hot pressing). The cellular structures were positioned in a graphite mold and then the PEEK powder was introduced into the mold in order to fill all the available volume between the Ti6Al4V parts and the mold walls. Then pressure and temperature were simultaneously applied, forcing PEEK to fill the open cells of the structure. The third part of this work was the mechanical and tribocorrosion behavior assessment of Ti6Al4V cellular structures impregnated with PEEK by performing compression and tribocorrosion tests.

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A Single-Step Method to obtain Additive Manufactured 3D Scaffolds with Tailored Surface Topography

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Surface topography and roughness are well-known to influence cellular behavior, but the majority of these studies have been performed in 2D polymeric substrates. There are very few reports regarding this influence in 3D mainly due to the challenge to transfer in a controlled manner the tailored surface characteristics onto 3D scaffolds. Additive manufacturing (AM) is one of the existing techniques that allows the processing of scaffolds according to specific 3D digital models based on the layer-by-layer addition of materials. In this work, by combining AM with wet-spinning, a non-solvent induced phase-separation that allows to obtain polymeric filaments with specific surface characteristics, we obtained a range of scaffolds with specific surface characteristics and assessed their effect on human mesenchymal stem cells (hMSCs) behavior. Poly(ethylene oxide terephthalate)/poly(butylene terephthalate) (PEOT/PBT) block copolymer (PolyVation, The Netherlands) was used to obtain the wet-spun AM scaffolds. PEOT/PBT was dissolved at different concentrations in different solvent combinations. For each combination, the solution was placed into a glass syringe fitted with a stainless steel blunt needle. A syringe pump (NE-1000, New Era Pump Systems Inc., USA) was used to control the extrusion of the polymer solution. A container with different PEOT/PBT non-solvent solutions was fixed to the fabrication platform and used as coagulation bath. Scaffolds were fabricated using a *XYZ* plotter (Envisiontec GmbH, Germany) as previously described. Scaffolds geometry and architecture were characterized by scanning electron microscopy (SEM) and laser scanning microscopy. hMSCs were seeded at two different densities and cell activity and morphology were assessed using biochemical assays and SEM. From the different PEOT/PBT solvent/non-solvent combinations studied, the use of chloroform as solvent and isopropanol and 90% v/v ethanol (in H_2O) as non-solvents allowed the most reproducible plotting of 3D scaffolds with defined geometry. These different non-solvents allowed the tuning of fiber-surface topography at the same time as the scaffolds were being produced. hMSCs cultured on the scaffolds adhered, proliferated, and produced endogenous extracellular matrix, but they behaved differently according to the initial cell seeding density. The effect of surface roughness and topography was more evident for cells seeded at a lower density. The differentiation assays indicated that, in this type of scaffolds, this is highly dependent on the fine balance between the surface characteristics and cell seeding density.

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Magnetic, electric, multiferroic, and plasmonic functional materials (A2)

Unidirectional porous PZT with improved pyroelectric and piezoelectric properties for energy harvesting applications

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Energy energy harvesting continuous to receive both industrial and academic interests since it provides a route for the realization of autonomous and self-powered low-power electronic devices [1]. This research demonstrates the significant benefits of using highly aligned porosity in energy harvesting piezoelectric and pyroelectric materials. Porous lead zirconate (PZT) ceramics with highly aligned pore channels (Figure A) and varying porosity were manufactured via a unidirectional freezing method, termed 'freeze casting' [2]. It was observed that on increasing the porosity level from 20 to 60 vol.%, the compressive strengths of the parallel and the series porous PZT were ~200% and 320%-580% higher than the conventional randomly distributed porous materials, respectively (Figure B). Due to the introduction of porosity and air into the ceramic, the permittivity in the porous freeze-cast PZT decreased significantly, which is beneficial to achieving a high piezoelectric and pyroelectric performance figures of merit, compared with the dense PZT. A complete thermal energy harvesting system, composed of a parallel-aligned PZT harvester unit and an AC/DC converter unit was constructed to successfully demonstrate the real-time operation of charging a storage capacitor (Figure C). These results indicated that the porous materials generated significantly more energy than the dense material when subjected to thermal oscillations. The results are of benefit for the further design and selection of promising porous pyroelectric and piezoelectric materials in devices for the energy harvesting applications. The maximum voltage of 14.7 V can be obtained in the capacitor utilising the porosity of 60 vol.% PZT with the fastest charging speed. The correspondingly generated 115 μJ electrical energy stored in the capacitor was reported to be sufficient to power a commercial temperature and humidity sensor generated from PTFE film [3].

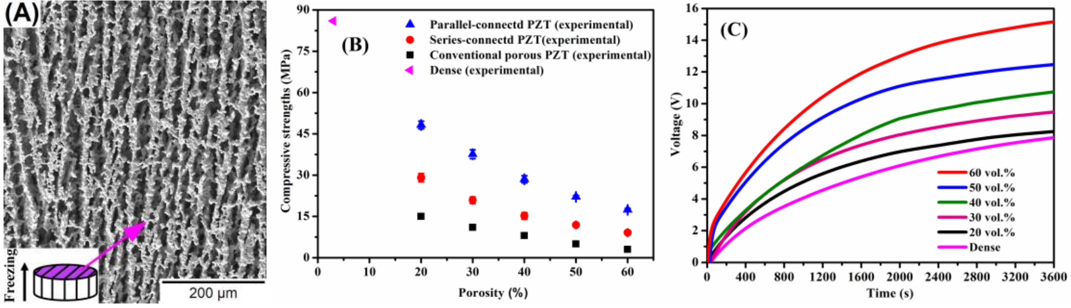

Fig. (A) SEM images of freeze-cast porous PZT. (B) Compressive strengths of conventional and freeze-cast porous PZT. (C) Charging voltage vs time plots of the dense and freeze-cast porous PZT.

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Crystal structure and piezoelectric properties of $Bi_{1-x}Sm_xFeO_3$ ceramics

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The $BiFeO_3$-based compounds are promising materials for technological applications due to their enhanced physical properties most pronounced near the phase boundary regions [1, 2]. Among RE-doped ferrites $Bi_{1-x}Sm_xFeO_3$ compounds attract particular interest as relatively small ionic radius of the samarium ion facilitates structural instability of the adjacent phases near a morphotropic phase boundary [3].

We have studied a structural phase stability and ferroic properties of the $Bi_{1-x}Sm_xFeO_3$ ceramics across rhombohedral-orthorhombic phase boundary ($0.1 < x < 0.15$). X-ray diffraction data confirm single phase structure with polar rhombohedral distortion for the compound x=0.1. The samples within the concentration range $0.11 < x < 0.13$ demonstrate two-phase coexistence - polar rhombohedral and anti-polar orthorhombic one, the anti-polar phase becomes dominant for composition $x = 0.13$. The crystal structure of the sample with $x = 0.14$ was estimated as pure anti-polar orthorhombic one. Piezoresponse force microscopy was used to attest ferroelectric properties. The PFM data testify a decrease in piezoresponse for the compounds upon increase of the amount of the orthorhombic phase. While maximal piezoresponse has been observed for the compound with $x = 0.12$ having dominant polar rhombohedral phase and minor anti-polar orthorhombic one. The PFM data obtained for the samples have permitted to get a polarization mapping for particular sample and to estimate an evolution of piezoelectric properties of these compounds. The PFM scans of the sample with x=12 demonstrate high piezoelectric response over the entire surface of the compound. A distinct domain structure can be ascribed to a majority of the grains, whereas some grains possess “neutral” contrast examined by both in-plane and out-of-plane channels. The PFM images show that most of the grains are constituted of multiple ferroelectric domains with different size and shape. It is suggested that enhanced piezoresponse observed in the compounds near the morphotropic phase boundary is associated with easier polarization extension associated with structural instability of this structural state.

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Ag-TiO_2 nano-heterostructures exhibiting gas sensing properties, visible-light activated photochromism with simultaneous plasmon-enhanced photocatalysis and antibacterial activity

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Achieving advanced multifunctional materials displaying coexisting properties is one of the most exciting and innovative research topics. We showed that Ag-TiO_2 nano-heterostructures, prepared via a green sol-gel method, exhibited purely visible-light activated photochromism with simultaneous plasmon-enhanced photocatalysis and antibacterial activity. Furthermore, this material proved itself to be highly sensitive for detection of acetone vapours at low concentrations.

Photochromic materials show reversible colour changes upon light exposure, and could play significant role in advanced devices such as photoswitches, photo-optical sensors, smart windows, photo-electronics and optical storage memories. Visible-light induced photochromism of these silver-modified (1-10 mol% Ag) TiO_2 nanoparticles (NPs) was monitored, and the change in colour experienced by the specimens was thoroughly investigated, with both spectroscopic and colourimetric analyses. Both the amount of silver present in the Ag-TiO_2 nano-heterostructure, and the visible-light irradiation time, dictated the degree and tuneability of the colour change, from pale yellow to dark blue/violet in Ag-modified specimens. The colour change was more rapid and extreme with increasing amounts of Ag, and the intensity and wavelength of the surface plasmon resonance induced under visible light also increased.

As noble-metal-modified metal oxide NPs are well known as visible-light harvesters, the photocatalytic and antibacterial activity were assessed. The former versus the abatement of nitrogen oxides (major atmospheric pollutants), the latter against Gram-positive and Gram-negative bacterial strains. Results showed that the Ag-TiO_2 possessed higher photocatalytic and antibacterial activity – when stimulated by a purely visible-light – than commercial Degussa P25. This indicated the suitability of our material for use in health care.

Sensing properties of the designed materials were also evaluated against acetone, a volatile organic compound whose presence in indoor environment can cause severe health risks. Ag-TiO_2 sensor exhibited the highest normalised response to acetone vapours at very low concentrations (<1 ppm) compared to previous TiO_2-based sensors reported in the literature.

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Turning biocompatible and biodegradable biopolymers into electric and magnetic flexible bionanocomposites

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Nowadays, there is a need for the development of low toxic and green materials in order to keep research as sustainable as possible. The use of biopolymers for materials development fulfills this criterion due to their biocompatibility and biodegradability. Here, we present novel sustainable bionanocomposites with chitosan or alginate as matrices and reduced graphene oxide and magnetite nanoparticles as fillers. The incorporation of different concentrations of these low toxic fillers into biopolymers gave rise to films with simultaneous tuned electric and magnetic properties. After preparation, we investigated the electrical and magnetic behavior from the macroscale to the nanoscale. Therefore, the magnetic properties were evaluated by SQUID and by magnetic force microscopy (MFM), while the electric conductivity was macroscopically measured in- and through-the plane and at the nanoscale by conductive atomic force microscopy (cAFM). The structural, morphological and mechanical properties, contact angle and magnetic hyperthermia response were also studied. The evaluation of electric and magnetic properties at nanoscale showed to be in good agreement with the results obtained at the macroscale. The electric conductivity and magnetic response increased with the increment of fillers content. It is observed a satisfactory dispersion of fillers throughout the matrices with the presence of agglomerates, responsible for local higher conductivity and magnetic response. The use of alginate as matrix promoted a higher electrical conductivity due to its intrinsic conductivity. Due to its remarkable properties, these bionanocomposites are suitable for a wide range of applications like enzyme immobilization, water decontamination, flexible electronic materials for nanoelectronic devices or hyperthermia treatments associated with drug delivery therapy.

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Synthesis, Structure, Optical and Magnetic Properties of New Multifunctional Lanthanide Complexes

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In Nanomedicine, lanthanide nanomaterials arise as interesting resources due to their unique magnetic and optical properties, combined with low toxicity characteristics. Being responsive to light, they offer an exceptional opportunity in diagnostic, image-guided drug/gene delivery and light-activated therapy. On the other hand, in Physics, lanthanide complexes are also exceptional candidates to host qubits, the quantum bits of information, allowing manipulation of the quantum states as required by quantum algorithms. The realization of an operational quantum computer is not far away and the use of lanthanide complexes in such computer is an extremely likely possibility.

We herein present a new family of Ln(III) complexes, featuring acetylacetonate as the counterion and different N,N´-donors as complementing coordination ligands. The synthetic procedure, in methanol solution under stirring and heating, gave product in 90-95% yield (based on Ln). Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol-dioxane solution at RT. The crystal structure of the complexes will be shown as determined by single crystal X-ray diffraction (XRD), with the geometry of the coordination sphere fully characterized. Absorption of light by the lanthanide-ligand ensemble will be revealed by diffuse reflectance and luminescence properties of the powder sample, measured under different excitation energies, will be discussed. The magnetic properties of the polycrystalline samples – determined as a function of temperature and field – will be shown, together with the change of such properties under irradiation. The potential use of this new family as multifunctional materials will be debated.

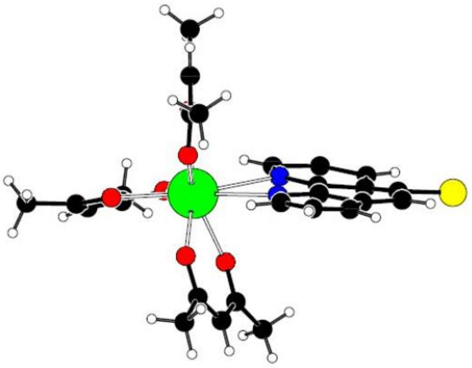

Figure 1. Molecular diagram of the Nd-acetylacetonate complex as determined by single crystal XRD.

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Oxyorthosilicates obtained by Laser Floating Zone: from photonic to electrical applications

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The aim of this work is the study of the rare earth doped oxyorthosilicates produced by the Laser Floating Zone (LFZ) technique. These silicates have a high chemical stability and allow incorporation of high concentrations of rare earth ions that yield different applications such as laser host materials, gamma ray detectors or scintillators, environmental barrier coatings (EBCs) and waveguides, among others. However, their production by general methods as solid state reaction or Czochralski (CZ) is somewhat problematic since such compounds typically require high temperature processing and environment control, resulting in a time consuming and complex process that increases fabrication costs and produces undesirable secondary phases as by-products. On opposite, crucible-free LFZ has been revealed as a suitable technique to obtain these compounds by a simple and fast process. Stoichiometric mixtures (1:1) of rare earth oxides raw powders (Gd_2O_3 or Lu_2O_3 or Nd_2O_3) with silicon oxide were processed by LFZ. The microstructure of the resultant materials has been characterized by SEM coupled to EDX. Raman and XRD studies were also employed to complete structural and compositional characterization. Thus, crystalline fibres of monoclinic Gd_2SiO_5 (GSO) and phase-separated ceramics of Lu_2SiO_5/Lu_2O_3 (LSO) and $Nd_2SiO_5/Nd_{4.67}(SiO_4)_3O$ (NSO) have been grown in descendent direction, ranging 10-35 mm in length and diameters of 1.5-2 mm. Powder and crystal XRD have been performed to check the high crystallinity degree of the GSO fibres produced. On the same way, XRD has revealed phase-separated ceramic fibres of LSO and NSO composed of monoclinic/cubic and monoclinic/hexagonal mixtures, respectively.

The optical characterization, accomplished by photoluminescence and photoluminescence excitation together with transmission studies, suggests that GSO and LSO fibres are promising candidates to be doped in order to develop new high optical efficient laser materials. In the same way, quasi-eutectic doped fibres of LSO could be implemented as matrix scintillators. As an additional effort, the Lu_2O_3 content promotes a photochromic effect on LSO fibres that could favor their use as UV sensor devices. On the other hand, the NSO derived fibres were electrically characterized, showing optimal properties to be applied as microwave dielectric components.

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High Temperature Giant Magnetoelectric Coupling in $BaTiO_3$:Fe auto-composites

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Multiferroics is one prominent area of Physics due to the outstanding applications that arise from these materials which led to the study of composites of ferroic materials, namely composites of ferromagnetic and ferroelectric archetypes [1-3].

We show results regarding polycrystalline $BaTiO_3$ which contained an overall 113 ppm of Fe. This specific kind of composite is a high-temperature extrinsic ME multiferroic, with very large relative spontaneous magnetization changes up to $\Delta M/M \approx 32\%$ and therefore corresponding to a ME coupling of $\alpha \approx 10^{-2}$ G·cm/V. These results originate from magnetic phase transitions which are correlated with the $BaTiO_3$ ferroelectric phase transitions, at temperatures confirmed by Raman Spectroscopy analysis of the 520 cm^{-1} ($T \approx 373K$) and the 487 cm^{-1} ($T \approx 330$ K) vibrational modes [4]. STEM/EDS mapping reveals that Fe distribution through the $BaTiO_3$ is quite inhomogeneous, tending to aggregate in specific locations, namely in the vicinity (between/inside) of the grain boundaries which should have a preponderant role in the reported magnetoelectric coupling [4].

To unveil the microscopic mechanism behind the observed sharp increase in magnetization near the structural transition temperatures of the $BaTiO_3$ matrix, a density functional theory study was made. We considered an atomic layer of Fe forming an interface with bulk $BaTiO_3$. For a particular metastable Fe atomic configuration, it was found that a low-spin to high-spin transition occurs in Fe, when the $BaTiO_3$ matrix changes from cubic to tetragonal. This surprising effect, due to the distorted octahedral environment of the Fe ions in the $BaTiO_3$ interface, would promote a sharp increase in the observed magnetization, in accordance with experimental data.

This work paves the way for a new kind of extrinsic ME multiferroic that could be applied in devices/industry when mass production of optimized $BaTiO_3$:Fe nanoparticles with the same characteristics as the ones presented in this work is achieved. Their applications would be a breakthrough since this magnetoelectric multiferroic operates well above room temperature.

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Role of topology in apolar-to-polar phase transition of hexagonal RMO_3 (M=Mn, Fe) improper ferroelectrics

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Progress in HAADF Cs corrected STEM characterization of ferroelectric (FE) domain and domain walls (DW) atomic structures of polar $P6_3cm$ phases of hexagonal RMO_3 (R = Y, Sc, rare earths and M = Mn, Fe) exposed a specific Z_2xZ_3 topology where FE domains of alternating positive and negative polarization (Z_2) separated by anti-phase domain walls with $2\pi/3$ phase shifts (Z_3) are distributed around topological vortices in 6-fold symmetry. Properties of the Z_2xZ_3 topological network are briefly recapped with support of additional elements revealed by atomic force (AFM), piezo-force (PFM) sensor force and optical microscopies. Interaction of topological vortices with atom clusters and dislocations leading to appearance of 4-fold and 2-fold vortex arrangements in doped/self-doped bulk materials are further also discussed.
The 6-fold vortex cores are intersections of FE domain volumes with three different trimerization phase angles and hence trimerization phase amplitude vanishes. The atomic structure of normal, apolar $P6_3/mmc$ phase is retained at linear topological defects which become the homotopy of cosmic strings from Higgs condensation of disorder [1]. Recent evidence that the dependence on cooling rate of the density of topological vortices created at the topological phase transition on cooling hexagonal $YMnO_3$, $ErMnO_3$, $TmMnO_3$ and $LuMnO_3$ single crystals from temperatures above Curie temperature (T_C) followed the Kibble-Zurek mechanism (KZM), being governed by universal scaling laws, was applied to re-accessed with success the conditions for observation of topological networks of 6-fold vortices in h-$LuMn_xO_{3\pm\delta}$ bulk ceramics. Dependences of topological phase transition points ($\simeq T_C$) and KZM coherence lengths on R^{3+} Shanon ionic radius in h-$RMnO_3$ phases were further investigated. For a constant density of topological vortices a fast growth of cooling rate by several orders of magnitude with the decreasing of R^{3+} radius from Y to Lu is first time reported here. Scarse data in bibliography on T_C and FE topological networks of isomorph hexagonal $(Lu,Sc)FeO_3$ phases and preliminary results of this study point to comparatively low values of T_C coupled to high densities of topological vortices attained only for the slowest cooling rates. Differences of internal energy of crystalline lattices of the two systems are further discussed.

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Green cellulose-based hydrogel stickers applied as gate dielectric in paper electrolyte-gated transistors

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Sustainability, industrial ecology and green chemistry are some of the main driving forces that have triggered the search for the development of new materials, products, and processes. [1,2] Nature offers a plethora of widely abundant materials, such as cellulose, to serve as starting building block sources for the design of eco-friendly advanced functional materials with tailored properties.[3]

In this work, an innovative approach of eco-friendly cellulose-based hydrogel electrolytes (CHEs) has been designed and engineered. The developed reusable and recyclable CHE stickers exhibit suitable electrochemical properties for application in electrolyte-gated transistors (EGTs) as gate dielectric. We report flexible indium-gallium-zinc-oxide EGTs on cellulose-based paper substrate gated by laminated CHEs, which operate at low voltages (< 2 V) with an on-off current ratio above 10^4, a subthreshold swing lower than 0.2 V dec^{-1} and saturation mobility reaching 7.5 $cm^2\ V^{-1}\ s^{-1}$. The flexible CHE-gated transistors exhibit environmental stability (> 1 month), good stability under stress, are able to operate at a bending radius down to 5 mm and with switching frequencies up to 100 Hz. Combining the flexibility of the EGTs on paper with the reusability of the developed CHE stickers is a breakthrough, which pave the way for next-generation green electronics based on biodegradable advanced functional materials allied with disposable/recyclable and low-cost electronic devices.

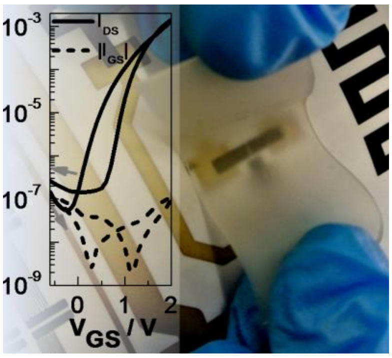

Figure 1 – Photography of the developed flexible and transparent CHE sticker and respective cyclic transfer characteristic curve of the bendable CHE-gated transistor on cellulose-based paper substrate.

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Comparative Analysis of Structural and Electromagnetic Properties of Cobalt Ferrite With And Without Addition of Niobium Pentoxide

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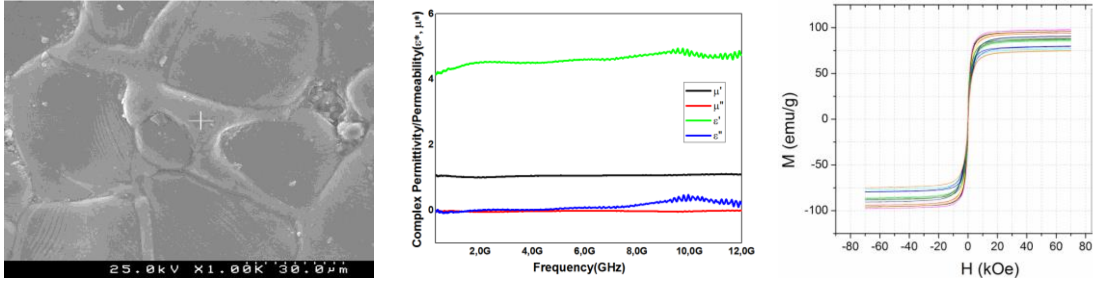
A comparative study of structural and electromagnetic properties of cobalt ferrites, with and without niobium pentoxide addition, and prepared by conventional solid state methods at different temperatures was carried out. Nb_2O_5 was added for the purpose of reducing the specific mass of the material while increasing its structural robustness, without significantly affecting its electromagnetic performance, as this cobalt ferrite was initially developed for potential application in encapsulation of sensors and coatings of aerospace structures. The structural properties were evaluated by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) methods. The complex electromagnetic properties were evaluated by means of complex permittivity and permeability measurements using transmission and reflection techniques (T/R), aiming to observe a Debye behaviour with different cut-off frequencies. In addition, room temperature measurements of the magnetisation were carried out by Vibrating Sample Magnetometer (VSM). The specific density measurements were performed by the Archimedes method, and indicate that it decreases with increasing niobium oxide concentration. The results of the structural evaluation allowed us to compare the grain size and to describe the microstructure of the samples. In this context, it was possible to observe the presence of an intergranular niobium-based phase in the intergranular regions, which appeared to fill in the spaces between the ferrite grains, separating the grain boundaries Figure 1(a) shows a SEM image (magnified 25000 times) of a sample doped with 10% of niobium pentoxide. (b) and (c) illustrate, respectively, the complex permittivity and permeability measurements of this sample, and the variation in magnetic hysteresis with Nb_2O_5 content. Regarding electromagnetic properties, a reduction of losses occurred with the addition of niobium oxide, which could minimise the attenuation of electromagnetic signals throughout the material. Finally, a series of complementary results discussing the influence of sintering temperatures on the structure and the electromagnetic behavior will also be presented.



(a) (b) (c)

Fig. 1 - (a) SEM imaging of 10% doped sample; (b) complex permittivity and permeability measurements; (c) hysteresis of all magnetic fields

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Fabrication and characterization of a DC magnetic field sensor based on magnetoelectric polymer composites

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Magnetic field sensors must have several characteristics, depending on the application requirements, and can be found in small integrated circuit devices, commonly placed in gadgets, domestic and industrial electronic utilities, among others. Magnetic sensors have thus become an essential measuring tool in a range of application areas including biomedicine, multimedia, automobile and military, just to mention some of them. From the different magnetic sensing technologies, the ones based on Hall Effect are those with the largest market share. Nevertheless, as the applications of magnetic sensing devices in areas such as automotive industry, navigation and electronics impose increasing demand for vector magnetometers with high precision, the inability on the precise measurement of the magnetic field vector with Hall Effect materials is a drawback. Additionally, industry constantly demand for smaller, cheaper, lower powered magnetic sensors, even when sensitivity is sacrificed.

In this work, the development of a DC magnetic field sensor based on a magnetoelectric (ME) PVDF/Metglas composite is reported. The ME sensing composite has an electromechanical resonance frequency close to 25.4 kHz, a linear response ($r^2 = 0.997$) in the 0-2 Oe DC magnetic field range and a maximum output voltage of 112 mV (ME voltage coefficient $\alpha33$ of $\approx 30\ \mathrm{V{\cdot}cm^{-1}{\cdot}Oe^{-1}}$). The sensing device, including the readout electronics, has maximum drift of 0.12 Oe with an average total drift of 0.04 Oe, with a sensitivity of $1.5\ \mathrm{V{\cdot}Oe^{-1}}$ ($15\ \mathrm{kV{\cdot}T^{-1}}$) and a 70 nT resolution. This feature is for the first time reported on a polymer-based ME device and compares favourably with a reference Hall sensor that showed a maximum drift of 0.07 Oe and an average error of 0.16 Oe, $5\ \mathrm{V{\cdot}T^{-1}}$ sensitivity and 2 μT resolution. Such properties allied to the accurate measurement of the HDC fields in the 0-2 Oe range make this polymer-based device very attractive for applications such as Earth magnetic field sensing, digital compasses, navigation and magnetic field anomaly detectors, among others.

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Tuning functionalized periodic mesoporous phenylene-silicas for CO_2/CH_4 separation

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The aim of this work is the design of periodic mesoporous phenylene-silicas (Ph-PMOs) for applications in carbon dioxide and methane separation. Novel PMOs are prepared by the functionalization of Ph-PMO materials with different amine groups through post-phenylene or/and grafting functionalizations. The pore size of both modified and non-modified Ph-PMOs are regulated by the size of the alkyl-chain in the surfactant template [1,2]. Materials with different pore sizes were used to understand the influence of the pore diameter on the CO_2/CH_4 separation [2]. The experimental research is performed in parallel with computational studies. A molecular simulation study, using the DFT method and a regular arrangement of phenylene-silica groups, of the ideal features of the adsorbent materials, for CO_2/CH_4 separation is made. It is used a simple model of the PMO wall obtained by the repetition of a unit cell with 3 phenylene rings, to select and evaluate interactions between gases and functional groups in the materials surface. The tendency between the ratio of the interaction energies between the wall structure of the Ph-PMO and the CO_2 and CH_4 molecules was in good agreement with the ratio of the Henry constants achieved by the adsorption technique. Therefore, a good synergy between experimental and computational tasks was implemented to optimize the resources, avoiding the synthesis of ineffective materials [3].

This work was developed in the scope of the projects UID/CTM/50011/2013 (POCI-01-0145-FEDER-007679), UID/MULTI/00612/2013, UID/ECI/04028/2013, NORTE-07-0124-FEDER-000011 | UID/EQU/500230/2013, PTDC/EQU-EQU/099423/2008 (FCOMP-01-0124-FEDER-010345), Investigador FCT, SFRH/BD/80883/2011, financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement.

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Nanotechnology Usability tool for optimization of nano-based products

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Industrial digitalization and circular economy are examples of manufacturing and business models that will be of great relevance in the near future, given the need to increase the rate between the quantity of products produced/sold and the resources (materials, energy, etc.) consumption. The relevance of nanotechnology for innovation and for the improvement of existing products is nowadays a reality. However, nanoengineering effective and practical application is still a challenge that must be assumed in order to define guidelines of intervention to a deep collaboration between stakeholders and with the ones who bring the technology closer and effectively to the market.

A Nanotechnology Usability (NTU) tool was developed with the main objective to diminish the gap between nanotechnology-based products developed in R&D centers and its implementation and effective usage, promoting optimized selection of materials and the use of eco-efficient production techniques. The NTU index is presented as a possible solution to be implemented for the increase of products on the market with an essence based on nanotechnology and being the result of an optimized selection of materials and the respective production techniques.

It is relevant to understand the all chain of nano-based product manufacturing, from the raw-material to the potential clients, considering existing nanomaterials, its characteristics, models, techniques and different processes for its production and/or manipulation, the current uncertainties related to nanotechnology, representing potential obstacles to a bigger usage. This was the main objective to develop the NTU tool that intends to gather information about a nano-based product with a specific application and increase its probability of success in the market, according to the society's needs and demands and, preferably aligned to the societal challenges. The need of a dedicated analysis tool to support a confident decision making process of enhancing or investing in a nanotechnology product or service is highlighted.

Overall, the main purpose of the NTU tool is to gather information from suppliers, developers, manufactures and users on the different (nano)materials, processes and attained characteristics, as well as features of competing products, evaluate this data in order to score its adequacy, cost and eco & social issues and by this means create the environment for an informed decision making process.

Piezo-resistive behaviour at high strain levels of intrinsically conductive polymers printed on a flexible polymeric substrate by a novel surface treatment

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Nowadays, flexible printed electronic (PE) are available, however, with a major mechanical limitation: high stretchability of the printed circuits. The literature, presents several strategies to achieve stretchable devices. Although effective for low strains, stretchability is highly constrained under higher mechanical strains. This study aims developing a new generation of good performance and lower cost printed system with conductive ink on a stretchable polymeric substrate, for novel stretchable PE devices. Therefore, a Drop-on-Demand inkjet printer with a piezoelectric printhead was used to deposit a thin film of an intrinsically conductive polymeric (CP) ink on a thermoplastic polyurethane (TPU) substrate. Two different CP ink were evaluated, namely, poly (thiophene-3-[2-(2-methoxyethoxy) ethoxy]-2,5-diyl) sulfonated (P3HT) and poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS). In order to promote adhesion between the ink and the TPU, the substrate surface was treated with a novel technique [1] increasing the substrate surface energy (by 45%), and consequently TPU wettability. The mechanical and electrical properties in response to applied strain of the CP ink printed on an elastomeric TPU were assessed. Achieved results raised a main concern about the P3HT feasibility. In contrast, the PEDOT:PSS printed substrate presented high stretchability able to follow and deform along with the substrate, without breaking or losing adhesion and its conductivity properties at 60 % strain. The CP ink piezo-resistive effect was demonstrated and high gauge factors (>300) were achieved (higher than the typical value for available flexible metallic strain gauges) showing the potential of the material to be used in high strain sensing applications. The simplicity of the structure, the flexibility and stretchability achieved is highlighted, in comparison to studies combining high cost materials and multi-step manufacturing techniques.

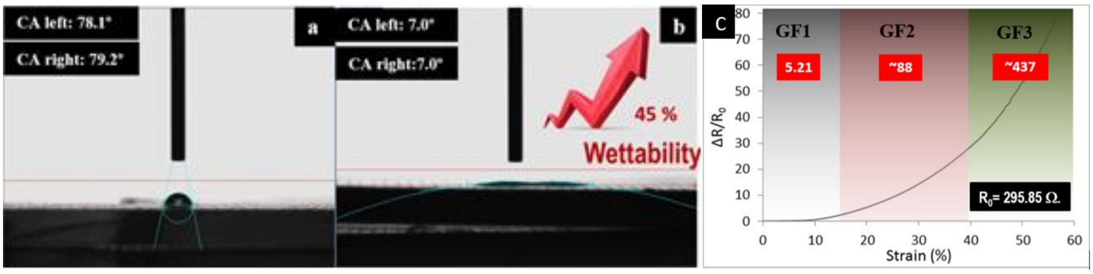

Fig. Drop of water on the: a) neat TPU substrate; b) SP-TPU substrate; c) Resistance changes with strain for surface treated TPU substrate printed with PEDOT:PSS ink.

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Temperature Phase Transition and Modification of Surface States in Self-Assembled Nanocomposites Based on CdSe/ZnS Quantum Dots and Dyes

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By virtue of their unique structures and complex interactions, the target nanocomposites based on semiconductor quantum dots (QD) and attached functionalized dye molecules have possessed quite a promising application in nanoelectronics, material science, biomedicine and sensing application. Here, we present a comparative analysis of structural dynamics and exciton relaxation processes in self-assembled nanocomposites based on TOPO- or amine-capped CdSe/ZnS quantum dots (QD) with attached functionalized dye molecules (porphyrins and peryilene bis-imides) in solutions and on surfaces upon temperature variation (77-295 K). In order to obtain more insight about these processes we used a combination of bulk and single molecule/single quantum dot experiments as a tool to precisely identify the interaction of exactly one QD with one dye molecule leading to a microscopic understanding of the QD-Dye nanostructures formation, ligand exchange and mechanisms of QD photoluminescence (PL) quenching dynamics [1]. In addition, time-resolved PL spectroscopy in combination with spectral deconvolution unravels that surface properties of QDs are a complex interplay of the nature of the dye molecule and the topography of the ligand layer across a temperature range from 77 K – 290 K. This includes a kind of phase transition of TOPO ligands switching the nature of surface states observed below and above the phase transition temperature. We have shown also that FRET QD→Dye plays minor role in the QD non-radiative exciton relaxation, but the driven formation of QD-Dye (1:1) nanostructures creates new energetically clearly distinguishable electronic surface states opening additional effective relaxation pathways which are sensitive to the specific nature of the respective dye.

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Study of the NLO properties of L- Histidine HCl-[$ErNO_3$]$5H_2O$ crystals

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Organic crystals have nonlinear optical effects (NLO) that make them attractive for applications in frequency conversion and optical processing. Among these we find the amino acids like l-histidine, and L-histiden HC. These compounds have nonlineaqr optical properties in some of their polymorphs. However their thermal stability is poor. It has been demonstrated that some mixed crystals of aminoacids with some nitrates improve properties like thermal stability and second harmonic emission. In this work, we synthesize L- histidine- HCl crystals doped with pentha hydrated erbium nitrate by slow evaporation at room temperature. The optical absorption spectrum recorded in the wavelength range of UV-vis revealed that the crystal has good optical transparency in the range of 350 to 1100 nm. The crystalline phase was determined by X-ray diffraction and the second harmonic generation efficiency of the crystal measured by using the Kurtz Perry modified method taken as reference the Urea SHG emission. Results obtained in this research shown that of L- Histidine HCl-[$ErNO_3$]$5H_2O$ with a 0.3% of Er (III) has an 0.65% SHG emission respect the Urea.

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Materials for environment and sustainable materials (A3)

Natural and synthetic sorbent materials performance for CO_2 capture: a comparative study

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Carbon capture and storage/use technologies are considered as viable key methods to reduce CO_2 emissions. The Ca-looping for CO_2 post-combustion capture is a very promising process based on the reversible chemical reaction of CaO and CO_2 to form $CaCO_3$. As important advantages the CaO-based sorbents can be easily regenerated, the CO_2 capture efficiency is especially high during the first carbonation-calcination cycles and the exhausted CaO can be used as raw material in cement production. The main limitation of this technology is the loss of CO_2 capture capacity by the sorbent throughout the several cycles, especially if natural limestone is used.

The present work focuses on the comparative study, of natural [1] and synthetic [2] CO_2 sorbents carrying capacity and stability, along the calcination-carbonation cycles. Limestone, dolomite and waste marble powder (WMP), a waste without commercial value, were selected as natural sorbents. The synthetic CaO-based sorbents were synthetized by the sol-gel method with and without activated carbon used as structuring pores generating agent during CaO sorbent preparation. All the sorbents were tested in Ca-looping cycle CO_2 capture tests for 10 and 20 cycles of carbonation-calcination reactions in a laboratory scale fixed-bed quartz reactor unit, using a gas mixture with a CO_2 concentration similar to industrial flue gas emissions [2].

The initial CO_2 capture capacity is similar for all the natural and synthetic sorbents, i.e., between 0.72-0.76 g of CO_2/g calcined sorbent, except in case of dolomite (0.61 g of CO_2/g calcined sorbent). The theoretical carrying capacity allowed by stoichiometry is 0.786 g CO_2/g CaO, which explains the values found for all the sorbents, except for dolomite due the MgO presence in the calcined sorbent. After 20 cycles limestone and WMP deactivation was 71% and 57%, respectively, whereas for dolomite and the two sorbents prepared by the sol-gel method was about 28%.

Usually, the CaO-based sorbents deactivation is considered to be caused by the sorbent loss of microporosity and growth of particles grain size along the cycles. The N_2 sorption technique was used to evaluate the BET surface area and pore size distribution and the X-Ray diffraction technique was used to evaluate the CaO particles size through the Scherrer formula. Morphologic aspects were examined by scanning electron microscopy. Besides the attractive results obtained for the synthetic sorbents, the possible integration of Ca-looping in industry implies a compromise between the sorbent performance with economic and environmental issues.

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Boron Detection and Scavenging Materials

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Boron compounds are used in many industrial applications, including the manufacture of glass and ceramics, insecticides, fertilizers, semiconductors, soaps and detergents, flame retardants, high duress compounds, and pharmaceutical drugs. Boron is necessary both to human health and agriculture but in trace amounts, but becomes toxic above ca. 2 ppm [1]. High boron contents in water might result from industrial eluents or from soils containing borates and borosilicates [1].

Boron is difficult to detect [2,3] and to remove from water. Here we present two new boron optical detection methods [2-4] and two scavenging methods, one based on thermoresponsive core-shell polymer nanoparticles (PNP), and the other on mesoporous silica nanoparticle (MSN) membranes. The polymer particles have a core of poly(methyl methacrylate) (PMMA) and a thermosensitive shell with a brush composed of a copolymer of N-isopropylacrylamide (NIPAM), 2-aminoethyl methacrylate (AEMH) and D-gluconoamidoethyl methacrylate (GAEM) boron-chelating diol-containing monomers. The MSN are surface modified with vicinal diol groups and crosslinked on cellulose acetate membranes.

Our systems feature high efficiency for boron detection and removal from water, with the possibility for portable use in field applications.

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Gold nanoisland-decorated TiO_2 for enhanced photocatalysis

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Photocatalysis has become an attractive process to remove contaminants from aquatic environments [1], [2], being titanium dioxide (TiO_2) the most used catalyst. However, there are some drawbacks concerning the use of TiO_2, namely the reduced spectral activation, restricted to the UV spectral range (< 387 nm), which corresponds to just 3 to 4% of the solar spectrum. Moreover, the high recombination of electron-hole during photocatalytic process also hinders TiO_2 efficiency [2]. To overcome this limitation, TiO_2 nanoparticles are usually doped, functionalized with noble metals or produced as nanocomposites, to narrow TiO_2 band gap and reduce the electron-hole recombination. This work reports on the development of TiO_2 nanoparticles decorated with gold (Au) nanoislands. Pristine TiO_2 and the Au/TiO_2 nanocomposites were characterized as well as their photocatalytic degradation efficiency with a ciprofloxacin (CIP) solution (5 mg/L).
The results showed that Au nanoislands on TiO_2 nanoparticles surface enhances photocatalytic efficiency towards the pristine TiO_2 nanoparticles.

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Bimetallic metal nanoparticles on carbon nanotubes embedded in polymeric membranes as supported hybrid catalysts for environmental applications

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One of the key areas of research today is the development and use of increasingly more efficient and economic catalysts to best take advantage of natural resources by consuming less energy. The unique properties that metal nanoparticles (MNPs) exhibit combined with the specific properties of carbon nanomaterials has derived in an enormous attention in many applications like heterogeneous catalysis [1]. Nowadays, interesting advantages are reported to be obtained with the development of bimetallic nanoparticles where the use of another metal allows to enhance their catalytic activity reducing the cost of the catalyst. An important challenge in heterogeneous catalysis is the recovery of the catalyst from the liquid reaction media to reduce the environmental impact. In this work, we studied the synthesis and incorporation of silver, copper and platinum MNPs into multiwall carbon nanotubes using the intermatrix synthesis technique [2] which includes two steps based on solution chemistry: 1) loading the functional groups with MNPs precursor via ion exchange and 2) formation of MNPs by chemical reduction of metal precursor. Making use of a procedure known as galvanic replacement [3] it is feasible to form bimetallic NPs. Once the MNPs-MWNTs were obtained they were incorporated into a polymeric membrane (PM) containing cellulose triacetate as polymeric support and 2-nitrophenyloctyl ether as plasticizer. All materials were characterized by FTIR, TGA, XRD and TEM. PMs were characterized by SEM. The metal content was determinate also via ICP-OES. The catalysts obtained were tested making use of the 4-nitrophenol reduction to 4-aminophenol as a model reaction. The reduction was carried out with sodium borohydride as the reducing agent. At least 90% of the total amount of 4-nitrophenol was reduced during the first hour.

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Active and transparent chitosan-genipin films: a promising approach for food packaging materials

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The high amount of foodstuffs loss due to their short shelf-life is of major concern not only to the industries, but also to the consumers. As a solution, active packaging materials are being developed. Herein various approaches have been studied. Biopolymers, namely polysaccharides, have shown promising results in the development of new active packaging materials. Their ability to readily form films with improved chemical, physical, mechanical properties and transport barriers to moisture, gases, flavor and lipids is crucial to prolong the products shelf-life. Beside, many polysaccharides have the scavenging and/or antimicrobial abilities that allow reducing some typical food deterioration reactions and the pathogenic microorganism's growth. In this work, chitosan, a biocompatible, biodegradable and non-toxic biopolymer easily recovered from crustacean industry byproducts, was crosslinked with genipin, a biodegradable compound that spontaneously interacts with the amino groups present on chitosan structure, yielding dark green active packaging materials. Further, aiming obtaining transparent materials, a two-way decolorization process was established: (i) an enzymatic pretreatment in which CotA laccase (a protein obtained from the *Bacillus subtilis* spore coat) oxidation occurred in the presence of 2'2-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS); (ii) a chemical reaction prompted by the hydrogen peroxide action. Different experimental conditions as pH, processing time and temperature were tested. Physical and chemical characterization including FTIR, ^{13}C CP-MAS solid state NMR, color, solubility, mechanical properties, wettability and antioxidant activity were determined. As result, an enzymatic pretreatment of chitosan-genipin films using 1 U/mL CotA-laccase mediated by 1 mM ABTS at pH 7 and 37 ºC for 24 hours followed by the hydrogen peroxide action using 5% (v:v) of H_2O_2 (pH 11) at 40 °C for 30 minutes led to transparent yellowish films. When compared with non-treated chitosan-genipin films, despite of this technology interfere with the films mechanical performance, it was maintained their antioxidant activity and stability under acidic conditions. Hence, the CotA laccase-ABTS/hydrogen peroxide system revealed to be a suitable approach to produce active and transparent chitosan-genipin films encouraging, therefore, their application as food packaging materials.

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Carbon based materials (A4)

Production and characterisation of alternative activated carbons – a full factorial design approach

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The application of wastes as new resources is gaining increasing attention by the scientific and industrial community once it is completely in line with the new paradigm of a circular and sustainable economy. In this context, the use of primary paper mill sludge, consisting mainly of cellulose, as precursor for the production of carbon adsorbents has already shown to constitute a promising solution, namely concerning its use for the removal of pharmaceuticals from water [1]. In this way, two great challenges of the scientific community - the remediation of contaminated water and the industrial waste management – should be addressed in an integrated approach. In this work, a full factorial design (FFD) was performed to study the influence of four factors at two levels in the production of an activated carbon by the pyrolysis of primary paper mill sludge and, consequently, in their physicochemical properties and adsorption capacities. Were studied the following factors: *a)* temperature of pyrolysis (under N_2 atmosphere) (650 ºC and 800 ºC); *b)* residence time (60 minutes and 150 minutes); c*)* type of activating agent (KOH and K_2CO_3); and *d)* precursor-activating agent ratio (1:1 and 10:1). These factors are known to influence the properties and the adsorbent performance of the final material. In order to choose the best experimental conditions, different responses were analysed, namely, the production yield, the adsorption capacity towards different pharmaceuticals (sulfamethoxazole, carbamazepine and paroxetine), the organic carbon content and the specific surface area (S_{BET}). Also, physical and chemical characterization of the materials with the best responses were performed by means of Fourier Transform Infrared spectroscopy, determination of the zero point charge, determination of the carbons' surface functional groups by Boehm's titrations, proximate and ultimate analysis, and scanning electron microscopy. Very little differences between the two chemical activating agents used and the two residence times tested were observed. The higher temperature (800 ºC) and precursor-activating agent ratio (1:1) showed the best adsorption performance but also resulted in the worst yields. Four of the set of conditions of the FFD analysis presented very good results for the adsorption of the considered pharmaceuticals, indicating that they are able to compete with the commercial activated carbons.

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Adherent and hard DLC coatings deposited by HiPIMS in Deep Oscillations Magnetron Sputtering (DOMS) mode

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Diamond-like carbon coatings (DLC) make up the largest proportion of thin film coating solutions applied in the automotive industry, notably for engine applications, drivetrain components and transmission parts. DLC combine high hardness with low friction coefficient, chemical inertness, high thermal conductivity and high refractive index, making them very attractive for a wide range of other applications. In order to comply with the current trends of rising operating temperatures and lower viscosity oils, component manufacturer are currently seeking to develop a new generation of DLCs coatings, with improved properties. The main limitations of the existing DLC solutions stem from high internal stresses and limited thermal stability. The stresses, often in excess of 10 GPa, limit the maximum achievable thickness of hard H-free DLCs due to adhesion problems. H containing DLC coatings, on the other hand, have lower hardness and are typically restricted to operating temperatures below 350^{o} C. The main objective of this work is to develop a new generation of significantly improved well-adherent and hard DLC coatings, with high sp3/sp2 ratio and good temperature stability. DLC films were deposited by deep oscillation magnetron sputtering (DOMS), a variant of high power impulse magnetron sputtering (HIPIMS). The bombardment energy was controlled by changing the substrate bias. In order to improve the film's adhesion an interlayer was deposited. In this work, the microstructure of the films was characterized using scanning electron microscopy, Raman spectroscopy and X-ray reflectivity. The mechanical properties (Hardness and Young´s modulus) of the films were also characterized.

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Conductive biopolymer-clay-graphene composite film doped with carbon nanotubes

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Carbon nanotubes (MWCNTs) have been used to prepare several nanocomposites with enhanced conductive properties for applications in several fields [1,2]. However, MWCNTs are too expensive for the industrial applications. Then, naturally occurring graphite, processed as graphene nanoplatelets (GNP), emerges as an alternative material for introducing conductivity into nanocomposites.

This work reports the preparation of stable water dispersions clay-GNP mixtures by using sepiolite fibrous clay and sonomechanical treatment. The doping of these systems with MWCNTs significantly increases their electrical conductivity [3]. It was attempted the development of functional nanocomposites by assembly clay-GNP hybrids with structural different polymers (alginate, gelatin, and polyvinyl alcohol). The alginate-based composites were the most interesting, being important the addition of the alginate only after the ultrasonic dispersion of the GNP and sepiolite. The dispersions lead to polymer-clay-GNP composites with enhanced mechanical properties. The in-plane conductivity of the films is always higher than through-plane conductivity because of the high tendency of graphene nanoplatelets to lie flat due to its 2D crystal organization. The doping of the composites with a very small amount of MWCNTs results in a significant increase of the electrical conductivity. Values of 2500 Sm^{-1} and 0.05 Sm^{-1} are achieved for in-plane and through-plane electrical conductivities, respectively, for alginate-based composites.

In conclusion, small amounts of MWCNTs together with GNP-clay systems can be used as nanofillers in the preparation of conductive composites, maintaining the mechanical properties, at low cost. The particular textural characteristics of the sepiolite component allows interactions with biopolymers, opening the way to functional materials for advanced applications due to their inherent conductivity afforded using GNP doped with MWCNTs.

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Bacterial cellulose and graphene nanostructures as promising nanocomposites for the development of new insulating and fire-retardant materials

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Driven by the need for new materials and technologies that progressively lead to fossil fuel reduction and help mitigate global warming issues, in the past decades, research efforts have been committed with the purpose of developing new energy efficient and lightweight composite structures, foreseeing applications in emergent sectors, such as construction and automobile industries. Cellulose foam is the greenest material that has proven to be a good insulation material due to its thermal and acoustic insulation features [1]. The energy efficiency of such foams may be improved by incorporating microencapsulated phase change materials (mPCMS) into insulating materials. Nonetheless, the flammability of these types of materials is a drawback for their application, therefore fire-retardant additives need to be added in order to satisfy the fire code safety requirements. Usually, boric acid is added, however, in wet conditions, boric acid is corrosive to other materials, as the case of metals. Recently, graphene and its derivatives have attracted the interest of researchers for its potential application as flame retardant additive~~s~~ [2]. In this work, new fire-retardant and insulating lightweight structures based on bacterial cellulose, carbon nanostructures (e.g. graphene oxide and reduced graphene oxide) and mPCMs were prepared by freeze-casting. The influence of carbon nanostructures and mPCMs content loading on the thermal, acoustic and mechanical properties were evaluated. The composite foamed structures presented enhanced thermal insulation and sound absorption properties. Furthermore, carbon nanostructures conferred fire-retardancy and improved the mechanical properties of the final materials. This study has developed a novel environmental friendly solution flame retardant composite cellulose foamed material with mPCMS with potential use for high-end insulation applications.

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A graphene-oxide-collagen scaffold as a versatile three-dimensional biomimetic microenvironment for tissue engineering applications

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During the past few years, graphene and its hybrids have become increasingly popular biomaterials for tissue engineering (TE) applications due to not only their excellent biochemical, electrical and mechanical properties, but also because of their potential to be combined with other materials in order to fabricate biocompatible composites with superior behavior. In this regard, graphene oxide (GO) has emerged as front runner to act like a functional building block of complex 3D cellular microenvironments since the oxygen functional groups located onto the surface of its sheets can be complementary used to directly enhance cell response and to be combined with specific biomolecules and polymers [1,2].

Thus, in this work we successfully explore the electrostatic interactions between the negatively charged GO sheets and the positively charged collagen (Col) particles in order to fabricate a self-assembled 3D porous scaffold capable of guarantee suitable biochemical and biomechanical features for a wide range of TE strategies, involving both static and dynamic cell culture protocols [3]. Indeed, the chemical, mechanical and morphological properties of the GO-Col scaffold were minutely analyzed and its capability to potentiate an enhanced cellular microenvironment was confirmed by preliminary biocompatibility tests using Rat Schwann cells. The versatility of the scaffold was also revealed through their compression-recovery features since independently of the degree of deformation applied (1%, 3% and 7%) via a bioreactor apparatus, its integrity was not affected. Additionally, these promising results boosted the adaptation of this GO-Col scaffold into the cartilage TE applications by innovatively incorporating inside the porous network an anisotropic electrospun scaffold able to mimic with great morphological accuracy the cartilaginous natural fibrous network.

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Symposium B - Structural Materials

Advances in ceramics, concrete, building materials (B1)

Revifeel PLUS: Ceramic tiles with improved thermal comfort

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Ceramic tiles are known for their intrinsic properties, such as high durability, water and chemical resistance and easy maintenance. However, for applications in warm residential areas (e.g. living rooms, bedrooms) or sun-exposed areas (e.g. areas surrounding pools), users generally choose materials with improved performance in terms of thermal comfort, such as wood tiles. Bearing in mind this limitation, CeNTI and Revigrés joined forces to improve the performance of ceramic tiles at the thermal comfort level, with the main objective of combining technical properties, design and comfort. From the project developments, three distinct and complementary technological solutions were achieved:

• REVIFEEL WARMUP: ceramic floor tiles with an innovative surface treatment that reduces the sensation of cold to the touch in indoor residential applications;

• REVIFEEL COOLDOWN: ceramic tiles with IR-reflective properties resulting from the direct additivation of ceramic raw materials during the tiles production; this technological solution aims to eliminate the sensation of excessive heat given off by ceramic surfaces due to exposure to solar radiation; • REVIFEEL COOLDOWN: ceramic tiles with IR-reflective properties resulting from the direct additivation of ceramic raw materials during the tiles production; this technological solution aims to eliminate the sensation of excessive heat given off by ceramic surfaces due to exposure to solar radiation;

• REVIFEEL HEATSYSTEM: ceramic tiles with an integrated heating system, a solution that is highly efficient, easy to install and maintain.

The work and developments carried out in the scope of Revifeel Plus project allowed to improve the ceramic tiles thermal comfort performance (temperature, sensation to the touch) suitable for flooring applications, namely for indoor (REVIFEEL WARMUP and REVIFEEL HEATSYSTEM) and outdoor applications (REVIFEEL COOLDOWN).

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Self-healing concrete with bacteria encapsulated in expanded clay

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Preparation process and the life service solicitations can cause damage on concrete's internal structure, creating cracks that tend to propagate and increase with time. This poses a potential risk of failure as water penetrates, corroding the rebar what considerably reduces concrete's life span. It is know that cement can exhibit up to a certain extent a natural ability to self-heal, a consequence of the long-term hydration phenomenon. Hence, some initial cracks can be spontaneously closed if the right conditions are met (humidity). This, however, will not be enough to repair most of the major cracks that are formed internally over a long period of use, so strategies need to be developed to achieve an efficient level of self-healing. Search for a more sustainable and durable concrete, less prone to cracking, lead to a new concept – self-healing. This concept, inspired by the natural ability of plants and human skin to spontaneously heal, inspired researchers to search for a method of conferring concrete with the ability to repair internal damage. The biological approach presents itself as a suitable alternative to achieve healing in concrete. In this work, bacteria were immobilized in expanded clay before being added to concrete. In order to incorporate the expanded clay, some of the aggregate was replaced within the concrete. This works presents the results obtained for the final mechanical strength and self-healing efficiency of concrete containing encapsulated bacteria.

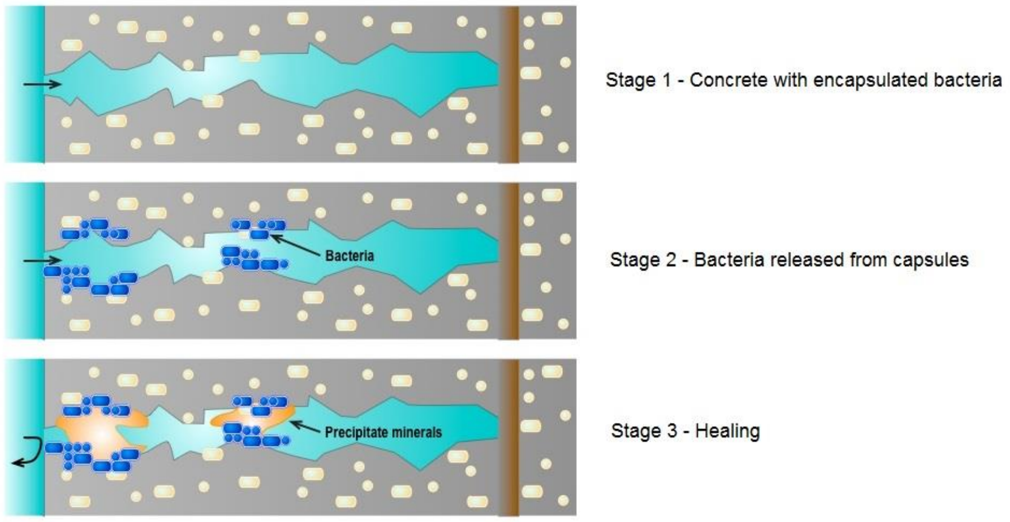

Figure 1 – self-healing mechanism in bacteria concrete

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Impact of coal and wheat husk addition on the properties of fired clay bricks

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Pakistan is an agricultural country and 70% of its population is directly or indirectly dependent on agriculture [1]. Pakistan has rich coal deposits, estimated to above 185 billion tones [2]. Presently, coal is commonly used as fuel in bricks and roofing tiles kilns, as it is an ideal fuel for kilns, especially for heavy clay products. In Pakistan, about 50% of mined coal is used in the brick industry, making it a huge market for indigenous coal, in particular for private investors [3,4]. A number of materials are used in construction industry. The choice and suitability of a specific material depends mainly upon its availability, nature of the project, individual preference, durability, proximity and economic considerations. The use of renewable agricultural by-products and other wastes as performance increasing additives in brick industry is gaining more and more ground with time [5-7]. The additives mixed in the brick clay burn out during the firing process, generating extra energy within the brick, and decreasing the total energy needs of the industrial furnace.

The use of by-products as additives in brick industry is gaining increased research attention due to their effective role in decreasing the total energy needs of industrial furnaces. In addition, these additives leave pores upon burning, causing a decrease in thermal conductivity and affect the mechanical properties of bricks as well. In the present study, various proportions of coal and wheat husk were used as additives in the initial ingredients of clay bricks. Microstructure, thermal conductivity, coefficient of thermal diffusivity, water absorption, shrinkage, compressive strength and bulk density of fired clay bricks with and without additives were investigated. Clay bricks containing 5–15 wt. % additives were found to be within the permissible limits for most of the recommended standard specifications.

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Mechanical characterization of cement pastes reinforced with pristine and functionalized MWCNTs

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This paper aims to characterize the mechanical behavior of cement pastes reinforced with pristine and functionalized multi-walled carbon nanotubes. To this end, the hardened density, compressive and flexural strength, modulus of elasticity and drying shrinkage of MWCNT-reinforced cement pastes were analysed. For the better interpretation of the obtained results, microstructural analysis was also carried out by means of scanning electron microscopy. The mechanical tests were performed at different ages, 7, 28 and 90 days, and shrinkage was measured up to 365 days.

Five different types of MWCNTs were studied, including two commercial aqueous solutions with MWCNTs with different aspect ratio, one type of pristine CNT in the powder form and two types of functionalized CNTs (COOH-treated and OH-treated MWCNTs). In order to cover cement pastes with different porosity, two w/c ratios were considered, 0.35 and 0.45. For comparison purposes, unreinforced pastes with equal composition were also tested regarding the same mechanical properties.

Experimental results show that the incorporation of optimized projected amounts of MWCNTs was effective to increment the mechanical strength of cement pastes. Depending on the type of CNTs and w/c ratio, the flexural strength, compressive strength and modulus of elasticity of MWCNT-reinforced pastes were up to 46%, 58% and 20% higher than those of unreinforced pastes, respectively. Moreover, MWCNTs were also effective in decreasing the drying shrinkage of cement pastes, especially at early ages, in which a reduction up to 87% was achieved when compared to reference pastes. The reduction of the long-term shrinkage at 365 days was as high as 30%. Finally, microstructural observation showed uniform dispersion and effective microcrack bridging of the MWCNTs phase.

It is concluded from this study that CNTs can effectively contribute for the reinforcement of cementitious materials, regardless of the w/c ratio. Different types of MWCNT and dispersion procedures led to distinct reinforcement efficiencies.

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Study of mechanical behaviour and correlations with physical and chemical properties of solid ceramic bricks in Asunción

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Given the whole research results presented at International Congresses such as IX SBTA 2011 at Belo Horizonte, Brazil, 1st I+I+D Fair 2015, F.I.U.N.A. held at San Lorenzo, Paraguay, IV ALCONPAT 2016, at Asunción and VII CONIMAT 2016 at Cusco, Peru, and the interest for these subjects, we continue researching on solid ceramic bricks quality jointed with mortars to form walls. As the former research established that bricks contribute in a larger way in its elastic and rigidity modules than the mortar, and that the final contribution is superior to those of the mortar, showing synergy between mortar and bricks in final bending and compression strength, these is shown in this paper by graphs and number after making more than 360 essays of these materials which makes walls. In this research we study not only the physical properties, but also analyze the chemical properties with traditional technologies and with EDX. The correlation between the raw materials physic and chemical properties and its compression and bending strength, brings up the importance to know these properties in raw materials in order to design and produce more efficient materials and with better performance. We combine two different raw materials from different soils in Paraguay to produce bricks in laboratory and study 20 different bricks offered in Asunción, selected in categories, to correlate its initial and final chemical and mechanical properties. Also other mechanical and physics properties are affected by chemical composition. The bricks have been categorized A, B, C and N/C (not categorized) according to Paraguayan Standard NP17 027 77 second edition of 2015, Specifications for solid ceramic bricks, and this research will help us to know how to design better bricks using laboratory equipment such as sieves, weighing scales, X Ray Energy Disperser, compression machine, micrometer, owen, electronic devices, and other to use appropriate materials or combining them to produce well categorized bricks using local technology towards getting better.

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Advances in metals and alloys (B2)

Assessing the thermomechanical processing steps of NiTi alloy production for orthodontic application

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The superelastic characteristics of NiTi alloys, combined with their biocompatibility place them in an interesting position for orthodontic application. The major challenges presented during fabrication of orthodontic archwires are the control of the hot-workability to reach the final dimensions and the capability to guarantee the functional properties required. This study presents an evaluation of the fabrication steps of NiTi alloys, from vacuum induction melting to the hot and cold gorging, aiming the production of orthodontic archwires in the framework of a joint project involving Instituto Mlitar de Engenharia (Rio de Janeiro, Brazil), Instituto Tecnológico de Aeronáutica (São José dos Campos, Brazil) and CENIMAT.

The structural, thermal and thermomechanical characterization of the different steps has been performed and the process parameters have been assessed, leading to several significant modifications of the major fabrication steps. The main focus of this analysis has been put on

- the impurities (C and O) control and their role on the hot workability,
- the Ni/Ti ratio and its influence on the functional characteristics,
- the effect of ageing treatments on the thermomechanical behavior.

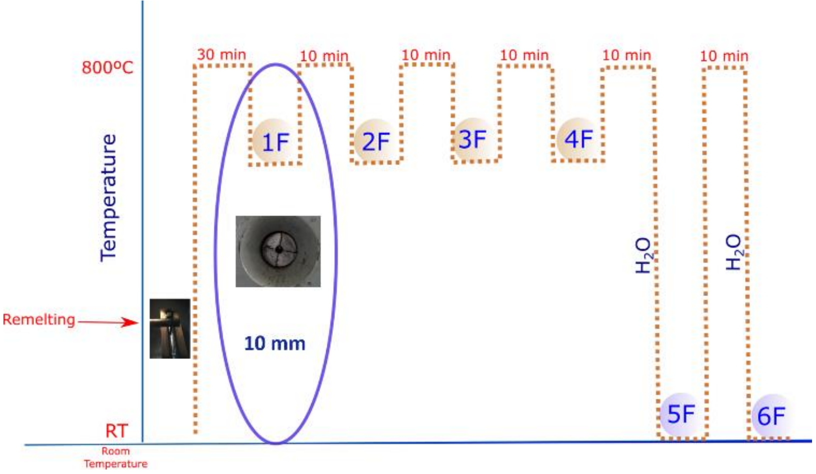

Figure 1 – Schematics of the fabrication steps of NiTi shape memory alloys.

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Study of the Effect of Corrosion on Nickel-Aluminum Bronze in Natural Waters

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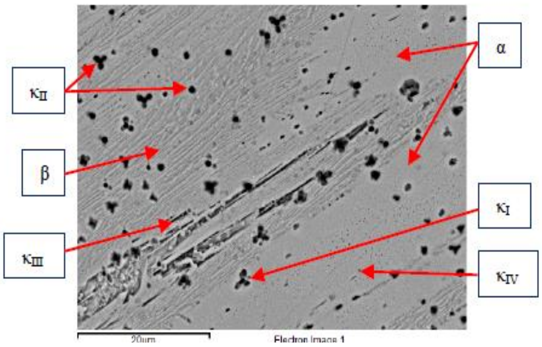
Nickel-Aluminum Bronze (NAB) is an extensively used alloy, particularly in marine environments, due to its excellent tenacity and resistance to corrosion. It is a family of alloys that is distinguished by having a significant presence of alloy elements such as Ni, Al and Fe in its chemical composition that alongside Cu make up the base of the alloy, and a high resistance to corrosion in numerous environments, particularly marine. Its high microstructural complexity, potentially a direct consequence of the thermal treatments they may experience, both in the cooling inherent to the actual solidification process during casting, an in any others that could occur in the manufacturing stage such as welding, has been the main reason for selection of this material.
To evaluate the corrosion behavior of NAB, different heat treatments were selected and the relationship between microstructural changes and corrosion behavior was studied. The microstructures of the as-cast and heat treated samples were characterized by optical microscopy and scanning electrode microscopy. Six different phases were identified: α-phase, β-phase and four intermetallic phases referred to κ-phases.



Phases identification of the as-cast NAB alloy

Electrochemical corrosion testing was carried out over 72 hours using the specimens selected on different natural waters under potentiostatic conditions. The corrosion progress on the different microstructural features were analysed in detail. Two types of corrosion, selective and general corrosion, were observed in the samples after being exposed to natural waters.

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Explosive welding of similar and dissimilar copper and aluminium alloys

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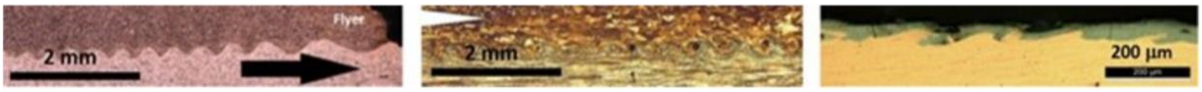
The main objective of this work was the analysis of explosive welded joints (EXW) between aluminium, copper and aluminium-copper plates and the influence of the variation of some welding parameters on the quality of the welding interface. The welds were in similar materials Cu-Cu and Al-Al and dissimilar Al-Cu, where the materials used were Cu-DHP deoxidized copper and AA6082 aluminium alloy, generally 3 mm thick. Two types of explosive emulsions (Eex + HGMS and Eex + EPS) were used, with different values of explosive ratio.

In the welds between similar materials the formation of wavy weld interfaces was observed, as shown in Figures 1a) and 1b), respectively for the copper and aluminium plates. The analysis of welds in larger magnification allowed to verify that the waves are regular and well defined, presenting dendritic pockets at the base and crest of some waves. These dendrites are proof that there was melting of the material in these zones. In general the welding interface presents a good bond, without cracks and with very small amount of pores. In these welds a small increase in hardness is observed next to the welding interface, due to the plastic deformation caused by the impact of the flyer.



a) b) c)

Figure 1 – Morphology of interface of weld between: a) Cu-Cu; b) Al-Al; c) Al-Cu.

On the contrary, the Al-Cu welds gave continuous fusion layers at the interface, as shown in Figure 1 c), mainly of aluminium, which led to further separation of the plates. This layer also shows some cavities, resulting from shrinkage of the material in the solidification, and some cracks, which suggests that it is brittle. The SEM-EDS analysis showed that the chemical composition varies from point to point of the layer having compositions similar to those of the intermetallic compounds $CuAl_2$, CuAl, Cu_4Al_3 and Cu_9Al_4. It has also been found that in the case of welds between dissimilar materials the higher the ratio of explosive and the distance between plates, the greater the formation of intermetallic compounds in the welding interface. The explosive emulsions used showed behaviour not suitable for the tests where aluminium is thrown against the base plate. In the welds of dissimilar materials the increase in hardness in the weld interface is greater due to the presence of intermetallic compounds.

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Joining of AA6082-T6 aluminium alloys by Friction Stir Welding: Mechanical characterization, modelling and numerical simulation

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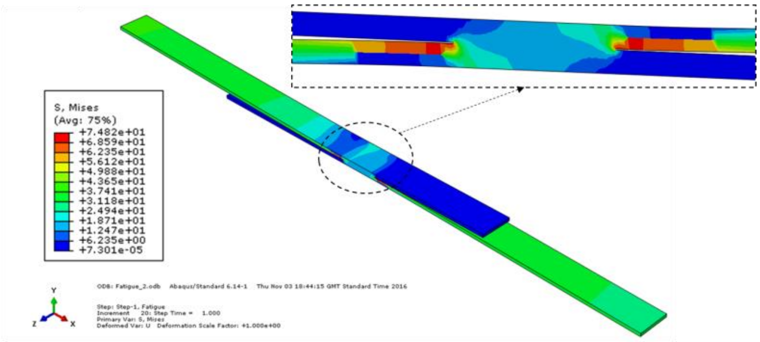
Nowadays, aluminium alloys are widely used in applications for the transportation industries, where lap joining is traditionally performed by riveting or fastening, which have the inconvenience of increasing the weight of the structure, or by resistance welding and related technologies, which have important limitations for the welding of aluminium alloys due to its low electric resistivity. This way, in the past few years, the application of solid state welding technologies, such as Friction Stir Welding (FSW), in the joining of aluminium alloys, gained increasing importance. In spite of this, the joining of very thin plates, as explored in current work, remains almost unexplored due to the enhanced difficulties in process control.

Friction stir lap welding of very thin plates, in AA6082-T6 aluminium alloy, was performed. The mechanical efficiency of the welds, in monotonic and cyclic loading conditions, was determined. Post weld heat-treatment was performed, for a selected set of welds, which displayed improved properties in monotonic loading. The as-welded and post-weld behaviour of the joints, in monotonic and cyclic loading conditions was compared, being found important differences in strength and failure mode. The results obtained show that the post-weld heat-treatment not only enabled to restore base material properties, but also had an important impact in the strength/structure of the bonding interface.

During mechanical testing of the as-welded samples, Digital Image Correlation (DIC) was used to perform strain data acquisition, which enabled to plot local stress-strain curves, for the different weld zones, and to assess the mismatch in mechanical properties and its relation with process parameters.

Modelling of the constitutive behaviour of the different weld zones also enabled to perform numerical simulation of the cyclic loading tests (figure below). Numerical simulation results, in conjunction with the metallographic analysis of the welds subjected to experimental testing, allowed to perform a deep analysis of the influence of mechanical/microestrutural mismatch, joint geometry and weld-defects, in joint failure.



Keywords: FSW, heat-treatment, mechanical behaviour, DIC, modelling, numerical simulation.

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Influence of ultrasound melt treatment in the corrosion of AZ91D-Eco alloy

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Magnesium alloys are widely used in a large variety of applications in the industry, particularly in biomedicine for instance on the manufacture of prostheses and other medical devices due their good mechanical properties as well as their characteristics of biodegradability and biocompatibility of the base material in the organism (1). However, the magnesium alloys present a fast degradation by corrosion phenomena which is considered as one main drawbacks of these kind of alloy. Recent studies show that the control of microstructure of magnesium alloys, through the chemical route by addition of rare earth metals such as Ca, Y, Nb and Ce, can refine the size of grain and morphology of intermetallic (Mg17Al12) improving the capability of the magnesium alloys to resist the corrosion phenomena (2).

Although the addition of chemical elements can decrease the corrosion rate the effect of these in the human organism, in case of use the medical devices produced in magnesium alloys, can be detrimental for human health. Thus, in order to overtake this negative evidence, the purpose of present work is to improve the corrosion resistance of the AZ91D-Eco alloy, by the refining their microstructure using an ultrasonic treatment of melt which is based on the physical process.

The AZ91D-ECO alloy was melted and held inside the crucible at different temperatures. After that, the acoustic radiator was immersed 10mm inside the melt and the liquid was sonicated isothermally during 2 minutes for each test temperature in order to obtain different levels of refination of microstructures. For the sake of comparison experiments were also carried out without ultrasonic sonication.

The evolution of microstructure was characterized by scanning electronic microscopy and the evolution of the rate of corrosion was performed with a characterization of the polarization curves with a scan rate of 1 mV s^{-1} in a 3.5% NaCl solution saturated by $Mg(OH)_2$. The results suggest that the rate of corrosion is influenced by the processing of melt as well as, in case of ultrasonic processing, by the parameters used (temperature and time of sonication).

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Corrosion behaviour of alternatives to the WC-Co hardmetal

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Cemented carbides and, more specifically, WC-Co are commonly used as drilling and cutting tools, in applications that require remarkable mechanical properties, i.e., outstanding hardness, fracture toughness and wear resistance, in different engineering fields such as the mining, oil and gas extraction.

For a long time, cobalt (Co) has been used as a binder for these carbides due to its well-known relationship with the WC, given by its good wettability and ductility, resulting on hard metal composites with enhanced mechanical properties, which are difficult to be achieved with other binders.

However, the price of Co has been continuously increasing with its rareness which led to the pursuance of different binder substitutes that could attain similar mechanical properties and processability. Another relevant problem is the corrosion of Co in some service environments which leads to the deterioration of the WC-Co composite and consequently to an early failure of the technical products.

The aim of this study is to assess different binder systems, in terms of their electrochemical behaviour and corrosion resistance in different corrosive media when compared with the common WC-Co system.

For this purpose, an electrochemical study was conducted using different techniques, namely measurements of the open circuit potential (OCP), in parallel with polarization curves (PC) and electrochemical impedance spectroscopy (EIS).

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Advances in composites and hybrid materials (B4)

Expanded corkboard core sandwich structure: low velocity impact and flexural properties

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The core material properties are fundamental to the overall performance of sandwich structures. Cork agglomerates and derivatives have been attracting some interest as alternatives to traditional core materials, particularly, polymer foams. Like cork, its agglomerates also benefit from high flexibility, elasticity, compressibility, and recovery properties, being outstanding natural energy absorber, which make them an interesting core material choice for sandwich structures. However, cork agglomerates usually exhibit higher density compared to polymer foams. Expanded black corkboards constitute a particular type of cork agglomerate with lighter densities, which could help make cork based sandwich structures with enhanced specific properties. Expanded corkboards are mainly used for sound and temperature insulation, and therefore, structural integrity is not a key feature - in fact, the absence of an added binder also contributes to the low density.

The present work investigates the use of existing black corkboards as core material in sandwich structures. The face-sheets, consisting of +/-45º glass fibre fabric reinforced epoxy resin were produced by resin infusion, and a polyurethane structural adhesive was used to assemble the sandwich structure. This scheme has been used in previous works which helps the comparison of the present construction to others differing only in core composition.

The sandwich structure was evaluated with respect to low velocity impact, three-point bending, and four point bending. Core shear properties were also evaluated through sandwich bending tests. Additionally, the core material was independently tested in tension, compression, and shear.

The results were analyzed to determine how the expanded corkboard sandwich construction compared to sandwich constructions with traditional cork agglomerates, polymer foams, or honeycomb core materials. In addition to work conclusions, suggestions are given regarding manufacturing agglomerates based on expanded cork more appropriate for structural applications.

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New Multi-scale Cementitious Composites Developed Using Carbon Nanotubes and Microcrystalline Cellulose

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Due to remarkable mechanical properties, various nanomaterials are now being considered as effective reinforcements of cementitious composites. In the present study, new multi-scale cementitious composites were developed using carbon nanotubes (CNTs) and micro crystalline cellulose (MCC) as a hybrid reinforcement system. To develop these composites, CNTs and MCC were homogeneous dispersed in aqueous suspension using ultrasonication energy and a nonionic surfactant, Pluronic F-127. These aqueous suspensions were then mixed with cement/sand mixture to fabricate the cementitious composites. Workability, mechanical properties and microstructure of the developed composites were thoroughly characterized. According to the experimental observations, flexural stiffness of cementitious composites improved strongly due to the hybrid reinforcements, as shown in Fig. 1. Also, flexural strength improved significantly (~13%) using 0.1% CNT and 0.2% MCC, dispersed using 3% Pluronic. The workability of the cement paste, on the other hand, was not significantly influenced due to the reinforcing materials. Future efforts are being directed towards optimizing the dispersion conditions of CNT and MCC to further enhance the mechanical performance of these new composites.

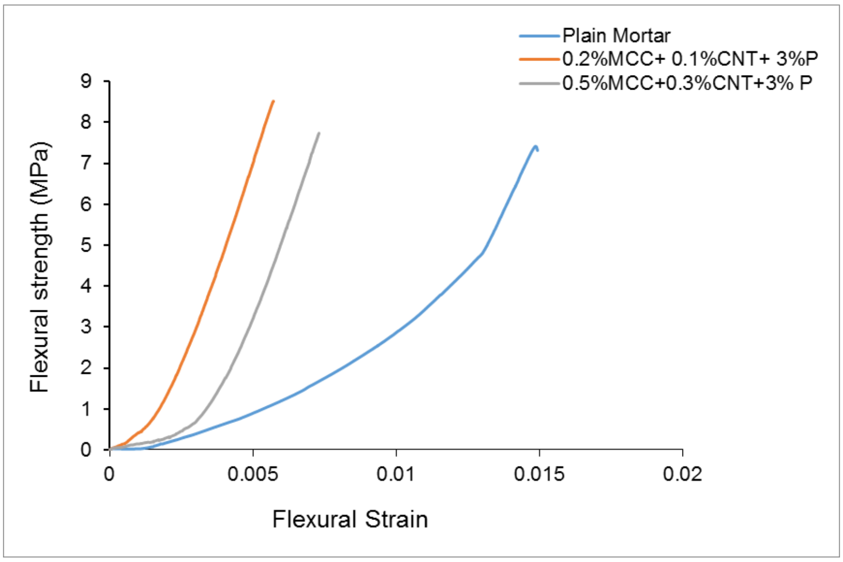

Fig. 1 Flexural stress-strain curves of plain cement and multi-scale cementitious composites

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Tailor-made carbon nanotubes dispersion in epoxy matrices through self-assembly with block copolymers

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Multifunctional properties of carbon nanotubes (CNTs) makes them a great candidate for application in reinforcement of high performance fibre reinforced composite materials (FRP). However, to maximize the property gain through their inclusion in the polymeric matrix, the nanotubes need to be properly dispersed within the resin. It is widely known that, mostly due to strong Van der Walls interactions between the nanotubes, their dispersion is difficult to obtain. In this work, we propose the use of block copolymers (BCP) - composed of two or more different linked polymeric segments – as effective surfactants for the dispersion of CNTs in an epoxy resin. The use of surfactants is a non-covalent method that can improve the nanotube dispersion.

Non-covalent methods are considered to be advantageous over mechanical and covalent methods. Mechanical methods can only stabilize temporarily the dispersions, while covalent methods can change the physical properties of the nanotubes.

The use of commercial BCPs for the dispersion of nanotubes in polymeric resin matrices has been recently reported, however, lack of information regarding the structure of the block copolymers makes it difficult to establish a relationship between structure and performance. BCP are capable to provide nanostructuration and to tailor nanoparticles distribution through self-assembly mechanism. This mechanism is widely dependent of the molecular design of BCP and on the interaction of each segments with the matrix and the (nano)particle to be dispersed. It is therefore expected that a suitable control of the BCP design will allow obtaining composite formulations with enhanced performance properties through tailored control of CNT dispersion and distribution.

In the present work, the influence of different BCP compositions in the dispersion of carbon nanotubes within an epoxy resin was studied. The BCP studied have different segments with distinct affinity for both the nanotubes and the resin matrix: one BCP have a segment which was expected strong interaction with CNT (polystyrene), one other have a segment with poor interaction for epoxy matrix and CNT (poly (butyl acrylate) and the last one have the same segment with introduction of acid functionalities which through that will increase their hydrophilicity. Rheological and dynamic mechanical analysis complemented with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed to evaluate dispersion.

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Fracture mechanisms of epoxy nanocomposites: influence of carbon nanoparticles with different geometries

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Enhancement in fracture toughness (K_{Ic}) has been a critical issue when it comes to epoxy application. This change in tenacity can be assessed through a variety of mechanisms that operate in crack propagation and a correlation made to the roughness of the fracture surface. The roughness in a fracture surface can be related to different toughening mechanisms, such as crack deflection, crack branching, separation between layers and plastic void growth. The present paper checked the effect of block copolymer (BC) in the nanoparticle dispersion and investigated the relationship between roughness and toughening mechanisms in hybrid epoxy nanocomposites with carbon nanotubes (CNT) and graphene nanoplatelets (GNP) nanoparticles. The compositions were prepared by means of sonication and in situ polymerization and fracture toughness was evaluated. The fracture surfaces of the specimens were evaluated by scanning electron microscopy and roughness measurements, and the dispersion was observed by transmission electron microscopy. All nanocomposites were tougher than standard systems, pure epoxy and epoxy with block copolymer. The increase in K_{Ic} of the nanocomposites compared to the pure epoxy was 34% for the hybrid nanocomposite, proportion of 1:1 (CNT:GNP) with 0.5 wt% total of nanoparticles and also containing 0.5 wt% of block copolymer; 35% for the system containing 0.5 wt% of carbon nanotubes and 0.5 wt% of block copolymer; and only 22% in the composition with graphene nanoparticles and block copolymer, containing 0.5 wt% of each. Systems with higher amounts of graphene showed the highest values of roughness and the main toughening mechanism is crack deflection/separation between layers of the graphene nanoplatelets. On the other hand, systems with more carbon nanotubes have a low roughness in the fracture surface and the main mechanism is bridging/break the nanotubes. Hybrid systems have more types of mechanisms that simple systems, with only one type of nanoparticle, however, some of these mechanisms are not effective in increasing the toughness and only increase the fracture surface roughness.

Keywords: Hybrid nanocomposites, epoxy, toughening mechanisms, roughness.

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Effect of carbon nanotube on the micro hot-embossed aluminium powder

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Manufacturing components from advanced materials can promote powder metallurgy industry when newly developed techniques like micro hot-embossing are used. Since the quality of sintered components strongly depends to the state of green samples, it is important to evaluate the homogeneity of constituents as well as the replicability of input materials. Processing metal matrix nanocomposites is prone to void formation and agglomeration and they will be intensified in micro scale dimensions. This study presents how adding multiwall carbon nanotube (MWCNT) to pure aluminium (Al) powder affects the state of micro hot-embossed samples.

Micro hot-embossing involves feedstock preparation and granulation, shaping, debinding and sintering. For this work, pure Al powder with D_{50} of 10 micron was mixed with 0.75 wt% MWCNT, based on a sonication technique [1]. A feedstock with 58(0.58) vol% of Al(CNT) was prepared [2]. Granulated particulates with particulate size smaller than 500 micron were hot-embossed inside elastomer and rigid dies. Replicability of green samples is highly affected by the solid content and critical conditions: temperature, pressure and holding time [2 and 3]. Binder material was thermally removed in Argon and Argon-hydrogenated atmospheres. Brown samples were sintered in the controlled atmospheres and high vacuum as well.

Scanning electron microscopy technique reveals that MWCNTs are distributed inside the binder system than the powder binder interface. This technique also shows that the constituents of green micro hot-embossed samples having CNT are more uniformly distributed than green samples without CNT. These nano reinforced samples do not break during demoulding step unlike non-reinforced ones. Infinite focus microscopy (IFM) reveals the increase of Sa (Arithmetic average of the absolute values of the roughness profile) of nano reinforced green sample for 45% compared with of the metallic die. It is contributed to the strengthening effect of CNT on the binder system. In case of using metallic die, in spite of having better replicability of narrow high aspect geometry, binder becomes sensitive to segregation. It can be resulted from high thermal conductivity of CNT. IFM also revealed that the height of the narrow high aspect micro wall of the green sample is 3.5% smaller than of the master die while the width of the micro wall is 5% larger than of the master die.

Preserving CNTs in brown samples after thermal debinding owes the period length of the process, i.e. the shorter the holding time, the more the preserved CNTs. Afterwards, the densification of brown samples is only obtained in high vacuum level, i.e. it is highly affected by the concentration of aluminium oxide shell (which is not broken during micro hot-embossing) and the compaction level. Hot isostatic pressing even did not increase the densification of pre sintered samples.

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Hybrid composites with tailored electromagnetic and dielectric properties based on shell-core polyamide microcapsules

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This work studies the possibility to develop hybrid composite materials with tailored electromagnetic and dielectric properties from shell-core polyamide 6 microcapsules (PAMC). PAMC were synthesized by activated anionic ring-opening polymerization of ε-caprolactam. The process was carried out in solution, in the presence of metal powders (Al, Fe, Mg), finely divided carbon allotropes – carbon nanotubes (CNT), carbon black (CB) and their mixtures, the typical sizes of the loads varying in the range of 0.5-50 μm. A recently developed and patented method was applied for the purpose [1]. By conventional melt processing PAMC were transformed into thermoplastic polyamide-based hybrid composites. This fabrication concept permits easy and simultaneous introduction into the polyamide matrix of different fillers, in wide concentration ranges and with controlled dispersion [2]. In such a way, PA6-based hybrid composites with tailored conductivity, magnetic and dielectric properties were prepared for the first time. Solid state NMR provided information on the structure at the molecular level of electromagnetic polymer hybrids and also about their capability to absorb radio waves. A loss of intensity or even complete disappearance of the NMR peaks related to the matrix PA6 was found in some hybrid composites containing mixed metal/carbon fillers, namely 3 wt% of Al and 7 wt% of CNT or CB. These initial results for radio wave absorption of the composites were complemented by detailed structural and morphological investigations of both PAMC and of the respective hybrid composites by electron microscopy, thermal techniques (DSC, TGA), X-ray diffraction and conductivity tests (AC/DC). The mixed metal/carbon allotrope loads provided significant improvement of both AC and DC conductivity reaching values of 10-01 Sm/m, which is an improvement of 9 orders of magnitude in respect to the neat PA6 matrix. In the Fe-containing hybrids the good conductivity is combined with susceptibility to magnetic fields. The results obtained allow the conclusion that the approach of transforming variously loaded PAMC into polyamide hybrid composites has potential in the preparation of microwave and radar absorbing materials, as well as in electromagnetic interference shielding.

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Synthesis of CNT–silica aerogels

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Even though aerogels have exceptional properties such as high porosity and specific surface area, low bulk density and thermal conductivity, the poor mechanical strength limits their application in several areas. The possibility of doping their structure with different compounds allows obtaining materials with different characteristics when compared to the native silica aerogels, which may lead to the development of new materials with properties not yet found. Due to the high mechanical strength of carbon nanotubes (CNT) [1], these materials are an interesting alternative to the mechanical reinforcement of silica aerogels. The combined properties of both materials, silica aerogel and carbon nanotubes, can open the way to new properties of the obtained porous and extremely lightweight materials, such as a high level of opacification, besides the mechanical effect. Here, the hybrid materials were synthesized from the mixture of organically modified silica precursors with CNTs by the sol-gel methodology. The tuning of the synthesis conditions led to differentiated properties of CNT–silica aerogels. These were appraised by a complete set of characterization techniques, such as contact angle, Infrared and Raman Spectroscopies, Scanning and Transmission Electron Microscopies.

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New Bio-based Multi-scale Composites Developed Using Carbon Nanotubes

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Multi-scale composites developed using carbon nanotubes (CNTs) attracted great attention due to their multi-functional properties such as improved mechanical performance, electrical and thermal conductivity, electromagnetic shielding, sensing of strain and damage, etc. In the present research, an effort has been made to enhance the mechanical properties of jute/epoxy composites through dispersion of CNTs within the matrix. Multi-walled CNTs were dispersed homogeneously within epoxy resin using ultrasonication energy and the nanotube dispersed resin was then used to impregnate the jute fabrics using a vacuum assisted resin transfer moulding technique. The developed multi-scale composites were characterized for mechanical and dynamic mechanical properties. As per the experimental results, incorporation of only 0.5 wt. % CNTs led to ~8% improvement in tensile strength and ~45% improvement in storage modulus of jute epoxy composites. The breaking strain of jute/epoxy composites improved significantly due to CNT addition, as can be observed from the stress-strain curves presented in Fig. 1. Therefore, these multi-scale bio-composites with further optimization can have potential application in various industrial sectors such as automobiles, construction, sports, etc.

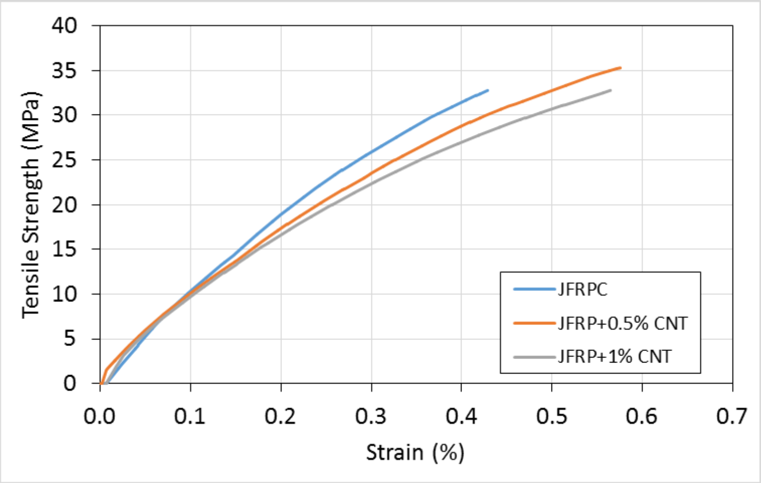

Fig. 1 Tensile stress-strain curve of jute/epoxy composite (JFRPC) and jute/epoxy composites containing CNTs

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Development of polymer/metal multilayer composites by “Spark Plasma Sintering”

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Polymer/metal composite materials and more particularly sandwich material systems or functionally graded materials (FGMs) represent an interesting and effective solution for the design of advanced materials. Sandwich composites, combining the low density of the polymer with the stiffness and the strength of the metal, are considered to be of great interest for high-demand engineering applications, especially in the automotive and aerospace industries. Their processing is conditioned by the materials used for the composite development and the design of the targeted parts. In this way, various methods can be used for developing these materials and among them, the most common are the hot pressing (HP) and the roll bonding (RB). In recent years, a consolidation process called - Spark Plasma Sintering (SPS) - was pointed out as it has proven its efficiency for sintering and joining dissimilar materials in various domains and more particularly for structural as well as biomedical applications. Nonetheless interface is still the weak point of multilayer composites due to the difference in chemical nature between materials to assembly and the improvement of interfacial resistance remains a challenge.

The aim of the present work is the development of polymer/metal assembly, exhibiting high macroscopic and microscopic cohesion, and thus interesting mechanical properties for structural applications. The use of a High performance thermostable polymer such as Polyimide (PI) or Polyetheretherketone (PEEK) was considered as it is consistent with the mechanical and thermal properties requirements for structural parts. The metallic counterpart used is an AA7020 Aluminum alloy developed by SPS at ISL in the framework of another study. A three-pronged approach was set up to improve the compliance between metal and polymer combining surface treatment, polymer reinforcement and coupling agent adhesion. The efficiency of each solution is discussed based on microstructural and mechanical characterizations.

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Nickel matrix composites reinforced by carbon nanotubes

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Carbon nanotubes (CNTs) have generated a great attention from the research community due to extraordinary properties as high stiffness, high strength and high thermal conductivity, combined with its low weight [1]. The use of CNTs as reinforcement material for metal matrix composites has been studied due to the potential hardening effect of these hard and stiff nanomaterials [2]. Furthermore, grain refinement strengthening has been identified in several CNT reinforced metal matrix composites. The CNTs dispersion through the metal matrix is the main challenge in the production of these nanocomposites due to the CNT agglomeration that influence the potential strengthening of the composite. Therefore, there is a great need for research on the production of metal matrix composites with a uniform dispersion of the CNTs. Previous work [3] revealed that Al-CNTs nanocomposites can be successfully produced through powder metallurgy using ultrasonication to perform the dispersion and mixture of CNT and Al powders. Ni-CNTs have also attracted some attention, however there are few studies that have used powder metallurgy as the production technique.

In this context, the aim of this work is to study the production of Ni-CNTs by powder metallurgy using ultrasonication to disperse and mix CNTs and Ni powders. The Ni powders (from Goodfellow) utilized exhibit a D50 of 25 μm with a purity of 99.5 %. To produce the composites, the MWCNTs (from FIBERMAX composites) were dispersed and mixed with Ni using an ultrasonicator during 15 minutes in isopropanol. The compacts, produced with 0, 0.5, 0.75, 1, 2, 3 and 4 vol% of CNTs, were sintered at 950 ºC during 90 min under a vacuum greater than 10^{-2} Pa. Thermal stability of the Ni sample and Ni-CNTs nanocomposites was evaluated by heat treatments at 700 ºC during 120 min. Microstructural characterization of the nanocomposites by SEM reveals that the CNTs are mainly observed in small clusters at grain boundary junctions. The Ni-0.75 vol% of CNTs revealed a better dispersion and smaller CNT agglomerates. These results were also observed in the production of Al-CNTs nanocomposites [3]. The effect of the CNTs in the grain size and texture of the Ni matrix was investigated by EBSD. The thermal stability evaluation revealed that the CNTs at the grain boundaries have a significant effect in the grain growth of the nanocomposites.

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Symposium C - Processing Technologies

Processing using laser/plasma/electric field technologies (C1)

Presentation of two different approaches to elaborate transparent ceramics for LASER and ballistic protection applications

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For last years, transparent polycristalline ceramics can be found in a various range of domains, such as medical, industry, defense and security. The development of these materials requires a poreless microstructure without impurities to avoid light scattering. As seen in the literature, transparency can be obtained by the application of a loading during the sintering step, such as Hot Press or Spark Plasma Sintering (SPS), or the combination of a pressureless sintering and Hot Isostatic Pressing (HIP).

On one hand, SPS process allows to obtain high optical quality in one step without post-treatment. Moreover, an additive helps to remove graphite contamination due to SPS tools.

On the other hand, pressureless sintering followed by a post-treatment by HIP is a suitable method to produce numerous and large ceramics of complex shape without the use of sintering aids. Nevertheless, this procedure requires considerable time.

Advantages and drawbacks of the two approaches to elaborate transparent ceramic will be illustrated with two examples: Er:YAG ceramic by SPS for LASER applications and MgAl2O4 spinel for ballistic protection of vehicles and soldiers.

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Alternative Sintering of Lead Free Potassium Sodium Niobate (KNN): Spark Plasma Texturing

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This talk is about an alternative method to sinter potassium sodium niobate ($(K,Na)NbO_3$, KNN) ceramics. KNN is a ferroelectric material, with a high Curie Temperature (Tc = 420ºC) and good piezoelectric response that can be engineered to match the piezoelectric performance of some of the most important lead based piezoelectrics. These assets make KNN one of the most promising lead-free systems. In spite of that sintering KNN ceramics is not trivial. The high sintering temperatures needed to densify this complex niobate oxide and the high vapour pressure of alkalines promotes the formation of secondary phases and hampers a full densification of KNN ceramics; hence their electromechanical performance. To solve this problem temperature and time for densification needs to be reduced or, in other terms, mass transport during the sintering step should be enhanced. It is now well known that the combination of pressure and electrical current during heating is a promising tool for rapid densification of ceramics at relatively low temperatures [1]. One of the most popular techniques among Field-Assisted Sintering Techniques (FAST) is Spark Plasma Sintering (SPS). There are recent reports on SPS KNN reporting KNN ceramics with densities around 96 % with enhanced dielectric performance [2-3]. Within this context in this work we present the results of KNN ceramics sintered by an alternative SPS method designated as spark-plasma-texturing (SPT) and defined as an edge-free SPS [4]. Here we report enhanced properties of KNN ceramics sintered by SPT. Dense ceramics (100%) with an average grain size $\bar{G} = 1.4\ \mu m$, $\varepsilon_r = 328$, $\tan\delta = 0.05$, $d_{33} = 125$ pC/N, g_{33} of 43.1×10^{-3} Vm/N, $P_r = 46.9\ \mu C/cm^2$ and $E_c = 9.4$ kV/cm were obtained. The comparison with SPT and conventional sintered KNN ceramics is presented and a phenomenological description is proposed.

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Structural and dielectric properties of laser annealed multiferroic nanostructures

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Nanostructured multiferroic materials presenting a coupling between their electric and magnetic degrees of freedom have been attracting much scientific and technological interest. By combining a piezoelectric ceramic and a magnetostrictive material the elastic interactions between both phases provide the coupling mechanism inducing a magnetoelectric behavior. A recent approach to create multiferroic magnetoelectric nanostructures is to take advantage of the film-substrate interfacial strain interaction in order to control or tune the electrical/ magnetic properties of the films. In this respect, $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ (BCZT), a strong lead free piezoelectric, and Metglas, an amorphous magnetic material with high magnetostriction, are potential candidates to form film-on-substrate multiferroic nanostructures with enhanced response. However, while BCZT needs deposition temperatures around 700ºC during film preparation, Metglas tends to decompose above 500ºC, hindering their combination in these multiferroic composites. Considering the low depth penetration of an excimer laser beam with wavelength of 248 mn inside a material, an alternative consists in performing a low temperature deposition of the BCZT phase, followed by a subsequent laser annealing step to crystallize the film.

As such, in this work we have studied the synthesis of multiferroic composites composed by BCZT thin films deposited by laser ablation with different oxygen pressures (0.03 mbar and 0.2 mbar), on Metglas substrates. BCZT was initially deposited at low temperature (400ºC). and then subjected to laser annealing with different fluences (0.05 J/cm^2 and 0.08 J/cm^2) and annealing times (up to 1000 seconds). The X-ray diffraction (XRD) results show that both the as-prepared films and the Metglas substrates were amorphous. No crystalline phases of Metglas, indicative of its decomposition, were observed on these samples. However, on the laser annealed films the perovskite-BCZT characteristic XRD peaks started to appear, with a relative intensity that increased with increasing annealing time. For annealing times higher than ~200 seconds a plateau was reached where the relative intensity was approximately constant. The SEM micrographs show dense films with thicknesses near 500 nm. A strong enhancement of the grain size with increasing laser annealing time was observed, indicative of the crystallization of the films. The dielectric properties show a tetragonal-cubic (ferroelectric) transition of BCZT at Tc ~ 90 that is broadened due to the nanoscopic grains composing the films. The slightly higher Tc relative to its bulk value is indicative of the presence of strain induced by the magnetostrictive substrate on the films. The influence of the synthesis conditions, particularly of the laser annealing step, on the electrical properties of the films will be discussed and presented.

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Upconversion luminescence of Ho^{3+} doped zirconia nanoparticles produced by pulsed laser ablation in water

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Luminescent oxide nanoparticles (NPs) doped with lanthanides (Ln) and transition metal (TM) ions have been reported as suitable alternatives to replace the conventional materials used currently in biological labeling due to its superior features, including higher chemical, thermal and photostability and lower toxicity. Within these materials, the ones having the ability to undergo up-conversion mechanisms, when pumped with near infrared (NIR) light, are of interest for *in vivo* biological labeling. The emission of visible light within the biological optical window, under NIR excitation, allows minimizing problems related to the low penetration depth of the excitation radiation, and with the autofluorescence and damage of the tissues that occur under ultraviolet/visible excitation.

Trivalent thulium (Tm^{3+}), erbium (Er^{3+}) and holmium (Ho^{3+}) ions are the most studied and effective optical centers that are incorporated in wide band gap materials for upconversion emission. Such is due to the singular electronic energy level diagram of these ions that show a ladder like structure, which allows the sequential absorption of NIR excitation photons, promoting the electron from the ground to intermediated electronic states (with long lifetime) and then to higher energy levels. In the past decade, a high effort has been applied in the production and in the study of the upconversion emission of these materials at the nanoscale. Typically, chemical strategies are applied to produce the upconversion NPs that are frequently time-consuming and give rise to NPs with low purity, not suitable for biological applications. In this work, NPs of zirconia doped with Ho^{3+} were prepared by pulsed laser ablation in liquids (PLAL). The possibility to produce stable colloidal solution, free of chemical precursors, in biocompatible solvents (such as water) is one of main advantages of PLAL relatively to other methods used to prepare NPs for biological labeling. In this technique, NPs are generated through the irradiation of a solid target, immersed in an appropriated liquid, by a high energy pulsed laser. Here, the NPs were prepared through the ablation of doped zirconia ceramic targets, immersed in water, using a nanosecond Q-switched Nd:YAG laser. Crystalline NPs with a spherical shape were successfully produced. The as-produced NPs show intense upconversion emission at room temperature when excited with 980 nm photons. Three groups of emission bands in the green, red and NIR spectral regions were observed and assigned to the characteristic intraionic transitions of Ho^{3+}. The role of holmium concentration and the effect of co-doping with Yb^{3+} ions in the upconversion luminescence was studied.

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Influence of liquid medium and laser fluence on production of silver nanoparticles by pulsed laser ablation

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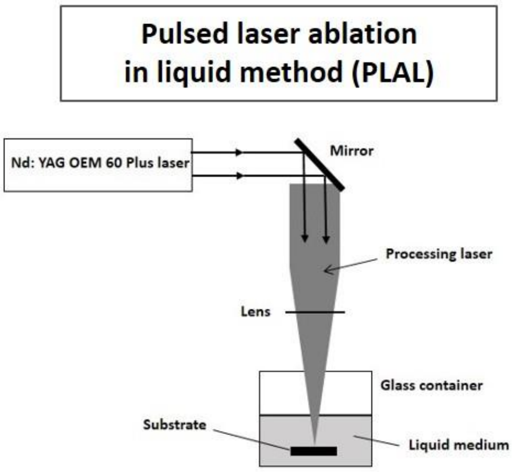
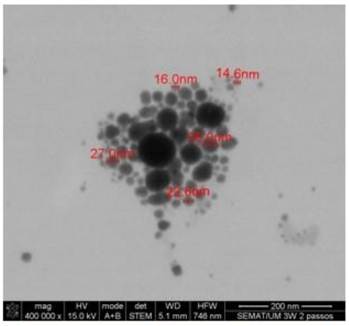
Synthesis of noble metal nanoparticles is currently an important research subject due to their extensive applications. Nanoparticles exhibit different characteristics and properties as consequence of a high surface area to volume ratio. In particular, silver nanoparticles (Ag-NPs) have unique properties, in contrast to larger-scale particles, such as optical, electrical, magnetic and antibacterial. Generally, the control of shape, size and size distribution is often achieved by different techniques including chemical and physical methods. Among others, the pulsed laser ablation in liquid (PLAL) has been attracting much interest for producing nanoparticles, since it avoids the contamination and the presence of impurity in the products obtained. Furthermore, this method allows producing stable colloids and nanoparticles with varying sizes. In this work, pulsed laser ablation method was used for synthesis of colloidal nanoparticles of silver target in different liquid environments (bidistilled water, acetone and ethanol) and laser fluence was also varied, in order to investigate the influence of these parameters on the characteristics of produced nanoparticles. Ultraviolet-visible (UV-Vis) absorption spectrophotometer and scanning electron microscope (SEM) were used for characterization of produced nanoparticles regarding to shape and size. The results showed that liquid environment and laser fluence have strong effect on charactristics of nanoparticles.





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Macro and microstructure properties of microwave fired porcelain

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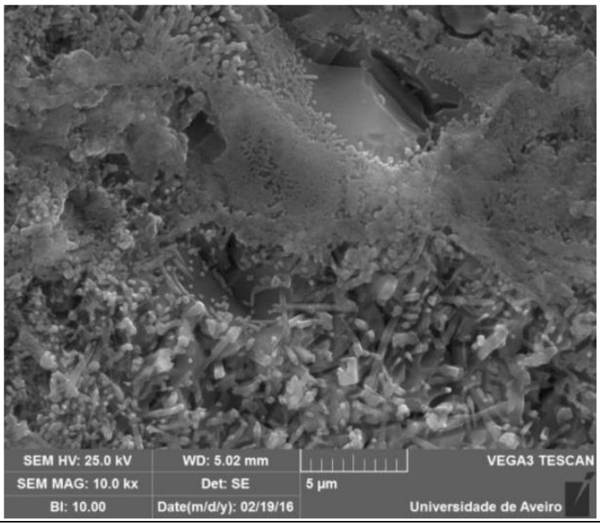
The industrial increasingly competitive environment leads to the exploration of alternative and more energy efficient technologies for the processing of ceramic materials, especially when high temperatures are required. Porcelain is one of those materials, were 50% of the total energy costs comes from the final firing stage, with natural gas being the most used energy source in industrial facilities. The microwave heating technology is presented as one option for ceramic materials firing. This heating technology presents shorter processing times, with costs reduction, and is less polluting. The microwave prototype bench oven presented has 6 generators in its core. Its operation, based on the permutation of the number of magnetrons promotes a more uniform heating of the material, avoiding the materials damage during sintering due to phenomena like the thermal runaway. Simulations of the electromagnetic field and temperature distribution are performed inside a microwave oven to understand these phenomena.

To measure the temperature, a thermocouple and a pyrometer were installed in the oven. To help in the firing, a silicon carbide (SiC) plate is used as microwave susceptor that also works as a base for the porcelain material. When compared with traditional ovens, our results show a reduction in the duration cycle, from room to the maximum temperature, of approximately 15% and with a displacement in the firing to lower temperatures. The impact resistance, porosity, density, X-ray diffraction and electron scanning microscopy of these materials are compared with those sintered by conventional methods, presenting similar characteristics.



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Copper thin films obtained by cathodic cage: Analysis of plasma confinement by increasing the thickness of the cage lid and the deposition parameters

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The deposition of thin films by plasma improves various physical, chemical and biological properties of surfaces such as hardness, wear resistance, corrosion, biocompatibility, bactericidal and fungicidal activities, etc. which contribute to the ennoblement of deposited materials. However, there are also some disadvantages, such as control of the atmosphere of the reactor, geometries of the parts to be deposited, understanding of deposition kinetics and reproducibility of results. The objective of this work is to study the deposition kinetics of copper thin films using the cathodic cage technique, changing the thickness of the cage lid, where the desired material will be extracted to form the thin film on the surface of the sample and its relation With the variation of treatment potency. Copper films are characterized as good electrical and thermal conductors, which justifies their use in microelectronics, according to the U.S. Environmental Agency (EPA) there are 282 types of bactericidal copper alloys, which enables their use in sterile environments. Thin films of copper were deposited on glass substrate, varying the deposition time, the current used in the process and the thickness of the lid of the cage. It evaluated the weight variation of both the cage and the deposited sample, defining the weight resulting from the depositions. The thin films were characterized by X-ray diffraction, scanning electron microscopy (SEM), atomic force microscopy (AFM), electrical conductivity and tribological analyzes (calotest, pin on disk).

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Performance Analysis of High Speed Steel (HSS) Drills Subjected to Different Surface Treatments to Plasma

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The plasma nitriding is performed in high speed steel tools to increase wear resistance of the cutting edge and reduce the tendency of the material machined to adhere and weld the output surface. This work aims to analyze the wear of high speed steel drills M2 under different parameters of plasma nitriding and / or deposition of titanium nitride film (TiN). The drills pass first through the nitriding treatment lasting for 3 hours, the temperature varying at 350 °C, 400 °C and 450 °C. The drills nitrided at 400 °C were further subjected to the deposition process of a TiN film. All drills were characterized by Vickers microhardness and tested in CNC machining center where the specimen was AISI 4340. A performance analysis of the different treatments was carried out, which concluded that the treatment resulted in better performance in machining was the nitriding treatment at 450 °C. The nitrided layer of drills was analyzed in a scanning electron microscope (SEM) and was made microhardness profile, where most nitrided layer was viewed in the drill treated at 350 °C, but it is noted that the hardness value increases with time of treatment, and that the deposition of the TiN film has low relevance in the performance of the drill.

Additive manufacturing (C2)

A new generation of x-ray computed tomography devices for quality insurance and metrology inspection in the field of additive manufacturing

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Keywords: micro-focus X-ray computed tomography (CT), laboratory CT system, industrial NDT, metrology

Summary: The YXLON FF35 CT system, is designed to achieve extremely precise X-ray inspection results for a wide range of applications while at the same time it offers user friendliness at highest level by a new intuitive touch interface control concept and further smart functionalities. In the presentation we will show representative applications focusing on the field of additive manufacturing and material science.

Introduction

Computed tomography has become one of the most important and powerful non-destructive testing methods - an achievement resulting from the continuous improvement of CT scanning and reconstruction methods, the enabling of increased precision and resolution and finally innovative concepts allowing for highest user friendliness to simplify the execution of successful CT experiments with high quality results.

Today´s range of CT applications is applied to nearly every industry, i.e. automotive, electronics, aerospace and material science. Here it is used for research and development, failure analysis, process and quality control, small series inspection, combined DR-CT inspection, defect and material analysis, assembly checks and, becoming more and more important, metrology, i.e. dimensional measurements.

Experimental Method

Experiments are performed by choosing one out of two different x-ray sources mounted side-by-side in the high precision laboratory CT system FF35. The FF35 CT is equipped with a digital flat panel detector. A granite base enables precise manipulation. The maximum scan field can be 300 mm in diameter or 500 mm in height. Reconstruction of the CT volumes is carried out by a filtered back projection algorithm. Data quality can be improved by applying a numerous variety of correction filters.

Results

Results of representative applications, e.g. from additive manufacturing, metrology and carbon fibre composites, will be highlighted during the presentation to demonstrate the performance of today´s laboratory CT devices and how they are used to increase the level of quality insurance processes.

Study of PLA properties obtained by 3D printing FDM process with FUZZY-PID temperature control and cooling system

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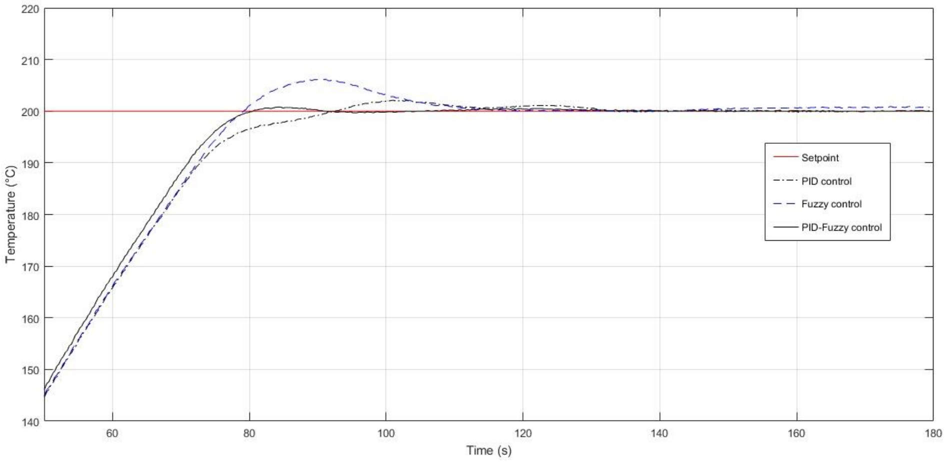
Currently the 3D printing systems for FDM (Fused Deposition Modeling) process with PLA (Polylactic Acid) use the open source control firmware such as MARLIN, REPETIER, and GRBL, among others. These systems apply a classical PID (Proportional Integral Derivative) control for heating the extruder. Heating up this element until stabilizes it for the PLA extrusion temperature, at 200 °C, takes about 180 seconds.

Nowadays it is common to use cooling systems on the extruder to reduce the probability of supports necessity and at the same time improving parts surface quality. These refrigeration systems cause perturbations in the process of extruder heating that must be corrected by the controller. A traditional PID control is not robust enough to keep a suitable extrusion temperature under these conditions.

This research presents the design and incorporation of a control system that optimizes the heating process, using the user's experience through fuzzy logic control, even combining both in a PID-FUZZY controller. Also with an additional cooling system, the mechanical properties (tensile tests) of the PLA are tested under different printing conditions; PID control and PID-Fuzzy, both with and without cooling system, and the results obtained will be discussed.

Figure shows the heating curve as function of the time with different control types. As one can see, the combined control allows a faster response towards a better temperature stabilization control. This effect will be analyzed in terms of parts mechanical properties to check the advantages of using it in low cost FDM 3D printers.



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Mechanical behavior of thermoplastic based composites processed by additive manufacturing

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Additive manufacturing has been experiencing an exponential growth and this tendency is going be maintained in the next years, with particular incidence in low cost printers. However, the industry is continuously requiring new features and new materials from the manufacturing process, namely composites with higher mechanical properties to produce functional parts. These new requirements creates a continuous pressure to design new components and printers able to process these more abrasive and high temperature materials, however it is well known that parts produced with these printers have lower mechanical properties than the equivalent ones obtained by injection molding. This research focuses on the analysis of samples printed in a low cost open source printer, comparing the mechanical properties obtained with the ones claimed by the filament supplier.

A commercial 1,75mm diameter PETG thermoplastic filament with short fibers was selected. The printer parameters were chosen considering this type of material and previous experience with this printer, processing ABS and PLA.

The mechanical, thermal and physical properties were analyzed and compared with manufacturer's reference data sheets in order to find out if there is in fact any reinforcement provided by the short fibers and what is the influence of the material extrusion by additive manufacturing in terms of properties degradation.

This work is divided in two separate parts. In the first section, FDM (Fused deposition modeling) process and thermoplastics reinforced composites characteristics will be reviewed. The second part focus in the characterization of several types of samples. Five flexural and five tensile samples were fabricated to characterize the mechanical properties. The dispersion of the fibers as well as their length and diameter are critical parameters influencing the mechanical behavior of the printed parts. This way, two small dimension cubes were printed; top face to show the printing pattern, and lateral view, to analyze the layer overlay effect. The filament was also characterized longitudinally and cross section.

Optical microscopy analysis revealed that the fibers were aligned along the filament and with the extrusion direction.

The obtained results show that the mechanical properties were roughly half of what was announced by the supplier as well as the fiber percentage.

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Porcelain powders formulation for indirect selective laser sintering

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Additive manufacturing (AM) is a disruptive conformation process whichprocess which allows the fabrication of parts / objects with complex shapes and functionallityfunctionality. It AM is well established for metallic and polymeric materials. However, in the case of ceramic materials there are still challenges to overcome and there is a need for systematic studies. Selective laser sintering (SLS) is one of the additive manufacturingAM techniques in which a laser beam is used to sinter/melt the material. Low melting temperature metals and polymers are well suited for SLS. In the case of ceramics, the sintering temperature is considerably higher and the crack formation and delamination in the ceramic body is one of the reported problems by when using direct laser sintering . Furthermore, the indirect way of selective laser sintering has been reported as a potential good option for the use of ceramic materials in SLS. In this process a sacrificial binder is used during the SLS process and it is removed in the forward steps.

In this work porcelain powder formulations, produced by Porcelanas da Costa Verde, were are prepared and used in indirect selective laser sintering studies. Polyamide was is used as sacrificial binder. Different formulation of ceramic/polymeric powders were are prepared and studied regarding pre-processing treatments, printing direction, different porcelain/binder ratios and reuse of powders. After the SLS process, several and different steps have been performed in order to achieve higher density. Between each step, dimension stability, microstructure, porosity and density have been monitored and analyzed and its relation with the processing cycle established. The results showed that the heat treatment of the ceramic powders is essential in order to be able to print porcelain. The increase in the porcelain powder content showed to increases the density of the final parts. It was shown that tThe reuse of powders showed to beis possible, what is currently of high importance from the industrial point of view, but SLS parameters must to be adapted for these formulations.

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MATERIAIS 2017
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EXPLORING MATERIALS... BRINGING SCIENCE SOLUTIONS TO THE WORLD
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A multimaterial approach for the next generation of high performance moulds

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The productivity of the injection moulding processes and the quality of the thermoplastic injected parts, depend on the polymeric material, on the injection equipment and peripherals and especially on the mould. Moulds are mostly fabricated on metals, in particular steel, aluminium and copper alloys. The mould should allow heat transfer during the injection moulding cycle. Traditionally, the moulds are held at a constant temperature which depends essentially on the type of polymeric material to be injected. However, for an optimum thermal cycle, the mould should be heated to near the melting temperature of the polymer during the injection phase and then cooled to allow the mechanical part extraction. The mould must therefore be optimized to have a high performance (both, thermal and mechanical) with reduced cycles for high productivity. In order to optimize thermal heat transfer, and to have the required mechanical properties, mould making must be based on three fundamental vectors: mould material, manufacturing process and optimized design (minimizing the thickness of walls, maximizing contact area with cooling and heating fluids, etc.). Production processes based on direct digital manufacturing were used, in particular the additive manufacturing process via Selective Laser Melting (SLM) and subsequent machining for finishing. The material used for the mould it was the H13 steel (AISI). This steel was copper coated in order to increase the thermal conduction properties and was processed by a SLM 125 machine with a maximum power of 400W. The processing parameters were selected in order to obtain mould inserts with high surface quality (minimizing the milling processes). The effect of the copper coating was analysed and compared to uncoated H13 steel. The combination of the three vectors referred (material, manufacturing process and mould design based on direct digital manufacturing) allows the integrated development of special tools / moulds with high performances. Moreover, the ability to accurately control the heating /cooling times and rates, allows the injection of plastic components with molecular orientations and degrees of crystallinity tailored to the application.

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Improving the performance of injection moulding through the application of additive manufacturing

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Automotive industry is one of the most competitive concerning time-to-market decrease, based on the optimized production of moulding tools. Additive manufacturing, namely Selective Laser Melting (SLM), can be an alternative to conventional machining processes for producing moulding tools due to its freeform capacity for generating complex geometries with no compromise on tool mechanical properties. This study aims to compare the performance of the injection moulding process by using metallic moulding inserts produced by both conventional and additive technologies.

The case-study selected for this research work is based on a parking sensor housing, which is a plastic part typically assembled on vehicle front and rear bumpers, therefore, with aesthetics concerns. The part possesses some challenging geometrical requirements for successful injection moulding such as wall thickness variations that may cause warpage and/or sink marks.

The application of tool inserts produced through additive manufacturing on the mould making industry brought to light a new competitive edge, where moulding tools can be optimized with conformal channels, enabling optimal cooling conditions and therefore, avoiding plastic part defects. To evaluate the impact of conformal cooling on this case-study plastic parts quality, injection simulations were carried out. Injection simulation results using conformal cooling channels provided excellent prospects concerning elimination of sink marks and injection cycle time reduction. Based on these results, the mould was reengineered in order to incorporate additive manufacturing components. Core, cavity and other mould elements were selected for the use of SLM and building strategies were studied, focusing the possibility of hybrid building, both to optimize time-to-tooling as well as building costs.

Post-processing operations were carried out to enhance surface finishing and material behaviour, in order to withstand the full demands of the injection moulding process.

Injection tests were performed to validate the expectations provided earlier by injection simulations. The results were as expected, enabling good quality plastic parts and a significant decrease on cooling time, and, consequently, on the overall cycle time.

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Influence of the thickness parts produced by SLM on the transformation characteristics of NiTi

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Additive Manufacturing (AM) is increasingly a technology with near-net-shape processing capabilities. Depending on the used technology, it is possible to obtain final products directly from the production equipment, with the same mechanical and aesthetic properties of products produced by other conventional technologies. Freedom of form continues to be the key point of AM, offering a production capacity of forms impossible to obtain by any other technology, because of its construction method of parts layer by layer. The Selective Laser Melting (SLM) technology is one of the many AM technics, and uses a laser beam to melt the bed of powder for each layer. The evolution of the SLM equipment allows the production of parts with better properties and also with larger dimensions. These characteristics make this technology increasingly used in the production of large parts for demanding markets such as the automotive and aerospace. The products for these markets are known for their quality requirements, which means that SLM parts must be free of defects. SLM can produce parts in metallic materials, including Nickel-Titanium alloys, also known as Nitinol alloys, which are characterized as Shape Memory Alloys (SMAs)-In the production of large parts by SLM it is necessary to guarantee the isotropy of the properties throughout the part extension. It is known that the processing parameters have great influence on the properties of the final product, and that the same parameters have different results for different scanning areas. The main target of the study is to evaluate the influence of the parts thickness on the homogeneity of chemical composition, microstructure and properties will be presented. Different thicknesses produced in optimized conditions of additive where the analyses were performed. This study intends to evaluate the isotropy in SLM production of large NiTi parts, in order to guarantee the quality of the final product.

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Coatings and interfaces (C3)

Protective coatings to avoid zirconia aging behavior

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Background: Tetragonal zirconia polycrystal (TZP) is a ceramic material known because of its high mechanical properties, achieved by a martensitic microstructural transformation that occurs in a presence of mechanical stresses. Because of that, bioinertess and aesthetical properties, TZP has been used as biomaterial, mainly to produce implant and prosthesis. However, when stabilized by yttria (Y-TZP), water molecules diffusion are able to promote this microstructural changing, reducing material flexure strength in a phenomenon called Low Thermal Degradation (LTD) or aging.
Objective: This work aims to produce dense layers of aging unsensitive materials, covering Y-TZP cores by dip coating process.
Results: Suspensions containing 12% mol ceria stabilized tetragonal zirconia polycrystal (Ce-TZP) and yttria partially stabilized zirconia (Y-PSZ) were produced using commercial powders (Hitachi and Tosoh respectively) in different solid contents. These suspensions were applied, by dip coating, in a Y-TZP core. Coatings were evaluated in terms of density by qualitative SEM analysis, which shown that dense layers could be obtained by using suspension without binder. Furthermore, coatings produced by one dip have shown better results than two or three dips, in terms of microstructure. Layers obtained in better conditions of process, i.e. higher density and lower thickness, were measured having about five micrometers for Ce-TZP and twenty micrometers for Y-PSZ. Accelerated aging tests were performed up to 18 hours for each layer material and no LTD was observed in core, as well in layers.
Significance: This paper provides a study of aging behavior of zirconia-based coatings applied to zirconia samples. In terms of aging, both layers applied (Ce-TZP and Y-PSZ) have shielded Y-TZP core from moisture diffusion, showing no phase changing in the end of process. Dip coating process is a strategic choice, once is possible to produce slim layers that can be reproduced in industrial scale.

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Using CO_2 supercritical fluid deposition to prepare functional thin film composite

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Oxide-based porous films may be seen as “bottom-up” platforms for nanotechnology, finding potentially applications at the microelectronics and photonics fields not only by means of the nanofabrication of functional ordered porous patterns with lateral thickness below 100 nm, but also by functionalization of the pores with molecules or nanoparticles.

In this work [1], a new concept to prepare nanocomposite thin films is explored. Two chemical-based bottom-up steps are used to design functional films including: i) block copolymer-assisted self-assembly of a porous matrix; and ii) impregnation of nanoparticles from a ferroic phase within the pores by supercritical CO_2 deposition. Porous nanopatterned $BaTiO_3$ thin films with *ca*. 17 nm of thickness are prepared using a cost-effective sol-gel solution containing a block copolymer and evaporation-induced self-assembly methodology. Hexagonal-arranged pores with diameter of *ca.* 95 nm, running perpendicularly to the substrate are filled with Ni nanoparticles using the supercritical fluid deposition technique from reduction of hydrated nickel nitrate in a supercritical CO_2-ethanol mixture at 250 ºC. Small Ni nanoparticles with 21 ± 5 nm nm are selectively deposited inside the pores of the matrix. Although through the MFM measurements it was impossible to confirm the magnetic behaviour due to the parallel orientation of the domains, SQUID measurements undoubtedly prove that a magnetic material was successfully deposited in the porous films of $BaTiO_3$.

The chemical composition of the porous matrix and of the nanoparticles can be modified by the use of different inorganic precursors. This novel strategy of functionalization based in supercritical fluid deposition to create nanocomposite materials is very versatile and can open perspectives for the application of these materials as nanopatterned media (magnetic data storage devices) as well as multiferroic materials.

[1] Castro *et al*. J. Mater. Chem. C, 2016, DOI: 10.1039/C6TC04232E.

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Aberration Corrected Analytical STEM and TEM for Multi-User Facilities

Felix Von Cube
Monocomp/Hitachi

In recent years the revolution in aberration correction technology has made ultrahigh resolution imaging and analysis routinely accessible on TEM and STEM. This presentation will show applications achievable with our high end microscope line up, ranging from 3D EDX analysis with our dedicated STEM (HD2700) to atomic imaging and mapping with the new soon to come multi user TEM/STEM (HF5000). Additionally, results of in-situ heating and gas exposure from our highly customizable 300 kV TEM/STEM will be presented. With this presentation I hope to give a small insight of the versatility and flexibility that Hitachi High-Technologies can offer in the field of transmission electron microscopy.

Selective metallization of flexible substrates by inkjet printing with electroless copper plating

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A new efficient approach for selective metallization of flexible substrates such as poly(ethyleneterephtalate) (PET) sheets has been developed (Figure 1). The method is based on the covalent grafting of a chelating polymer film poly-4-vinylpyridine (P4VP) able to complex metallic palladium ions which then serve as catalyst for a copper electroless plating step. A solution of P4VP containing the palladium ions (II) catalyst is firstly inkjet printed to form a metallization primer. This primer is then photo-grafted onto the surface using a flashlamp. By a photo-oxidation process, light allows the formation of free radicals on the P4VP layer in contact with the substrate. Thus, covalent adhesion between the substrate and the P4VP is achieved. A selective copper layer is finally grown on the activated primer by a copper electroless plating process. The grafted primer layer enhances the copper adhesion. A resistivity - measured with four probes - as low as 2.1 μΩ.cm (sheet resistance equivalent to 84 mΩ/□ for 250 nm thickness) is obtained, which is only 20% higher than the one of bulk copper. This new low-temperature process only requires a plating bath and is thus compatible with low-cost thermally unstable flexible polymer substrates and R2R printing processes. The final metallic layer notably shows a very good adhesion on PET substrate and good stability in ambient atmosphere.

This approach is a very attractive way to achieve localized plastic substrate (such as PET, Kapton) metallization under ambient conditions.

Due to the versatility of the process in terms of flexible substrate type, different applications can be targeted such as RFID, Plastronic, interconnects for flexible electronic.

Keywords: copper electroless plating, inkjet printing, printed electronics, flexible substrate, antenna

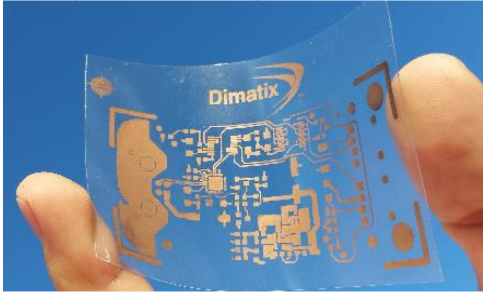

Figure 1: Copper patterns obtained on flexible substrate by electroless process after the primer printing, light-induced grafting and metallization steps.

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On the role of the energetic species in TiN thin film growth by reactive DOMS in Ar/N_2

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The properties of TiN films deposited by DCMS strongly depend on the composition of the discharge since the N_2 fraction is the main deposition parameter controlling the poisoning of the target and, thus, the flux and energy of the species bombarding the growing films. Accordingly, the properties of the films are also intimately linked to the N_2 fraction.

In this work TiN films were deposited by DOMS, a variant of HiPIMS, with increasing N_2 content in the discharge gas. The IEDFs of the plasma species were acquired with EQP, crystalline structure characterized by X-ray diffraction, chemical composition evaluated by EDS, microstructure by SEM and hardness measured by nano-indentation. The results show that TiN films deposited at low N_2 fraction grow under relatively low intensity bombardment conditions that favour the formation of [111] preferential orientation. On the contrary, TiN films deposited at higher N_2 fractions are grown under heavy bombardment by the plasma species as can be deducted from their structural properties - less crystalline films, high compressive stresses formed and decrease of the grain size.

The increased bombardment of the films with increasing N_2 fraction was attributed to changes of N species energy flux as corroborated by the IEDFs. The evolution of the films properties was accounted for by assuming that the energetic metallic and monoatomic nitrogen species interact with the growing film through different mechanisms and thus they have differentiated effects on the films properties. The structural properties of the films are mainly influenced by the bombardment by energetic N species while the microstructure of the films and their hardness mainly depends on the bombardment by energetic Ti species.

The different roles of the energetic metallic and monoatomic nitrogen species in the growth process of TiN films implies that proper control and balance of the two types of bombardment are mandatory in order to optimize the properties of the TiN for the targeted application.

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Microstructure and Hardness Enhancement of Multilayer CrN/MoN Films

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Transition metal nitride thin films are widely used as hard and wear-resistant coatings in cutting tool or manufacturing industries. However, their efficient outputs may be improved by applying multilayer design. The report is focused on study and characterisation of structure and mechanical properties of Chromium and Molybdenum multilayer nitride films. The films were obtained using Arc-PVD deposition on stainless steel substrates in vacuum-arc unit "Bulat-6". The total coating thickness varies from 8 to 15 µm when individual layer thickness is in range from 20 nm to 1 µm. Experiments were performed on 6 samples with 12, 24, 44, 88, 180 and 354 layers with different individual layer thickness.

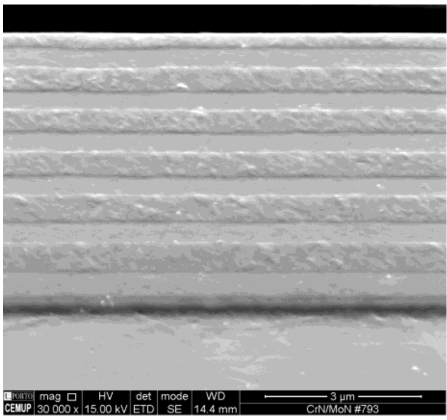

Fig. 1 – SEM-image of cross-section CrN/MoN multilayer film.

Elemental composition was evaluated using energy-dispersive X-ray spectroscopy (EDS) and wavelength-dispersive X-ray spectroscopy (WDS). Surface morphology and cross-section were characterised with scanning electron microscopy (SEM). X-ray diffraction measurement (XRD) and electron backscatter diffraction (EBSD) were used for structure characterisation.

The similar internal structure of Chromium and Molybdenum nitrides results in their similar diffraction patterns and, related to this, difficulties of overlapped peaks identification. To define phases which are present in considered films, the X-ray techniques of low angle methods were used. Grazing incidence X-ray diffraction and in-plane X-ray analysis have allowed to study only top surface layers of samples and receive patterns separately from CrN and MoN.

The relations between microstructure, bilayers thickness and mechanical properties have been found.

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Interface Characterization of Industrial Slide-Contact Bearings Coated with Tin Based Alloys

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Slide-Contact Bearings are mechanical devices often employed in high speed rotary machinery under heavy loading conditions, suitable for shaft large dimensions. The main applications include producers of energy (thermal, hydro and nuclear plants), cement industry; manufactures of turbines, generators, motors, among others.

The Slide-Contact Bearings have to fulfil certain tribological and mechanical requirements so that mechanical device performance is satisfactory. To assure those requirements the steel bearing surfaces are usually cover with anti-friction alloys, which provide the surface properties modification, namely corrosion resistance increase, wear and friction coefficient decrease [1].

Therefore, the adhesion mechanism between the anti-friction alloy and the steel substrate should be strong enough to prevent bearing damage. In order to achieve an effective joining process between bearing surfaces and anti-friction alloy, some requirements must be present, to establish a solid, cohesive and strong connection. Babbitt alloys have many beneficial properties, such as good compatibility with steel, ability to embed foreign particles, high thermal conductivity, good wettability, flexible conformability and antifriction property [2]. Hence Babbitt alloys, namely tin based and lead based are widely used.

In this study, were applied different conditions of DIN St52 steel substrate and surface preparation. The interface between steel substrate and the Tin based alloy (Tego V738) was characterized in order to understand the influence on bearing performance.

For such purpose, the gravity casting of the Tin based alloy was performed over the steel substrates and the microstructure, chemical composition, hardness and the adhesion at the interface was investigated.

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Synthesis and structural characterization of fluorine-alloyed WS2-C coatings produced by reactive magnetron sputtering

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Transition metal dichalcogenides are well-known 2D materials by their lubricating property although they present low load-bearing capacity and environmental sensitivity drawbacks. WS2 is commonly alloyed with carbon (WS_2-C) in order to get good mechanical and tribological performances and overcome those issues. Furthermore, specific mechanical applications like lubrication procedures in devices' assemblage processes require special surface wettability character. In this work, W-S-C coatings doped with fluorine (F) were deposited in a semi-industrial magnetron sputtering machine, aiming to reach controlled water/oil wettability while getting good frictional properties. An Ar/CF_4 reactive gas mixture was used for incorporating F and C in the films. Two WS_2 targets and one Cr target (for adhesion interlayer) were used to deposit the coatings in glass, silicon and steel substrates. Morphology and chemical composition/bonding was characterized by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), Raman and X-ray photoelectron (XPS) spectroscopies. The coatings' microstructure was evaluated by X-ray diffraction (XRD); while the mechanical properties such as hardness/elastic modulus and adhesion were respectively characterized by nanoindentation procedures and scratch testing.

The results revealed that for lower CF_4 partial pressures the fluorine content in the coatings increased without significantly change the structure and morphology in relation to pure WS2-C coatings. However, for higher CF_4 partial pressures, the F content in the coatings unexpectedly decays to residual values and high at. % of oxygen in the coatings are measured. Furthermore, the F insertion in the coatings led to the deterioration of the mechanical properties. In regard to water/oil wettability of the developed coatings, the insertion of F (5 at. %) led to a water contact angle (WCA) of 40 ± 2º and an oil contact angle (OCA) of 15 ± 2º; comparatively to the non-fluor doped coating which had a WCA of 46 ± 5º and a OCA of 18 ± 1º.

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Effect of high dosage on the short-fibber-carbon-reinforced epoxy composites machining process

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Carbon fiber reinforced composites are being successfully used in many applications in result of its good mechanical, thermal and electrical properties. Short fiber reinforced polymers fill the gap of mechanical property between the continuous-fiber laminates and the unreinforced polymers. The study of short-fibber-carbon-reinforced epoxy composites is important and relevant because there is not a complete understanding of machining process to these materials and its complex effect is little known subject.

This paper studies the machinability and the tensile properties of short-fibber-carbon-reinforced composites epoxy, under high dosage condition, manufactured by compression moulding, potentially used in automotive and aeronautic industries. This work intends to give a small contribution to the best use of this industrial process. The paper reports the effect of fiber dosage of reinforcing on tensile strength and stiffness modulus and also on the machinability, considering four cutting speed, two values of fiber length and two different values of dosage, when combined in mass fraction, 43% wt, 75% wt of resin and fiber. For this purpose, the impact of cutting conditions on surface roughness and temperature during process was studied. This research is looking to identify the machining behavior to variation of dosage on short fiber composite.

This preliminarily findings could be potentially used at new studies or applied in automotive and aeronautic industries right away, they are likely to be of great interest to the vision scientists, researchers, and trainees who work at industry.

Highlights; Study the machinability on high dosage short-fibber-carbon-reinforced epoxy composites.
Effect of the machining parameters on cutting temperature, surface roughness and tensile properties.
Plate manufacturing by compression moulding process.

Keywords; Composite, Machinability of composites, Short fibber composite, Mechanical properties

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Reinforcement Sputtering Functionalization and influence on the interface reaction of 410L- SiC_p stainless steel composites

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The aim of this work was to investigate the reactivity between SiC particles (SiC_p) and 410L stainless steel (SS) alloy. The SiCp were functionalized by the sputter coating of: (i). titanium and (ii) titanium and nickel. 410L SS-10wt.SiC_p composites were produced by Powder Metallurgy (PM).
The surface and interface structures of the functionalized SiC_p were investigated by SEM/EDS. The observations by SEM/EDS revealed the coated layer of the sputtered titanium or titanium-nickel. The interfacial bonding between SiC_p and sputter-coated titanium and Ti/Ni was investigated and discussed.

Keywords: stainless steel, SiCp, MMCs, interface reaction, Sputter coatings

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Structural studies of the hydrogenated silicon thin film deposited by RF magnetron sputtering

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Hydrogenated nanocrystalline silicon films have become the subject of great attention due to their remarkable properties for microelectronics and solar cells technology. The structural changes in intrinsic silicon thin films deposited by radiofrequency (rf) magnetron sputtering at room temperature (Ts = 35°C) are investigated as a function of the rf-power. The aim of this work is to get more insight into the effect of the rf-power. By varying the rf-power from 200 W to 500 W, and keeping all other parameters of the plasma constant (the total pressure is fixed at 6 Pa, the plasma gas mixture of 30% Argon and 70% H_2 and the target-sample holder distance of 50 mm). The composition and the microstructure of the films were analysed by FTIR, atomic force microscopy (AFM), optical transmission measurements (OT) and Raman analysis. The results indicate that the film deposited at RF_power equal to 200w has amorphous structure. The films deposited at RF_power above the 200w have nanocrystalline structures. The grain size, the volume fraction and thickness increase with increasing rf-power.

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Recycling (C4)

Inorganic polymers reinforced with glass fibre waste for construction materials

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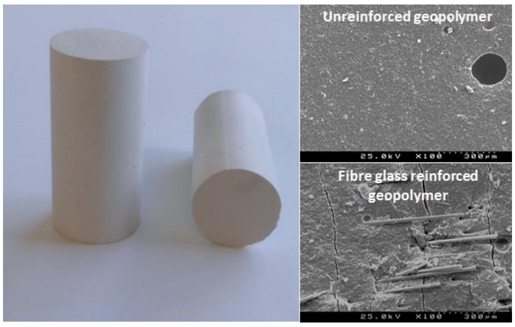
Despite the good mechanical performance of Portland cement-based materials, their production is becoming perceived as unsustainable [1] due to the massive CO_2 emissions coming from the decomposition of calcium carbonate and combustion of fuel cells. Recent data shows that the production of 1 ton of Portland cement generates 0.85 ton of CO_2 [2], accounting to around 5-7% of the total CO_2 anthropogenic emissions [3]. In this context the development of new building materials with reduced environmental footprint is of the upmost importance. Inorganic polymers (also known as geopolymers) emerge as a promising and environmental friendlier alternative to Portland cement [4]. These binder materials are synthesized by alkali activation of silica and alumina rich materials at relatively low temperatures. In this study the feasibility of using glass fibre waste as reinforcement material in the production of metakaolin-based geopolymers was evaluated. The influence of the fibre size and content on the tensile and compressive strength of produced inorganic polymers was investigated. Results show a 162% and 76% improvement, respectively on the compressive and tensile strength for composites containing 3 wt.% glass fiber waste. These results demonstrate feasibility of using unexplored glass waste fibre as reinforcement agent in the production of environmentally friendly binder materials, which may prevent the landfilling of huge amounts of this waste material.



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Development of Eco Composites based on Slate Residues

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During the last few years, several studies have been carried out in order to develop composite materials incorporating natural materials as reinforcement agents in a polymeric matrix. The sustainability of resources and materials is one of main trends in the building industry. Thus, eco composites reinforced by mineral fillers, such as slate, has been assumed as a special target on this area.

The processes of slate's extraction and polishing, a metamorphic rock, generate a large amount of by-products (about 40%), which are considered waste So, the main purpose of this development is to give a new life to these residues, which are in the form of powder, creating added-value products. The composites were developed through the incorporation of the mineral fillers in a thermoset bio-epoxy matrix, which is an ecological resin and consequently environmentally friendly.

However, this type of reinforcement presents low compatibility with polymeric matrices. In order to overcome this problem, a silane agent was used. Silanes are coupling agents that allow improving the compatibility between organic and inorganic materials, improving the adhesion between the slate and the bio-epoxy matrix.

Samples were produced by compression moulding process with and without incorporation of silane on slate residue. The particle size of the slate used was lower than 500 µm and the content added to the resin was 50 % and 70 %.

Afterwards, in order to evaluate the influence of silane in the improvement of the adhesion between the slate and matrix, flexural tests were performed, according to EN ISO 178. Besides the mechanical characterization, other tests were performed, such as Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS), to evaluate the chemical compositions and particle sizes of the samples. The results showed that the adhesion between slate residue and bio-epoxy matrix as well as the mechanical properties can be improved by the application of silane agent.

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Physical and mechanical properties of eco-reactive powder concrete

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Large quantities of used tires and bottle glass are dumped in nature annually worldwide creating cumbersome discharges. The valorization of these wastes in the manufacture of cement materials could constitute an interesting ecological and economic alternative. However the characteristics and the durability of the developed products should be acceptable. This paper presents a contribution for the development of ecological concrete, lightened by waste rubber aggregates (RW) and with increased compactness by the incorporation of glass bottles powder (GP).

Rubber aggregates (0-4mm) were obtained from the milling of used tires. They were used replacing crushed sand in concrete mixes by volume rates of 10%, 20%, 40% and 60%. Moreover, the glass powder was used as cement substituent by mass with a fixed rate of 15%. The workability, fresh unit weight, compressive and tensile strengths, and deformability were experimentally determined and analyzed.

The best compressive strength with respect to RW replacement rates were obtained with 10% and 20%. The compressive strength further improved with the incorporation of the glass powder. It has played an important role in the decrease of porosity of the mixtures and the improvement of the indicators of sustainability such as the compression resistance and the permeability. The deformability of rubberized mixtures is higher than reference concrete. So, the ductility increases with the increase of the RW replacement rate. Furthermore, the developed rubberized concretes with GP presented the most resistant and deformable behavior under the action of compression compared to the reference rubberized concrete.

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Transformation of Textile and Wood Waste in new Products

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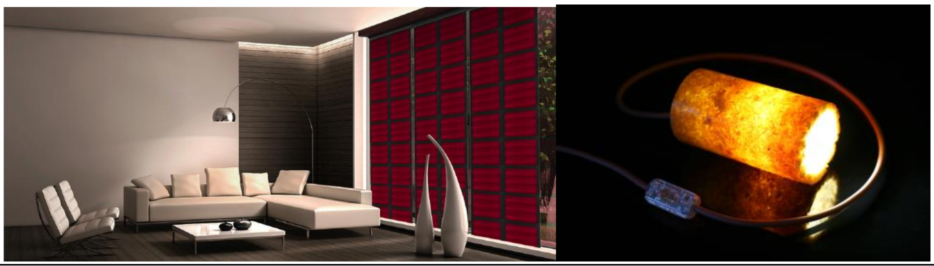
The Master's program in Product and Industrial Design of University of Porto is a partnership between the Faculty of Fine Arts and the Faculty of Engineering. The course is a project-based learning, aiming to develop competences and skills in the area of product and industrial design, and all the teaching staff is committed with the main project taught in each semester of the first year. The multidisciplinarity between designers and engineering creates methodologies and principles to be applied in the development of innovative projects in partnership with companies and non-profit institutions. In the period of 2013/16, students had the opportunity to participate in a European Project about Community Service Engineering. This project had concerns about the sustainability of our planet.

As it is well known, each year the natural resources are sold-out earlier in the year than the nature capacity to reset them. Human being must be aware of this problem, changing the basic patterns of consumption and manufacturing. Ecological concerns should be directed towards a new design orientation, through the use of industrial waste recycling that is normally devalued, without being assigned a new application.

This work aims to promote the reuse of two types of industrial wastes. The main objective is the idealization and conception of products that valued textile and wood residues, through the creation of new raw materials. It is necessary that design and engineering become the vehicle for raising awareness of waste reuse, giving design a commitment to minimize the environmental impact.

The idealization of products that reuse materials, presenting better environmental performance, are considered as a factor of importance for sustainable development. In this way, new solutions were created for textile and wood waste, in an innovative way, with the materialization of products, associated with the areas of furniture and luminaires. The solutions validated in concepts, were understood in processes of residue transformation, namely the fabric and sawdust. Through aggregation processes between the textile waste and contact glue, a shape memory alloy (nitinol wire) was incorporated in order to produce an innovative curtain that changes shape with the sunlight incidence. Through agglutination processes with a synthetic resinous binder, sawdust was shaped to preserve the wood natural color. The results obtained are very promising, as one can see in figure.



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Symposium D - Characterization and Modelling

Physical, chemical and structural characterization (D1)

Raman and infrared reflectivity studies of $LaTaTiO_6$ polymorphs

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Ln$TaTiO_6$ compounds have fundamental and technological interests, because they show appropriate dielectric parameters for microwave (MW) and electronic applications, they can serve as hosts for U and Th radiative wastes, and present interesting features linked to an *aeschynite-euxenite* transformation around a morphotropic phase boundary [1-3]. Indeed, for *Ln* ions with lower atomic number ($Z \leq 66$, Dy) *Ln*$TaTiO_6$ crystallize into an orthorhombic structure of *aeschynite* type belonging to the *Pnma* space group, while for $Z \geq 67$ (Ho) the structure is still orthorhombic but of an *euxenite* type (*Pbcn*). Within each group, the materials show very similar structural, dielectric and vibrational spectroscopic responses. However, the results obtained for $LaTaTiO_6$ usually did not match the properties of other lower Z compounds; for instance, it presents a lower dielectric constant and negative temperature coefficient of resonance frequency, τ_f [1]. In addition, DRX and Raman patterns of $LaTaTiO_6$ ceramics completely differ from those of *aeschynite* and *euxenite* *Ln*$TaTiO_6$ [1,2], which was attributed to the presence of multiphase. Despite that, the material shows quite good MW dielectric properties, and, therefore, it has been considered as a good candidate for MW dielectric applications. Recently, Kasunič *et al.* have showed that $LaTaTiO_6$ presents polymorphism, and that phase pure orthorhombic *aeschynite* and monoclinic *C2/c* structures can be obtained, depending on the sintering conditions [4]. This find rises the controversies about the structure and properties of the material in the literature, and induced us to perform additional investigations to fully understand the physical behavior of $LaTaTiO_6$. Thus, in this paper, we present structural and vibrational spectroscopic investigations of the orthorhombic-to-monoclinic polymorphic transformation of $LaTaTiO_6$ ceramics, as a function of the sintering temperature. Phase pure compounds were investigated by Raman and infrared reflectivity techniques. The Raman spectrum of the *aeschynite* $LaTaTiO_6$ appears to be very close to that of $PrTaTiO_6$. Raman and infrared spectra of monoclinic $LaTaTiO_6$ ceramics were obtained for the first time. Polarized Raman spectroscopy allowed determining (and assigning) all the non-polar modes of the material into the monoclinic phase. Infrared reflectivity spectra allowed determining the main polar modes that contribute to the dielectric response. The intrinsic dielectric parameters obtained by this procedure match well those found by MW techniques. [Work partially funded by FAPEMIG and CNPq].

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Thermal ageing of an epoxy observed with positron lifetime and mechanical tests

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The epoxy resins are cross-linked polymers with excellent chemical and thermal stability. They are important engineering materials used in structures subjected to complex mechanical, hygrothermal and chemical loadings and many other applications. The long-term behavior of these materials is still a challenging issue, but whose knowledge is crucial to ensure the integrity and reliability of structures based on epoxy resins. Inside the overall problem of durability of polymers, is the physical characterization of the ageing under isothermal conditions, especially for ageing temperatures lower than the glass transition temperature [1].

This study analyses the physical ageing of a commercial epoxy at constant temperature: 30, 40, 50, 60 and 70°C. The Fourier transform infrared spectroscopy (FTIR) was used to monitor the chemical integrity of the material composition, and it was found that the material is unchanged during the ageing program. Differential scanning calorimetry (DSC) was employed to determine the glass transition temperature as well as to describe the evolution of the physical ageing characteristics through changes in the endothermic peak temperature and enthalpy of relaxation. All these thermal quantities showed an exponential increase to the equilibrium with the ageing time. The specimens, after a well-controlled rejuvenation process, were subjected to mechanical study. Three points bending tests were performed under monotonous and relaxation loading, to evaluate the effect of physical ageing on elastic and viscoelastic behavior.

To attempt an explanation of the different macroscopic mechanical, physical, and chemical properties of the epoxy, the specimens were also measured with Positron Annihilation Lifetime Spectroscopy (PALS) [2]. The preparation of this PALS experiment used a relatively high activity source of Na-22 in order to obtain high counting rates and to achieve a statistically significant counting (more than 106) within a time that does not interfere with the ageing process (about 2 hours). This choice inevitably affected the time-resolution of the positron lifetime (~275 ps). Although the resolution, it is possible to observe and describe the spectrum of the long component lifetimes, and to draw a trend of physical ageing process on the free volume fraction (FVF) of the epoxide resin. Fig. 2 shows the trend of FVF as function of the ageing time for the epoxy samples staged at a constant temperature of 30ºC. Complete analysis of the results for three samples series (30, 40 and 50 ºC) will be presented and it comparison supports that the structural relaxation effects are more difficult to observe temperatures closer to the glass transition temperature, but the observed ageing time was too short in order to identify a equilibrium value for the free volume fraction.

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Mechanical characterization (including at nanoscale) (D2)

Validation of cohesive laws for static strength estimation of adhesively-bonded joints

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Nowadays, the use of adhesives is widespread in such a manner that it covers different market sectors, such as the aerospace, aeronautic, automotive and sports industries. In fact, the use of adhesive bonds in mechanical structures has been growing in the replacement of conventional bonding methods such as brazing, riveting, fastening and welding. In general, adhesive bonds offer several advantages, such as the weight reduction, reduction of stress concentrations, easy fabrication, good fatigue behaviour and possibility to join dissimilar materials. The industry´s growing interest in adhesive bonds is based on the increased reliability of the strength prediction methods to adhesive structures. In this context, Cohesive Zone Models are available, which allow simulating damage growth in structures, after introduction of previously estimated cohesive laws in numerical models. One of the most important stages of this predictive method is the estimation of the tensile and shear cohesive laws; so it is highly important the existence and validation of accurate methods for obtaining these laws.

This work aims the validation of tensile and shear cohesive laws, estimated by the application of the direct method, in order to predict the failure of bonded joints under mixed-mode loading. In this context, single and double-lap joints were tested with different overlap lengths and adhesives with distinct ductility. The adhesives Araldite® AV138, which reveals high strength and low ductility, the Araldite® 2015, a moderate ductility and intermediate strength adhesive and the SikaForce® 7752, with low strength and high ductility, were considered. The cohesive laws in pure modes enabled obtaining simplified cohesive laws with triangular, trapezoidal and linear-exponential shapes, which were tested for each one of the adhesives. The validation of the referred cohesive law shapes was accomplished by comparing the numerical predictions with the experimental tests. A peel and shear stress analysis in the adhesive was also performed, in order to understand the influence of stresses on the joints' strength. The use of the direct method allowed obtaining accurate strength predictions, providing the most adequate cohesive law shape for each set of adhesive/joint geometry. Moreover, for the considered geometric and material conditions, this study allowed concluding that no significant errors are committed by choosing a less suitable law.

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Determination of Mechanical Properties of aluminium AA6061 and HSLA420 steel using Inverse Analysis

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In sheet metal forming industry there has been an increasing interest in numerical simulations including also inverse engineering methods. This is mainly because the trial-and-error techniques, long used in the past, are no longer economically competitive. So, new optimization strategies are introduced and implemented, which lead to more precise parameters of constitutive models.

The occurrence of the new sheet metals like high strength steels, used in the automotive industry to manufacture lightweight components with complex shapes, or aluminum alloys, with their advantageous strength to weight ratio, the determination of mechanical properties exhibits new technological challenges. In this context, identification algorithms of mechanical characterization are needed to predict material behaviour during sheet metal forming processes [1].

The purpose of this paper is the identification of material behaviour of high strenght HSLA420 steel and aluminium alloy AA6061, using an experimental reference test associated with an optimization algorithm, to minimize the difference between experimental and numerical results.
In order to evaluate and validate the proposed methodology, the identified material parameters from inverse analysis are compared to experimental uniaxial tensile test data.

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Effect of σ and χ phases on micro residual stresses in cast super duplex stainless steel

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Cast duplex stainless steels (DSS) are advanced materials which offer an excellent combination of mechanical properties (high strength and toughness) and corrosion resistance. This performance is a result of an accurate balance between ferrite (α) and austenite (γ), achieved by controlling chemical composition and processing parameters, such as solution annealing temperature and holding time. However, DSS are prone to formation of detrimental secondary phases at elevated temperature, in particular sigma (σ) and chi (χ) phases. During solidification, a multiphase microstructure is formed, consisting on α, γ, and secondary phases, with different coefficient of thermal expansion (CTE), elasto-plastic properties, *crystallographic structure* and local texture. Thus, thermal residual stresses are introduced, which affect the quality of near net shape castings.

The main purpose of the present work is to determine the influence of σ and χ phases on local residual stresses, their magnitude and gradient~~s~~. For this aim, micromechanical modelling of a DSS is performed by means of a finite element software package (OOF2). This is a software designed to analyze the macroscopic response of the material from experimental micrographs. It can combine the image information with characteristics of the phases in the microstructure. The microstructural analysis of DSS in as-cast and ~~-~~annealed condition~~s~~ was performed by optical microscopy (OM) and scanning electron microscopy (SEM) using backscattered electrons (BSE).

OM does not provide enough resolution to distinguish between σ and χ phases, however SEM-BSE mode has proven to be more suitable for identifying those phases, as is shown on figure 1a. Due to differences in chemical composition σ phase (richer in Cr) appears light gray, while χ (richer in Mo and W) appears white. To perform the numerical simulations, the micrographs were loaded into OOF2 and the material~~s~~ properties were assigned to the phases: Young's modulus, Poisson's ratio and CTE. The material response to an applied thermal stress is shown on figure 1b, revealing high concentration of stresses at secondary phases interfaces and/or at γ and α interfaces. This is a result of the differences in the CTE between the phases, having α the lowest CTE (10.4×10^{-6} ºC^{-1}).

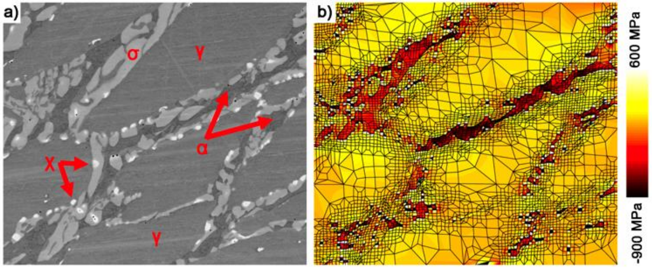

Figure 1 – a) SEM-BSE microstructure of DSS in as-cast condition; b) hydrostatic stress in response to thermal stress with free boundaries.

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Local Texture Characterization of Stainless Steel Cladding using Neutron Diffraction

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The influence of heat treatments on the texture and residual stress fields of weld cladded samples is discussed in this study. The samples were elaborated from carbon steel plates, cladded with three layers of stainless steel filler metals by submerged arc welding. Different samples were prepared: as welded and as welded plus two relevant industrial heat treatment, one at 620° C for a holding time of 1 hour and the other at 540° C for a period of ten hours. Local texture measurements were carried out by neutron diffraction. A gauge volume of 3 x 3 x 2 mm^3 at each cladding layer (at depths of 2 mm, 5 mm and 7.5 mm) for each sample was used. Texture results indicated that there exists an annealed cube component in all the studied samples. Based on the measured pole figures the calculated orientation distribution functions data were used to calculate the Young's modulus with respect to the main welding directions. The calculated anisotropic Young’s modulus is shown and discussed. Residual stresses in depth are analyzed by means of neutron diffraction and mechanical methods. Both methods will be presented and compared. The results shown that the sample treated to 620^{o}C, presented the highest residual stress relaxation.

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Fracture behaviour of sheet metal materials for different stress triaxialities

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Currently, multimaterial and lightweight design is being used in car body-in-white structures, which promotes the use of different metallic materials or non-conventional grades and they include mild steels, high strength steels and aluminium alloys. However, the introduction of non-conventional grades in the automotive industry introduced new challenges in sheet metal forming processes [1]. The behaviour observed with conventional materials is not applied to these high strength steels and aluminium alloys, therefore the conventional models can lead to a poor prediction of the actual material behaviour, in particular in cases where internal damage is associated with larger plastic deformations.

These factors together with the increasing complexity of plastic deformation technology have led to a successive approach to the concept of virtual production, namely, the numerical simulation of plastic forming processes and the extension of their use to the whole process of components production [2]. In this paper, experimental tests were performed on sheet metal materials, namely an aluminium alloy AA6061 and a high strength steel HSLA420, to investigate the fracture behaviour for different levels of stress triaxiality (linear and complex loading paths). These experimental tests allow the calibration and validation of selected constitutive models and damage models to be implemented and developed in finite element analysis, in order to predict damage initiation and fracture location on materials under this study.

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Assessment of standardized methodologies for fatigue design of shafts: DIN 743, FKM and AGMA 6001

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Machine element design has been experiencing a significant change, from the traditional approaches based on analytical and parametric analyses, to a full computational analysis mainly based on finite element methods. However, the design of some machine elements needs to consider multiple effects that cannot be modelled using the standard software for finite element analysis, requiring the access to external databases or to specific standards and methodologies. In addition, from the industrial point of view, the application of established methodologies allows to obtain faster and cheaper solutions for the common machine elements.

The fatigue design of rotating shafts may be carried out using a variety of standard and non-standard procedures, and constitutes an example where it is imperative to access different design factors and methodologies only available in specialized software and literature. This article addresses three current methodologies available for fatigue shaft design: German standard DIN 743; the German guideline "Fracture Mechanics Proof of Strength for Engineering Components" proposed by the Research Committee on Mechanical Engineering (FKM) and the US standard AGMA 6001-D97. These methodologies are briefly presented in this communication.

Comparisons between these three approaches are not found in the literature and may be needed for practical applications. Therefore, a typical rotating shaft design problem, with different stress concentration details, is assessed using these three methodologies. The different adopted factors, the respective limitations and the differences in final safety factors are also discussed in the article.

Advanced characterization using microscopy techniques (D3)

Exploring stresses in $K_{0.5}Na_{0.5}NbO_3$ thin films by in-situ TEM sintering

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The need to remove lead from the electronic devices was imposed by the European Union in 2003 [1]. Although in 2012, the used of lead in lead zirconate titatane (PZT) based dielectric ceramics was exempted of this prohibition, due to impracticable implementation, there is a current need to find alternative lead free piezoelectrics. PZT is the piezoelectric material of choice in sensors and actuators and the market leader in microelectromechanical system devices. In the search for lead-free piezoelectrics, sodium potassium niobate (KNN) is a promising substitute for PZT. KNN exhibits a high Curie temperature but its electromechanical properties need to be improved to produce competitive KNN-based materials. It is well known the dependence of the electromechanical properties on the microstructure, namely texture and grain size [2,3], which can be affected by applied stresses or presence of internal stresses developed during sintering, as in thick films deposited on rigid substrates [4-6].

It is proposed in this work, to study the effect of temperature and time in the microstructure development of KNN thin films, assessed by *in-situ* transmission electron microscopy (TEM).

RF sputtering was used to deposit the KNN thin films in a sodium chloride (NaCl) dummy substrates with a [100] normal orientation. The thin films were heated up at different temperatures and for different times and then the substrate was dissolved using water. This allowed us to observe the microstructural development by TEM and identify the crystallization starting temperature before starting the *in-situ* experiments. *In-situ* heating in TEM is going to be performed to observe the evolution of the microstructure.

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Locally inducing and mapping of structural transformations in Ni-Mn-Ga thin films by scanning thermal microscopy

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Ni_2MnGa is a ferromagnetic-shape-memory alloy with two main structural phases: austenite (high temperature) and martensite (low temperature). The structural transition temperature (T_M) is strongly dependent on sample composition [1]. The formation (elimination) of martensitic twin boundaries when the sample is heated above (cooled below) T_M results in dramatic changes in the sample's topography which can be sensed by Atomic Force Microscopy (AFM). We present a study of locally induced structural transformations by nano-thermal analysis performed with a Scanning Thermal Microscope (SThM) [2], based on AFM, on a 400 nm Ni-Mn-Ga thin film. The Scanning Thermal Microscope thermal tip (radius ~ 100 nm, sensitivity of ~ 1 Ω/ºC and 50 nm spatial resolution) simultaneously heats and determines temperature locally, while acting as a conventional AFM probe. As the tip heats a specific location, cantilever deflection is measured and changes in the structure below are signaled. The Ni-Mn-Ga thin film local structural transformation is marked by a discontinuity in the cantilever deflection curve, which occurs at different temperatures for different locations in the sample. Mapping of the sample's T_M values was performed (Fig.1). T_M ranges from 344 K to 359 K. A 15K interval of T_M values was also found in magnetization versus temperature SQUID measurements, although shifted to lower temperatures by ~ 9K. An accentuated decrease on the T_M distribution around 354 K (Fig. 2) is consistent with the compositional narrowing observed in the material's phase diagram. [1] This work shows how nano-thermal analysis can be used to map T_M inhomogeneity at the nanoscale for systems with structural transitions such as Ni-Mn-Ga.

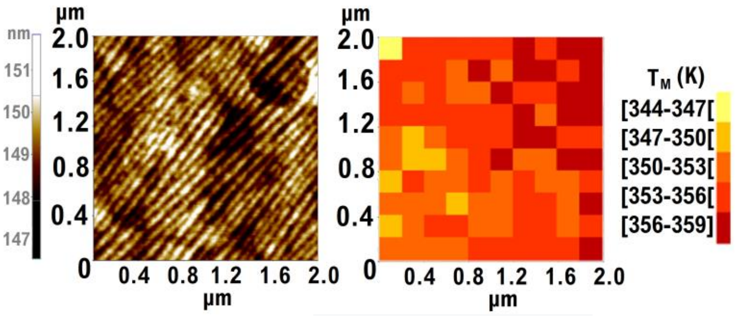

Fig. 1 Topography of 2x2 µm^2 of the sample (left) T_M map for the same area (right)

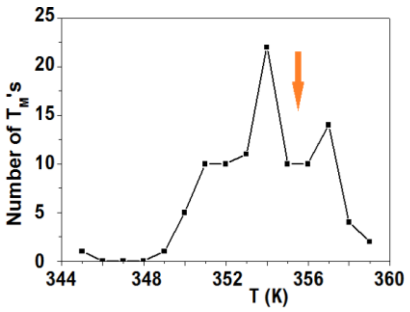

Fig. 2 Distribution of T_M for area in Fig. 1

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Materials modelling (Advanced atomistic algorithms, computer simulations) (D4)

Numerical Modelling of Welded T-Joint Configurations using Sysweld

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Advances in the computational tools for welding process simulation have been noteworthy, allowing to assess complex phenomena, as is the case of welding distortion and residual stress. The most advanced tools take into account the thermo-metallurgical and thermo-mechanical changes that take place during the welding processes. Considering these changes and the materials properties at the different temperature values, it is possible to obtain reliable models of the welding processes.

In this communication, T-joint welded configurations are investigated, considering arc welding and laser beam welding processes. For this purpose, the commercial software ESI Sysweld was adopted, since it is one of the most advanced tools for this purpose. These models are based on finite elements; therefore, a mesh sensitivity analysis was performed in order to evaluate the minimum element size required for accurate results.

Results for a T-joint between a steel tube and a steel plate using laser beam welding (LBW) and arc welding were obtained. The laser beam welds presented a significant reduction of the heated affected zone and, consequently, the tensile residual stresses are confined to a smaller area.

In arc welded double side T-joint, different procedures were explored in order to understand the influence in the residual stress; the second pass does not increase the maximum residual stress, however it increases the area with tensile residual stress, Fig.1 .

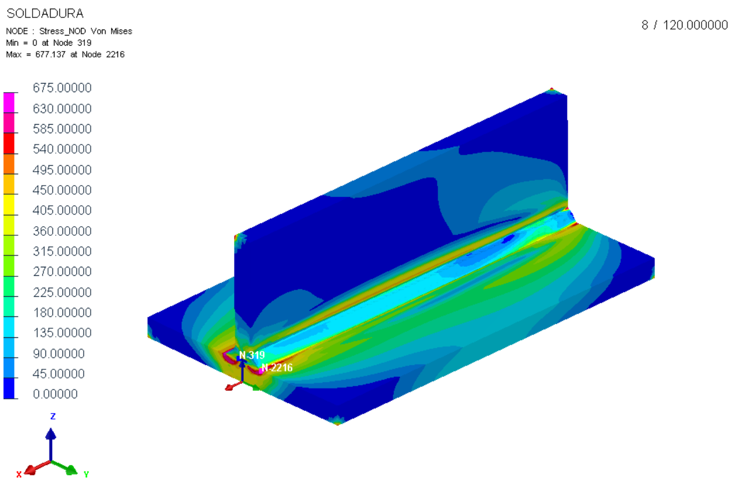

Fig. 1. Equivalent von Mises residual stress for a T-joint with double side weld.

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Finite element modeling of the mechanical milling and physical characterization of copper powders

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Copper-matrix composites, used for electromechanical applications, are often produced by mechanical alloying (MA) in attrition mills. Understanding MA and the influence of milling parameters on powder properties is therefore valuable. In this work, materials characterization techniques and finite element method (FEM) modeling are used as tools to study that influence.

Pure copper powder was milled for times of 10 minutes up to 8 hours, in a planetary ball mill with a copper vial and copper balls. The variables analyzed were ball size and the presence of a process control agent, isopropyl alcohol. The samples were characterized by XRD, SEM, Vickers hardness measurements and particle size measurement by laser diffraction.

Powders milled with isopropyl alcohol (wet), which lowers welding rates, showed faster and more significant particle and crystallite size reduction and faster powder shape changes. For 8 hours, wet-milled powders showed size reductions of 80% compared to 25% size reduction for dry-milled powders. Green hardness and density depended significantly on powder shape and size, not showing a direct correlation with milling time and powder strain.

2D FEM milling simulations were carried out considering spherical powders. Variables studied include ball velocity and size and powder packing and spacing. The most significant factor responsible for increased stress and strain in the powders was more spacing between particles.

Results from both pure copper milled samples and FEM simulations correlate and may suggest that having lower welding rates and more separated particles is the overriding factor to faster particle size reduction.

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First principle computational study of Hydroxyapatite structures, properties and related materials

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First principles studies and calculations of bulk and modified Hydroxyapatite (HAp) were carried out using different density functional theory (DFT) based on local basis (in AIMPRO code) and plane-wave (in VASP code) methods. The data obtained were used for studies of HAp structures and physical properties (e.g., density of electronic states—DOS) and for the modeling of various defects in HAp, especially for oxygen vacancies in HAp surface layers, which can also determine HAp photocatalytic properties. HAp has many other specific structural peculiarities and physical properties, which have important roles at the surface. The biomineral HAp is the main mineral constituent of mammal bone and the most important biomaterial for bone regeneration. Studies have shown that the creation of surface charges (polarization) increases the adhesion of osteoblast cells, and enhances their reproduction and growth. One of the main applications of HAp as a biomaterial is in the field of bone repair and bone replacement in the form of bioimplants. HAp's biocompatibility makes it very attractive in this field, as state-of-the-art bone implants are made of metallic titanium, whose surface could oxidise to TiO_2 substrates, which are coated with a thin HAp layer on the surface. The HAp layer improves adhesion to the surrounding bone, and provides a scaffold for bone growth. Therefore, it is very important to study interactions between Hap and TiO_2. On the other hand, TiO_2 is one of the most popular photocatalysts. There are two major polymorphs for TiO_2: anatase and rutile, having different band gap energies, of ~3.2 and ~3.0 eV, respectively. The investigation of their band gap energies is very important for many applications. All data obtained were analyzed using both approaches, AIMPRO and VASP, and compared with other models and experimental data. This study was supported by RFBR grant 15-01-04924.

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Comparative analysis of the diffusion-controlled thermal annealing of radiation defects in simple oxides and piezoelectric PLZT ceramics

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The radiation-resistant insulators (MgO, Al_2O_3, BeO etc) are important key materials for fusion reactors, while response of piezoelectric PLZT ceramics to high energy irradiation is of great interest because of their possible application in strong radiation environments such as thermonuclear reactors. It is very important to predict/simulate not only the kinetics of diffusion-controlled defect accumulation under neutron irradiation, but also a long-time defect structure evolution including thermal defect annealing. Here we developed and applied the advanced theoretical approach based on the formalism of the correlation functions suited much better for the study of defect kinetics and aggregation than generally accepted rate equations.

On the basis of our calculations, we estimated the migration energy of the *F* centers and interstitial oxygen defects O_i, their interaction energies and metal colloid size upon annealing. We simulated the *F*-type center annealing after electron, heavy ions or neutron irradiation as a bimolecular process with equal concentrations of the complementary *F* and O_i defects. It is controlled by the interstitial oxygen ion mobility, which is much higher than that of the *F* centers. The *F* center annealing begins at temperatures 500-700 K, when both *F* and F^+ centers are practically immobile, due to the recombination with mobile O_i defects. It is demonstrated how the shape of the *F*-annealing curves is determined by two control parameters: E_a and effective pre-exponential factor and strongly depends on irradiation conditions.

The appropriate migration energies were obtained from available in literature annealing kinetics for electron, neutron and ion- irradiated oxide crystals (MgO, Al_2O_3, $MgAl_2O_4$, BeO, ZnO, PLZT etc). The results obtained are also compared with recent *ab initio* calculations of interstitial oxygen migration (MgO and Al_2O_3).

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a-SiC:H photodetector in VLC system with RGB LEDs

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Energy saving LED lamps constitutes main elements in Visible Light Communication (VLC) technology as they can be used for communication purposes. Several applications derive from this technology, and indoors positioning is a field where VLC can be used with success, overcoming main advantages related to GPS signals that are strongly absorbed by building infra-structures. Several applications of the proposed technology are predicted, such as guidance of users inside large buildings, location-based services, automation of some inventory management processes, etc..

The work presented in this paper supports the viability of a navigation system based on Visible Light Communication (VLC) for indoors applications. The system design uses RGB LEDs and an a-SiC:H photodetector. The system has four transmission optical channels supplied by the modulation at two different frequencies of the RGB LED internal red and blue chips. Each cardinal direction becomes thus assigned to a specific set of optical excitation, dependent on the wavelength and frequency of the modulated RGB LED.

An optoelectronic characterization of the devices used in the integrated system is presented to support the main results, namely the decoding strategy. The photodetector is a multilayered pin-pin heterostructure based on a-SiC:H on a glass substrate and inserted between two transparent electrical contacts. It works as an optical filter in the visible range, presenting a selective spectral sensitivity dependent on the external optical bias (wavelength, intensity and direction of incidence on the device), that enables the amplification and/or attenuation of specific wavelengths when properly biased with steady state optical illumination.

Each navigation direction is assigned to the presence of 2, 3 or 4 optical signals of characteristic frequency and wavelength. In order to infer the navigation position a dedicated algorithm based on the photocurrent signal measured under front and back bias was developed. First, it is necessary to identify the wavelengths that contribute to the photocurrent signals, which are related to the device wavelength filtering properties. Front biasing is used to detect the red wavelength and back biasing to detect the blue wavelength. Secondly, as signals of the same wavelength may be modulated at different frequencies it is necessary to detect the frequencies present in the output signal, which is done using Fourier analysis.

The viability of the system is demonstrated through the implementation of an automatic algorithm to infer the photodetector cardinal direction. Additional research on the light intensity is presented to investigate the accuracy of the spatial position along a cardinal direction.

A capacitive optoelectronic model supports the experimental results and explains the device operation. A numerical simulation will be presented.

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Modelling and simulation of thin-film coatings for optical applications

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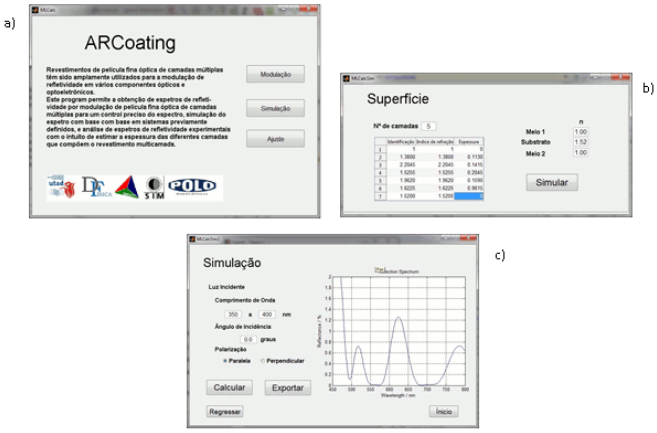
The continuing researching process to seek the best performance of optical components has conducted to a no stop search. In the field of Anti-Reflection (AR), a continuous improvement of software instruments is need to better modulate, simulate, and analyse the reflectivity spectrum as well as the transmission spectrum [1].

We have developed a simulation program for the reflectivity spectrum of dielectric multilayer optical coatings using MATLAB. The input data are from the full description of the system and compute the reflectivity spectrum to the analysis of experimental reflectivity and estimate the layer thickness of the deposited materials. In order to perform the computation, we used the characteristic matrices to calculate the reflectance of an assembly of thin-film layers [2].

The simulator built in a MATLAB environment takes the advantage of the numerical engine and programming tool, but also the built in tool to create a graphical user interface (GUI) which we wanted to be quite interactive and user-friendly. The result is shown in Fig. 1. The reflectance spectrum shown in the Fig. 1 was for an antireflection coating consisting of five layers whose structure was optimized in order to have a reflectance less than 10^{-3} in the range between 400 nm and 800 nm. [3] The simulator perform other computation depending in the input data such the adjustment of a curve where the fitting parameters are the thickness of the different layers of the coating.



Revestimentos de pelicula fina óptica de camadas múltiplas têm sido amplamente utilizados para a modulação de refletividade em vários componentes ópticos e optoeletrônicos.
Este program permite a obtenção de espetros de refletividade por modulação de pelicula fina óptica de camadas múltiplas para um control preciso do espectro, simulação do espetro com base com base em sistemas previamente definidos, e análise de espetros de refletividade experimentais com o intuito de estimar a espessura das diferentes camadas que compõem o revestimento multicamads.

Nº de camadas 5

	Identificação	Índice de refração	Espessura
1	1	1	0
2	1.3800	1.3800	0.1130
3	2.2045	2.2045	0.1415
4	1.5255	1.5255	0.2045
5	1.9620	1.9620	0.1590
6	1.6225	1.6225	0.9615
7	1.5200	1.5200	0

	n
Meio 1	1.00
Substrato	1.52
Meio 2	1.00

Luz Incidente
Comprimento de Onda
350 a 400 nm
Ângulo de Incidência
0.0 graus
Polarização
● Paralela ○ Perpendicular

Figure 1 – The layout of the ARCoating simulator: a) Main window; b) Thin-Film Multilayer Structure; c) Five layers antireflection coating reflectance spectrum.

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The possibility of use of ferrocene-substituted conducting polymers in paraquat electrochemical detection

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Paraquat is one of the most used non-selective herbicides [1], killing green plant tissue on contact, also used in modeling of oxidizing stress. Nevertheless, besides of its toxicity for plants, it is highly toxic for humans and animals [2]. Thus, the development of an exact, precise, sensitive and rapid method of its detection is really an actual problem [3].

As paraquat is a redox-active substance, the electrochemical methods may be applicable to it and chemically modified electrode may serve good the detection of paraquat [3]. One of the substances, frequently used for electrochemical analysis is ferrocene (Fc), but, in the case of paraquat, no electrochemical detection method involving has been developed, and its development leads he research to resolve the problems like:

- Indefinition in ferrocene mechanism of action with paraquat;
- The possible presence of electrochemical instabilities, accompanying the system, like oscillatory behavior, yet observed for paraquat in [3] (Fig. 1)

In this work, the possibility of use of ferrocene and ferrocene-derivatized conducting polymers as an electrode modifier in paraquat electrochemical detection was studied. The correspondent mathematical model was developed and analyzed by means of linear stability theory and bifurcation analysis. It was detected, that the steady-state stability in this system are maintained on a vast topological parameter region, being compromised only by capacitance changing effects of electrochemical reactions. The possibility of electrochemical instabilities in this system has also been evaluated.

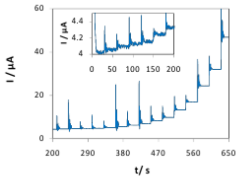

Fig. 1. Current oscillations, observed during the electrorreduction of paraquat, accompanied by its successive addition. Used from [3] under permission of Centre of Excellence in Electrochemistry of the University of Tehran, Islamic Republic of Iran

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QSPR Modeling Applied to High Molecular Weight Polymers: Ductility Characterization from Elongation at Break

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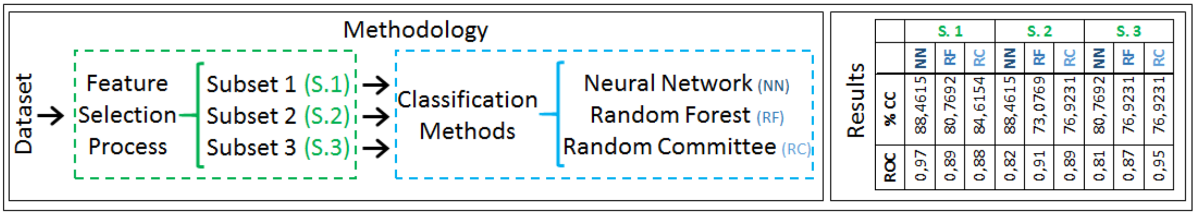
New polymeric materials with specific requirements are designed to satisfy a demanding market and the study of the mechanical profile of a polymer helps to define its application range. During last years, we are proposing virtual testing tools based on Quantitative Structure-Property Relationships (QSPR) to assist the polymer designers prior to the synthesis, obtaining savings in times and costs. QSPR models estimate a target property of chemical compounds from variables that describe their molecular structure. In this work, we present classification QSPR models for ductility characterization of polymeric materials, using information provided by tensile test experiments in order to classify polymer ductility based on elongation at break. Figure 1 schematizes the proposed methodology. The models are computed from a dataset of 77 linear amorphous thermoplastic polymers with high molecular weight [1]. The first step detects alternative subsets of relevant molecular descriptors related to the target property using a feature selection method [2]. These subsets are contrasted by an expert via a visual analytics software tool [3]. From this analysis, we conclude that an experimental parameter of the tensile test, cross head speed, plays a central role in all models. Finally, QSPR models are inferred by different machine learning methods. The output of these models allows classifying a new virtual material under design as ductile, fragile or undefined. The model with the highest performance correctly classifies 88.46% (%CC) of polymers and has a receiver operating characteristic (ROC) curve equal to 0.97. As conclusion, this QSPR model can predict if a material will be ductile or not in early phases of polymer design, previous synthesis, with high confidence.



		% CC	ROC
S. 1	NN	88,4615	0,97
	RF	80,7692	0,89
	RC	84,6154	0,88
S. 2	NN	88,4615	0,82
	RF	73,0769	0,91
	RC	76,9231	0,89
S. 3	NN	80,7692	0,81
	RF	76,9231	0,87
	RC	76,9231	0,95

Figure 1. Methodology and experimental design of QSPR models using classification methods.

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Posters

Symposium A - Functional Materials

Bio-inspired materials and materials for healthcare applications (A1)

Synthesis and Characterization of Hydroxyapatite Coating on Titanium by Sol-Gel Method

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Materials for biomedical applications have been extensively investigated in the last years by several researchers, mainly to technological applications in the health area to the clinical uses, with the aim to substitute the bone in an orthopedic surgery.

Problems like metal ions release, bone resorption, inflammatory and painful symptoms, have been reported in many cases. Even the development of new classes of materials has not been able to overcome all the mentioned drawbacks.

To improve the properties of these materials, the main goal of this work is to develop titanium oxide (TiO_2) coatings, containing zirconium (Zr) and hydroxyapatite (HA) nanoparticles, by sol-gel process, deposited on titanium substrate.

For gel synthesis a solution containing 165 ml of ammonium hydroxide (NH_4OH), 7 ml of phosphoric acid (H_3PO_4) and 228 ml of H_2O, has been mixed with another solution composed of 39,5g of calcium nitrate ($Ca(NO_3)_2$) dissolved in 150 ml of H_2O. The final product has been submitted to a heating process for water evaporation. The titanium parts (substrate) have been anodized in 0,1 M of oxalic acid ($H_2C_2O_4$), prior to gel deposition, in order to obtain an TiO_2 barrier coating. For films deposition of the gel on the oxidized titanium substrates, the dip-coating process has been applied. After the gel deposition, the parts have been placed in the oven for a heat treatment as follow: 450 °C for 1 hour, 700 °C for 1 hour with 1°C per minute of temperature increment. The number of layers on the substrate surface varied from 1 to 3.

For sample characterization, crystal structure of the films evaluated has been evaluated by X-ray diffraction (XRD), chemical stability by voltammetry and potential balance. The morphological and chemical quantitative analysis has been realized by field emission scanning electron microscope (FDSEM) with EDX detector. The diffraction analyzes of x-rays showed that it was possible to coat the titanium substrate with TiO_2 inter-layer and hydroxyapatite by sol-gel process. The electron microscope images indicate a non-uniform deposition surface; which might be explained by a low adhesion rate of the film. The results of X-ray diffraction showed the formation of an intermediate phase of zirconium phosphate (ZrP_2O_7). According to the analyzes of SEM, EDX and XRD, it has been detected the formation of hydroxyapatite layer ($Ca_{10}(PO_4)_3(CO_3)_3(OH)_2$.

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Novel biopolymer-silica hybrid nanoparticles prepared by a non-emulsion method

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In recent years, great progress has been observed in new methods of surface modification of functional nanomaterials envisaging targeting applications. Among these materials, biopolymer–silica hybrids have drawn attention as promising materials owing to their unique properties and potential applications in distinct fields [1,2]. These materials benefit from the flexibility and reactivity of polymer functional groups and the structural robustness and chemical inertness of the inorganic moiety. The development of hybrid materials derived of polysaccharides has experienced remarkable growth due to attractive properties of polysaccharides such as biocompatibility, biodegradability, low cost and availability. Nevertheless, owing to the poor compatibility between polysaccharides and common silica precursors, the formation of biohybrid materials is not a trivial task and the control of the hybrids size and morphology often requires the use of emulsions.

Herein, we report a non-emulsion method for preparing spheroidal and uniform biopolymer–silica hybrid particles, using distinct polysaccharides (κ-carrageenan, chitosan and starch). The biopolymer was firstly treated with an alkoxysilane that contains isocyanate groups. Then, the resulting compound was mixed with a silica precursor (tetraethyl orthosilicate, TEOS) and the mixture underwent hydrolysis and condensation under alcoholic basic conditions to yield uniform spheroidal hybrid particles via a sol-gel method [1]. The resulting materials were extensively characterized using electron microscopy (SEM) (Figure 1), solid state NMR, thermogravimetric analysis, FTIR spectroscopy and elemental analysis. We anticipate that the materials described here will have impact on the application of biohybrids, namely in areas in which the minute size and spherical morphology are relevant such as in drug delivery and bioimaging.

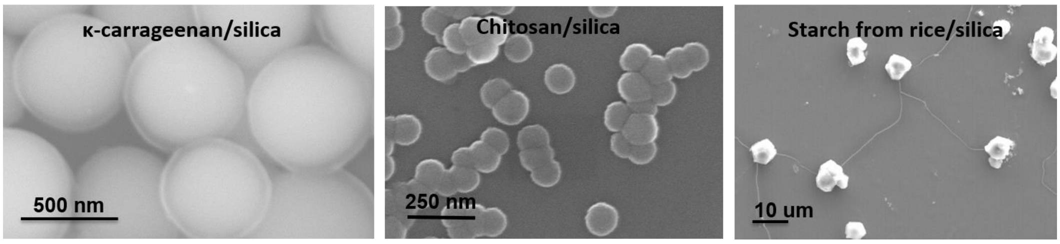

Figure 1-SEM images of biopolymer/silica hybrid particles.

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Degradation of Modified membranes for periodontal Regeneration

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Nowadays, the frequency of diseases or trauma that cause tissue loss is increasing rapidly. Therefore, new solutions capable of facilitating tissue regeneration are urgently needed.

In the particular field of dentistry, the loss of the periodontal structure is still a frequent issue to which several diseases may contribute. Hence it is imperative to develop adequate structures able of promoting a rapid rehabilitation of the affected tissue.

The objective of the following study was to develop composite membranes of collagen and hydroxyapatite for periodontal regeneration. This goal implied the membrane production and characterization followed by the study of its degradation in physiological medium. Pure collagen and composite membranes filled with hydroxyapatite were produced by lyophilisation and by electrospinning and some of them were also pressed under controlled conditions. Hydroxyapatite nanosized particles were synthesized by chemical precipitation. All the produced materials were characterized by techniques including XRD, SEM/TEM, zeta potential, gas adsorption and FTIR spectroscopy. The results showed that the membranes exhibit a bioactive behavior when in contact with simulated body fluid, thus pointing out a high potential for applications in dental tissue regeneration.

To study the membrane degradation profile in a phosphate buffer solution (PBS) mimicking human saliva, the time variation of the protein concentration in the PBS was evaluated by optical density and also by SDS-PAGE. The results revealed that membranes prepared under different conditions do behave differently during degradation. It is thus concluded that the degradation rate of the composite membranes may be controlled by adequate manipulation of its processing steps. Pressing showed the higher rate of degradation during time. This result opens the possibility of tuning the degradation of the collagen membranes modified with hydroxyapatite according to needs imposed by regenerative strategies of dental tissues.

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Calcium phosphate cements as local drug delivery

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A sustained and locally drug delivery strategy is an attractive alternative to conventional systemic delivery method, oral or parenteral, bringing several advantages that include: i) facility to reach the infected tissue; (ii) decrease risk of bacterial resistance to antibiotic therapy; (iii) low amount of drugs and preclude repetitive administration (iv) therapeutically effective level, and (v) cost effective [1,2]. Therefore, considerable effort has been evaluated in order to develop potential cement pastes for bone regeneration with ability to incorporate drugs relevant for different therapeutic needs. Calcium phosphate cements, well known for their excellent osteoconductive and injectable capabilities, allow the incorporation of drugs and active principles in the material due to their low-temperature setting reaction and intrinsic porosity [1].

The aim of this work was focused on the development of calcium phosphate based cements for biomedical applications, including a drug in their composition. Different calcium phosphate based cements were studied, varying the nature of the starting powders, their size and particle size distribution and liquid to powder ratios, in order to evaluate their influence on porosity, mechanical properties and crystalline phases of the cements and relate these features to the rate of drug release. An aqueous solution of citric acid was used as setting liquid and levofloxacin, a fluoroquinolone antibiotic, was used as a model drug. The results showed that addition of the antibiotic did not significantly affect the mechanical properties and porosities of the cements. However, in the presence of levofloxacin, there was an increase in the initial and final setting times of the cements. The drug release rate was relatively high, with an identical profile for all cement formulations tested, being not possible to relate the drug release rate with the cement properties evaluated, namely porosity. This fact is probably due to the migration of the antibiotic to the surface by diffusion process during the dry step of cement samples. In order to clarify this point, future studies related to the homogeneity of drug throughout cement ceramic matrix will be evaluated.

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Nanostructured magnetic platforms for the sustained delivery of anticancer drugs

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Platinum(II) drugs are effective anticancer agents against many malignancies including testicular, ovarian, bladder, head and neck, small-cell, and non-small-cell lung cancer [1]. Cisplatin (cis-diclorodiamineplatinum(II) - CDDP) is one of the anticancer drugs most widely used in clinics, owing to its ability to bind to genomic DNA. However, as most of the other small-molecule anticancer drugs, its clinical use is conditioned due to high toxicity and severe side effects, namely nephrotoxicity and neurotoxicity, as well as due to incidences of Pt associated drug resistance [2,3].

The emergence of nanotechnology had a significant impact on the drug-delivery field and nanoparticles (NPs) are at the leading edge, with many potential applications in clinical medicine and research. Due to small size, nanoparticulate drug carriers might facilitate the delivery of the drugs on nanosized porous tumor vasculatures. In addition, the incorporation of magnetic nanoparticles provides magnetic features, which enables site specific drug delivery to be envisaged using magnetically driven carriers [4,5].

Herein, the development of novel nanosized carriers with magnetic properties, for the guided transport and controlled delivery of CDDP is reported. These carriers encompassed magnetic iron oxide nanoparticles encapsulated within amorphous silica shells, chemically modified with adequate functional groups for conjugation of CDDP. The resulting materials were characterized using Fourier-transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD) and zeta potential measurements. The nanoparticles were loaded with CDDP and the drug release was monitored along time spectrophotometrically at physiological pH in in vitro conditions. The results will be discussed in the context of the potential application of these materials in controlled drug delivery.

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Electrospun composite polyurethane- ZnO biomembranes for vascular graft applications

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Vascular diseases are presently the number one cause of death, responsible for more than 17 million deaths worldwide. Particularly in Portugal 29.5% of all deaths in 2013 were due to vascular-related failures. The main solutions are the use of autologous and donor grafts, but its limited availability and rejection risk still represent serious drawbacks. Artificial devices based on synthetic polymers appear as promising alternatives although unable to completely restore natural functions. Therefore, tissue engineered blood vessels are actively being investigated.

The objective of the following study was to develop electrospun composite biomembranes from a synthetic polymer - Polyurethane (PU), and an inorganic filler - zinc oxide (ZnO), to use in the repair and regeneration of vascular structures. PU was chosen due to its confirmed biocompatibility and tunable mechanical properties and, ZnO nanoparticles were blended in the membrane in order to promote antibacterial activity and selective toxicity.

Both composite constituents were characterized by XRD, FTIR and SEM-EDS. ZnO particles were further characterized in terms of size distribution (Coulter counter) and specific surface area using gas adsorption technique and BET method.

Nanosized ZnO particles, either synthesized by chemical precipitation or commercially available, were incorporated (5 %wt) into a PU matrix previously dissolved by THF: DMF (1:1) at room temperature. Electrospinning was used to fabricate the composite nanofibers by feeding the suspension to the cylinder collector at a flow rate of 3000μL/h with an applied voltage of 27kV and 17 cm distance from the collector. Random fibers were collected and characterized by Scanning Electron Microscopy (SEM), thermal analysis FTIR and XRD.

The morphology of the composite fibers produced and their diameters distribution indicate that the electrospun fibers may be a promising alternative to the existing synthetic matrices. The ongoing studies on the physical, chemical and mechanical properties of the composite fibers will allow to deepen the exploring work here reported.

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Influence of fiber orientation on the mechanical response of piezoelectric poly(vinylidene fluoride) electrospun fiber mats

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Since numerous cell functions are regulated by mechanical signals, the specific microstructure of biomedical materials can play a key role in inducing specific cell responses. Biomaterials processed in the form of electrospun fiber mats have already been explored to mimic different types of extracellular matrix in the human body [1, 2]. The tensile properties of such biomaterials are of large importance as they will determine suitability of the materials for specific applications. Further, as human body shows both aligned and randomly oriented cell/tissues it is imperative to determine how fibrous substrates with different orientations behave under mechanical solicitation, in order to fully understand their characteristics for tissue engineering (TE) applications [3].

Poly(vinylidene fluoride) (PVDF) is a piezoelectric polymer with the highest piezoelectric, pyroelectric and ferroelectric responses, among polymers. This polymer and its co-polymers have been also largely used in TE applications. For example, in skeletal muscle TE, the aligned morphology of electroactive PVDF fibers improve the directional growth of myoblast cells [4].

In this work, PVDF aligned and randomly oriented fibers were produced and the influence of fiber orientation on the stress-strain behavior was investigated. It was found that the Young’s modulus depends significantly on the stretch direction in the oriented fiber mats, being independent of the deformation direction for the randomly oriented fibers. Nevertheless, with the applied stress, all samples undergo a reorientation of the fibers towards the stretching direction and a decrease of the fiber diameter. The behavior is similar for pristine and composite fibers, the latter incorporating cobalt ferrite magnetic nanoparticles.

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Study of NiTi orthodontic wires with actuating forces

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In this study, a class of NiTi orthodontic wires with different actuation forces was analyzed. Varying actuation forces on the same orthodontic wire, allow the optimization of repositioning the different types of teeth. The wire was separated into three sections (Posterior - section 01, Intermediate – section 02 and Anterior – section 03, Figure 1). The phase transformation temperatures in each section were determined by DSC analysis. The mechanical behavior was analyzed by three-point flexion tests at four different temperatures (5, 20, 27 and 37 ºC). The measurement was realized in water with controlled temperature. In parallel, a three-point flexion test was performed by TMA analysis in the temperature range (5 to 40 °C). These tests allowed us to determine the evolution of the actuation force as a function of the temperature: This study shows a comparison ~~with~~ of the different sections on the same wire, providing a better understanding of the behavior of these functionally graded materials.

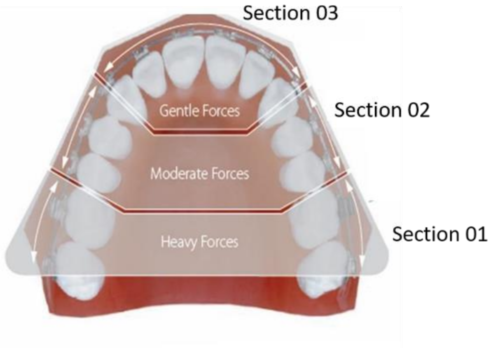

Figure 1 – NiTi Orthodontic wire with different forces sections (Ortho Organizers)

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Production of polycaprolactone/boron and calcium-containing silicate hybrid nanofibers via a combination of electrospinning and non-aqueous sol gel process

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Organic/inorganic hybrids are attracting increasing interest for biomedical applications since multiple properties such as mechanical strength, hydrophilicity, biocompatibility and chemical signaling can be integrated and tuned according to the nature and ratio of the organic and inorganic components. Polycaprolactone (PCL) is a synthetic polyester, semi-crystalline and biodegradable, that is widely used in tissue engineering since it exhibits mechanical properties suitable for a variety of applications and viscoelastic properties that allow its processing through different fabrication technologies.[1] However, PCL is hydrophobic and lack in appropriate biological cues for regeneration. On the other hand, inorganics such as bioactive glasses, largely used to repair hard tissue, have recently shown angiogenic abilities widening their use for the repair of soft tissues as well.[2] Within bioactive glass compositions, boron and calcium are two elements that have demonstrated to promote angiogenesis. In this study, the feasibility of producing PCL/ boron and calcium silicate hybrid submicron fibers for soft tissue applications was investigated via a combination of electrospinning and sol gel. Common sol gel processes to produce biocompatible inorganic networks require the use of water that precludes the use of many suitable biodegradable polymers that are hydrophobic and not water soluble such as PCL. The production of hybrids using PCL and aqueous based sol gel inorganics has been attempted and resulted in a constrained incorporation of the inorganic component to approximately 16% wt.[3] Here, we developed a non-aqueous hybrid solution that allows the electrospinning of submicron and nano size hybrid fibers containing up to 60% of the boron and calcium containing silicate. Chemical structures and thermal properties of the fibers were investigated by FTIR and solid state NMR, and by TGA and DTA, respectively.

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Mechanical caracterization of bovine cortical bone and the role hydration-dehydration cycles

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The hydration, dehydration and rehydration cycle do not change the structure of hydroxyapatite examined by X-ray diffraction (XDR). The collagen structure, as measured by FTIR-ATR, is not changed by dehydration. rehydration does not seem to be quite effective in replacing the initial water content of bone tissue. Mechanical bending tests demonstrate that the dehydration increases the longitudinal modulus of elasticity, the elastic toughness and the tensile strength. Thus, the dried tissue exhibits a brittle mechanical behavior, whilst the hydrated and re-hydrated tissues exhibit a ductile behavior.

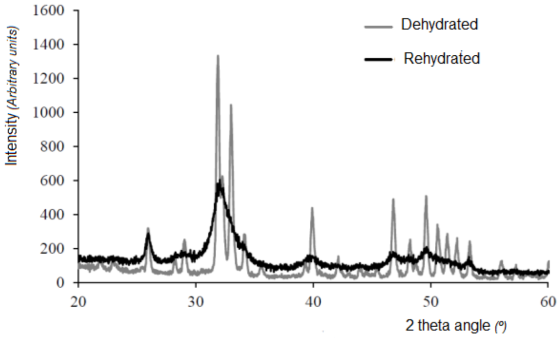

Fig. 1 – Comparison on the XDR patterns of the dehydrated bone and rehydrated bone. The dehydrated bone resembles the characteristic pattern of the hydroxyapatite.

The storage time of the samples does not appear to influence the longitudinal elastic modulus. But the water content of the tissue shows a slight reduction determined gravimetrically after storage at -20ºC for 161 days.

The bone tissue was also analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In the context the conclusions drawn were:

- The samples thermally dehydrated (at atmospheric pressure and at a temperature of 40 °C) contains water in the same state of the samples initially hydrated.
- The water bounding in the rehydrated tissue is weaker than the water in the samples initially hydrated.
- The thermal dehydration treatment performed in this study (at atmospheric pressure and at a temperature of 40°C) just partially removes the water from the bone tissue. However, it is not possible to know, based on the DSC and TGA results, if the removed water is only free water or it also includes a fraction of water in a bounded state.
- Rehydration does not seem to be quite effective in replacing the initial water content of bone tissue.

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Influence of electrical polarization on the bioactivity of chitosan/hydroxyapatite porous scaffolds for tissue engineering

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Chitosan (CS) and hydroxyapatite (HAp) are biomaterials used in tissue engineering. HAp a ceramic similar to the natural apatite in hard tissue has been widely used in bone regeneration. CS is a biopolymer with many biomedical applications. On the other hand, studies started in 1990s show that electrical polarization of the surfaces of HAp increases its ability for osteointegration and bone regeneration.

A porous scaffold composite was developed to mimic the trabecular bone. Also, in order to better mimic the natural HAp of bone, powders composed of nanorods were produced from commercial micrometric powders of hydroxyapatite supplied by Altakitin® and used in the scaffolds preparation. The studied compositions were 100% CS and 75%CS/25%HAp (%wt/%wt).

The scaffolds were electrically polarized by contact polarization. A DC electric field was applied during 1h at 130°C and the efficiency of polarization was investigated using the thermally stimulated discharge current (TSDC) technique.

Bioactivity tests were performed by immersion of the samples (polarized and non-polarized) in simulated body fluid (SBF).

TSDC results show that non-polarized samples of CS already exhibit same charges. Positive polarization enhances the charge deposited in the surface while the opposite effect visible with negative polarization. CS has higher deposition of electrical charges compared to CS/HAp samples.

SEM (scanning electron microscopy) and EDS (Energy-dispersive X-ray spectroscopy) were used to study the effect of charging on bioactivity. Images show that after 1 day of immersion in SBF the CS samples exhibit deposition of calcium phosphates crystals. While for the CS/HAp scaffiolds it is already visible at end of 1 day and for 7 days of immersion a apatite layer has been formed. The non-polarized CS has higher deposition of apatite at 7 days of immersion in SBF than the polarized CS but for the CS/HAp composite the higher deposition is observed on the negative surfaces. No enhancement of apatite formation is observed on positive surfaces compared to non-polarized.

In conclusion the negatively surfaces of CS/HAp porous scaffolds show the highest bioactivity.

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Synthesis and characterization of hemicellulose hydrogels with incorporated magnetic nanoparticles

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Magnetic nanoparticles represent very promising materials in medical applications. As potential drug carriers, magnetic nanoparticles have received wide studies owing to their unique properties. Hydrogels are hydrophilic, polymeric networks with possibility to incorporate different functionalities in the physical or chemical cross-linked network in order to produce “intelligent” or “smart” hydrogels. These smart hydrogels response to environmental signals such as temperature, pH, ionic strength, and electric and magnetic fields. In order to obtain stimuli-responsive hydrogels we have incorporated magnetic nanoparticles in it. The hemicellulose hydrogels were prepared by free radical polymerization of hemicellulose and maleic acid in the presence of cross-linker (N,N'-methylenebisacrylamide) and a redox initiator system (ammonium persulfate and anhydrous sodium sulfite). The chemical structure of the prepared hydrogels were analyzed using Fourier transform infrared and Raman spectroscopy. The surface morphology of the prepared hydrogels were observed using a scanning electron microscope.

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PLA-ZnO nanocomposites with anti-bacterial characteristics

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Lying in the gap between bulk materials and atoms or molecules, nanoparticles (NPs) continue to raise intense research aiming to explore their size-dependent properties which are not yet fully understood. When combined with bulk materials, NPs may endow their peculiar properties to the resulting nanostructured composite.The use of biopolymers synthesized from monomers of natural origin helps to replace current petroleum based plastics offering a cheaper and environment friendly alternative. Poly(lactic acid) (PLA) is a biodegradable biopolymer well known for its interesting biomedical properties. Adding a PLA matrix with ZnO NPs fillers, a nanocomposite (PLA/nZnO) may result with the benefits of the nanosized filler properties, as for instance its anti-bacterial behaviour. The study of PLA/nZnO nanocomposites is the target of the present work. ZnO NPs were synthesized using a solution chemical precipitation method while the structure, morphology and surface properties were characterised by using XRD, FTIR, SEM, TEM, BET, DSC and Zeta-potential techniques. PLA/nZnO nanocomposites (0-5 wt% of ZnO) were prepared by solvent casting method using dichloromethane as the solvent. The alterations of the PLA structure, microstructure and crystallinity with the addition of ZnO was investigated by XRD, SEM, FTIR and DSC. The samples were also mechanically tested for tensile strength using a UTM and submitted to anti-bacterial testing to analyse the effect of the ZnO nanofiller using both gram positive and gram negative bacteria. It was found that as the concentration of the filler increases, the antibacterial activity of the samples also increases.

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Photocrosslinkable hyaluronan-pectin cell-laden bioink for 3D-bioprinting

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Extrusion bioprinting is a biofabrication approach where 3D cell-laden scaffolds are produced by using pressurized air or mechanical forces to print prepolymer solutions into a platform. Nevertheless, the development of bioinks with good printability features concomitant with suitable environments for cells is a challenging task. The aim of this work is to create a heteropolymeric system combining methacrylated hyaluronic acid and pectin to develop a bioink with improved printability features while enabling cell viability during and after the printing process, for skin tissue engineering applications. Hyaluronic acid is a physiologically relevant component of the extracellular matrix able to produce highly viscous solutions and already used in skin regeneration products. Pectin is a plant derived polysaccharide used in the food industry but hardly explored in the tissue engineering field. In this work, hyaluronic acid and pectin were modified with methacrylate groups and combined in different concentrations so that proper rheological and mechanical properties could be achieved. Hydrogel discs were produced by photopolymerization by exposing different formulations to UV light in the presence of a photoinitiator. Rheological properties of discs were assessed upon incubation in culture medium. To produce cell-laden hydrogel discs with improved cell adhesion, both polysaccharides were modified with thiolated RGD sequences by a Michael addition type reaction. Even though hyaluronic acid solutions were characterized by their high viscosity, shear storage modulus values of gels solely made out of this material were far lower than gels produced including pectin. On the other hand, despite producing low viscosity solutions, pectin strongly enhanced the stiffness of the produced hydrogels during the time of incubation, as the presence of divalent cations led to a secondary ionic crosslinking between carboxylic groups in pectin chains. Preliminary studies on cellular response were performed by embedding of human dermal neonatal fibroblasts within the polymeric matrix. Cells remained viable and metabolically active throughout the culture time, as verified by Live/Dead and resazurin metabolic assays. Overall, this photocrosslinkable hyaluronan-pectin system explores the intrinsic characteristics of both materials by using hyaluronic acid to tailor bioink viscosity and modulate cell response while pectin provides the possibility to adjust mechanical properties of photocrosslinked hydrogels by secondary ionic crosslinking events.

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Development of e-skin thin film sensors for blood pressure measurement

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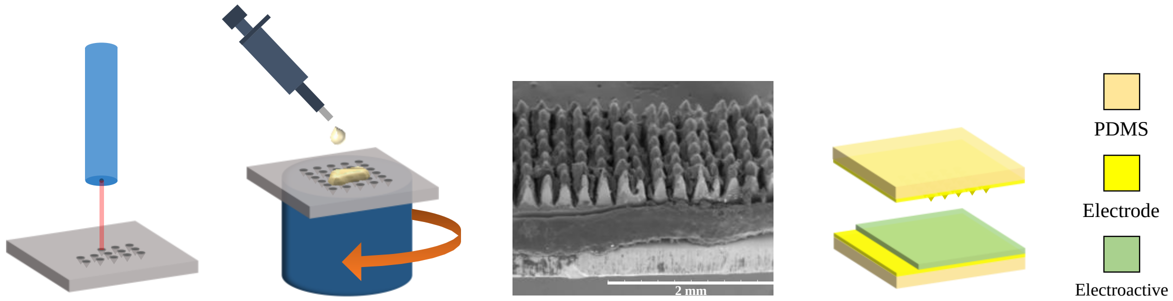
The subject of electronic skin (e-skin) is being widely investigated with the aim of pursuing its use on prosthetic or robotic limbs, or even on human skin for vital signals assessment. In fact, the monitoring of blood pressure would be greatly improved if performed through a flexible pressure device incorporated on an e-skin platform, contrasting with the current approaches that are bulky, noisy, and uncomfortable for users. Nowadays, e-skin devices aimed to monitor blood pressure are usually composed of: a flexible substrate in contact with skin, among which polydimethylsiloxane (PDMS) is a popular option; an electrode on top of that substrate; the sensing component that transduces the blood pressure to an electrical signal, detected by the electrodes of the device; another electrode over the sensing component; and finally one last layer to encapsulate and isolate the full device, usually of the same material as the first substrate. The flexible substrates may be micro-structured to enhance the detected signal. Typically, these devices are produced through techniques that are both expensive and time-consuming. In this work, we propose low cost alternatives to produce such e-skin devices, which minimize the dependence of clean room facilities and allow a faster customization. Those alternatives include the use of laser for the production of micro-structured PDMS films, and electroactive polymeric films for the transducer component. An illustration of the fabrication steps is outlined in figure 1.



Acrylic mold patterned by laser

PDMS thin film deposition on patterned acrylic mold through spin-coating

SEM image of a microstructed PDMS thin film produced with an acrylic mold

Schematic of a final device proposed in this work

Figure 1: Illustration of the preparation of e-skin sensor.

New Functional Bio-MOF Material for the Treatment of Osteoporosis

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Metal-Organic Frameworks (MOFs) are a class of materials formed by combining different metal ions and organic linkers. The different properties of the components allow the preparation of a wide range of materials with several applications. The present work focuses particularly on the development of a new functional bio-MOF material for the treatment of osteoporosis.

The new bio-MOF material is designed to provide a more efficient therapy for osteoporosis by combining the therapeutic effectiveness of alendronate (a bisphosphonate that attenuates the extensive bone degradation, characteristic of osteoporosis disease) with the administration of calcium (an important oligo-element for bone health). After being prepared by hydrothermal synthesis, the new alendronate-calcium MOF material will be characterized with resource to several advanced characterization techniques, such as Powder X-Ray Diffraction (PXRD), Nuclear Magnetic Resonance (NMR), Fourier Transform Infra-red Spectroscopy (FTIR), Thermogravimetry (TGA) and Scanning Electron Microscopy (SEM). Taken together, these results allow distinguishing new materials from those already reported. At the same time, these techniques provide information about the new functional bio-MOF material, such as its purity (PXRD and NMR), structural features (FTIR), thermal behavior (TGA), or even particle morphology (SEM), which could be of extreme relevance for the following steps concerning their bio-applications.

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Mechanical Properties of Bioactive Dual Layer Materials

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In dentistry, the rehabilitation of edentulous patients with dental implants has become increasingly important since tooth loss could lead to several problems on the dental arch such as bone resorption or neighboring teeth movements. These problems can consequently promote masticatory functions problems and other tooth loss.

Currently, Ti6Al4V is the most commonly used material for dental implants, due to its good biocompatibility, high corrosion resistance and Young's modulus (YM) closest to bone when compared to other metals. However, the YM of this material is still high when compared to bone, which can lead to stress-shielding effect, and consequently bone resorption and implant failure. Poly-ether-ether-ketone(PEEK) has become a good candidate for these implants not only due to its good biocompatibility, high wear resistance and excellent thermal and chemical stability but also due to its lower YM when compared with metallic materials. Ti6Al4V and PEEK bioinertness can be overcome by adding bioactive materials such as hydroxyapatite (HAp) and β-Tricalcium Phosphate (β-TCP), that are similar to the mineral phase of the bone matrix. In fact, many studies have focused in improving bioactivity of bioinert materials by using bioactive coatings on their surface. However, during implantation, delamination can occur, compromising their bioactive role. Biocomposites are a good solution to avoid delamination, once the bioactive materials are embedded in the matrix, promoting therefore good mechanical and bioactive properties.

In this work, dual layer materials were produced by hot pressing, with the first layer being composed by the metallic or polymeric material and the second one is a biocomposite, where the matrix is the polymeric or metallic material reinforced by 10vol.% of HAp or β-TCP.

This work evaluates the mechanical properties of these dual layer materials, comparing them with unreinforced Ti6Al4V and PEEK, and with Ti6Al4V-HA, Ti6Al4V- β-TCP, PEEK-HA, and PEEK-β-TCP composites.

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New wood composites with application in footwear heels

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1. Introduction

Fashion and classic shoes apply frequently heels made of wood agglomerate´s. These heels are produced through a series of time consuming steps often involving manual work and chemicals.

2. Objectives & Methods

The main objective of the present work was developing wood composites processable by extrusion and injection molding that result in heels presenting good physical properties and appearance. With this goal, specific wood materials were incorporated in selected thermoplastic materials, in the range of (10 to 50)% (w/w) and relevant properties were evaluated and fine-tuned.

3. Results

Hardness increases gradually with increasing wood addition. These results can be attributed to the more rigid material nature of the additive compared to the polymer. The composites developed present, namely: (1) Capacity to retain the nails or adhesives used to fix the heels to the shoe components; (2) Superior lateral impact strength; (3) Good resistance to water and wear; (4) Aesthetics, “touch” and “sound (when subjected to impact)” similar to the wood agglomerate heels, and (5) Adequate quality-cost ratio. Composites coloring and surface finishing was also studied and successfully established.

4. Originality & Conclusions

The project designed a patent pending original concept that results in wood composite heels having superior properties obtained by sustainable production processes.

Note: A complete operational pilot production process was implemented. The final results will be presented to the audience.

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Polarized films of chitosan and hydroxyapatite for bone regeneration

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The increase of bone diseases and fractures has evoked great interest in the development of biomaterials for use in bone replacement and regeneration.

Recently has increased the interest in combining chitosan, a natural polymer, biocompatible, biodegradable and flexible, with hydroxyapatite, a bioactive bioceramic, osteoconductive and with good mechanical properties. Simultaneously, several studies have shown that electrical polarization of hydroxyapatite, enhances osteointegration and therefore bone regeneration.

The influence of the electric polarization in the bioactivity of chitosan and chitosan/hydroxyapatite films was studied.

Chitosan and chitosan / hydroxyapatite films were produced by preparing homogeneous solutions that were poured into Petri dishes and subsequently dried. Some samples were polarized by contact at 130ºC for 1 hour under the action of a 4.5 kV/cm constant electric field. Also samples were thermally treated, i.e., kept at 130ºC for 1h (but no electric field was applied). This way it was possible to differentiate between the effect of temperature and the combined effect of temperature + field. TSDC (Thermally stimulated Discharge Current measurements) was used to investigate the polarization and the amount of electric charge in thermally treated, polarized and non-polarized samples.

Samples were also characterized by FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-Ray Difraction) and DSC-TGA (Differential Scanning Calorimetry- Thermal Gravimetric Analysis).

Bioactivity assays were conducted by immersing samples in simulated body fluid solution (SBF) at 37°C. Non-polarized, positive and negative polarized surfaces were characterized by Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy, SEM-EDS, to evaluate and compare the deposition of apatite crystals in order to determine which surface would promote a greater osteointegration. Results indicate better bioactivity for the negative charged surfaces, followed by positive ones and finally by non-polarized (but thermally treated). Comparing CS with 70%CS/30%HAp (wt/wt) films bioactivity is significantly higher in the composite.

The process to obtain the films needs to be further developed in order to improve reprodutibility and eliminate by-products for the preparation.

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Histological alterations induced by gold nanoparticles on seabream *Sparus aurata*

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Gold nanoparticles (Au-NPs) are known for their excellent physico-chemical properties with great value of applications on several fields namely on medicine. The increase of manufacture and use of these nanomaterials may lead to their release into the environment polluting water bodies. Fish are sentinel species for different chemicals released into the aquatic systems. The present research aims to evaluate the effects of Au-NPs on the histology of gills, liver and spleen of *Sparus aurata*. After synthesis Au-NPs were coated with polyelectrolytes (positive and negative). Samples were then chatracterized by UV-Vis spectroscopy, and dynamic light scattering. Results are shown on Table 1. Citrate Au-NPs, Positive coated Au-NPs, and negative coated Au-NPs showed absorption spectra peak at 519.62 nm, 520.48 nm and 523.38 nm, respectively.

Table 1. Characteristics of nanoparticles: size, polydispersity index (PDI), and Zeta potential assessed by DLS.

Nanoparticles	**Size**	**PDI**	**Zeta potential**
Citrate Au-NPs	22.8 nm	0.460	-50.29
Au-NPs coated with PAH	62.81nm	0.605	19.1
Au-NPs coated with PSS	82.43nm	0.46	-22.73

Sea bream juveniles obtained from a fish farm were divided into 5 groups (n=7 each): control, and exposed to 5 and 25 µg/l of Au-NPs - citrate coated, coated with a negative (PSS), and positive (PAH) electrolyte. Animals were exposed for 5 days after which they were sacrificed and liver, and spleen removed for histological analysis. Ethical handling procedures were taken in all experiments.
In conclusion, the results of this study showed degenerative histopathological changes on the liver of all Au-NP exposed groups, when compared to control. In addition, a wide range of anomalies were observed within gills, evidencing possible implications on fish health. Further studies are being conducted to explore other endpoints of toxicity.

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Preparation and characterization of chitosan vessels to biomedical applications

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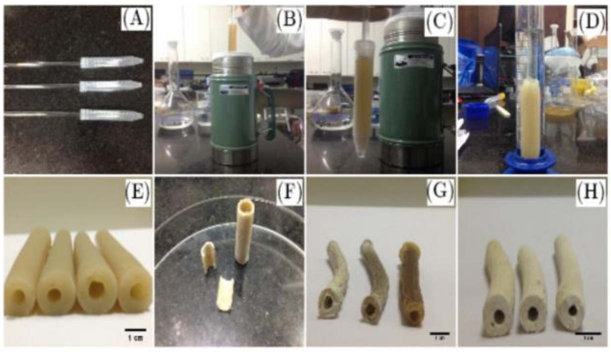
Chitosan, a copolymer of glucosamine and N-acetyl glucosamine, is a polycationic, biocompatible and biodegradable polymer. Because of its unique physicochemical and biological properties, chitosan has shown up to be a polymer of great potential in a range of biomedical applications, including in the Tissue Engineering field. Tissue Engineering is a field of the Health Sciences concerned with the development of substitute biological structures that can therefore act restoring, preserving or improving tissue functions. Scaffolds, biomaterials constructed from biopolymers, are structures that houses cell cultures during growing and proliferation processes, and for that reason such structures have been extensively studied to biomedical applications. In this work, it was produced porous and nonporous scaffolds in the form of cylindrical conduits with different concentrations of plasticizers added to a chitosan-made solution with potential applicability in the field of cardiovascular health. Chitosan vessels were prepared according to two distinct methods: gelation and neutralization of chitosan solution and freeze-drying. Glycerol was used as a plasticizer. In order to do that, we have optimized methodologies of scaffolds production from already-existing protocols. The results have shown some differences among the samples characterization parameters, such as porosity, absorption of water in physiologic media and mass degradation, in function of their compositions.



Images taken of scaffolds preparation method.

The morphology of scaffold was monitored using a Scanning Electron Microscope (SEM) indicated an adequate porosity. The effect of plasticizer on thermal behavior was verified in this investigation. The thermal behavior showed that occur a substantial mass reduction in order of 60 % to samples manufactured with CH solution. Samples produced with solution CH/GLY had mass reduced in order of 40 %.

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Effects of ZnO-NPs on Histology of Gilthead Seabream, *Sparus aurata*

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Zinc oxide nanoparticles (ZnO-NPs) are used for a multitude of purposes, including on biomedical field. An overview of the benefits and possible impact of these nanomaterials on both environment and human health was recently reported (Beegam *et al*., 2016). Features of these nanoparticles (e.g. size, shape, surface charge and agglomeration) may lead to different biological effects such as genotoxic, mutagenic and cytotoxic effects on fish. Therefore, in the present work a 96h assay was performed using the gilthead seabream *Sparus aurata*, a species with a great economic value, to evaluate microanatomical alterations induced by these particles on gills, liver and edible muscle.
ZnO-NPs were sinthetized by controlled double-jet precipitation method. A volume of 100 ml of preheated water (90ºC) was added to the reactor with stirring rate of 500 rpm, followed by 100 ml each of a 0.02 mol zinc nitrate and 1.6 mol trithanolamine (TEA) solution, introduced simultaneously through glass tubes at a constant flow rate. The additions were carried at different flow rates namely 9 ml/ min, 7 ml/ min and 14 ml/ min. The system was kept for 30 min at 90 ºC, under continuous agitation. Particles were separated from the supernatant solution by filtration and washed with ultra pure water. The powders were then dried in oven at 75ºC overnight. The crystal structure of ZnO particles was characterized by X-ray diffraction and their size determined by scanning electrone microscope.
Sparus aurata (4-5g, ±7 cm length) purchased from a fish farm (Spain) were grouped into five (n=7 each): control, zinc chloride, ZnO-NPs (7 ml/min; 9ml/min and 14ml/min). A dose of 1mg/L of each type was added to the tanks. After 96h exposure period animals were sacrificed, weighted and organs were removed, and fixed in 10% buffered formalin for standard histology. Ethical procedures were applied during experiments.
No remarkable alterations in histology of edible muscle were noted. However, changes in gills and liver were shown in all groups exposed to ZnO particles. Possible implications for human health are highlighted in this study.

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Plasmonic behaviour of noble nanoparticles (Au, Ag) dispersed in AlN

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Thin films composed by plasmonic nanoparticles, such as Au or Ag, dispersed in a dielectric matrix (e.g. TiO_2, Al_2O_3, AlN, etc.) are of great interest for a wide range of technological applications, namely in plasmonic sensing (e.g. detection of gas molecules or biological agents), due to their unique plasmonic properties. Most of these applications are based on the excitation of surface plasmons (SPs), in the case of metallic surfaces, or localized SPs, in metallic nanoparticles or nanostructures (e.g. fractal structures). The optical properties of the noble nanoparticles are regulated by their geometric characteristics (distribution, size and shape), but also by the dielectric function of the host matrix. The possibility of using AlN as a host matrix for plasmonic nanoparticles, and nanostructures, of Au or Ag, and how their concentration and distributions influence their optical response, will be discussed in this presentation. The thin films were deposited by reactive DC magnetron sputtering and submitted to post-deposition thermal annealing, in order to promote the growth and coalescence of the nanoparticles. After the annealing treatment, different size distributions were obtained and hence changes on the optical responses were observed. The plasmonic behaviour depends on the type of metal and concentration as well as on the annealing temperature. The films present tuneable resonance peaks in the visible range and different absorption band characteristics, which might be important for application in LSPR-sensors and Surface-Enhanced Raman Spectroscopy (SERS).

Selective reference:

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The influence of pressure on the sintering of Ti6Al4V-ZrO$_2$ materials for biomedical applications

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The development of design approaches for biomedical applications using conventional and well accepted bio inert materials is an actual challenge. This work is concerned with the effect of sintering pressure on the interface reaction between titanium alloy (Ti6Al4V) and zirconia (ZrO_2), on the density and mechanical properties of the Ti6Al4V-ZrO_2. For this purpose, different sintering pressures were performed (P=5, 20 and 100 MPa). Image analysis and chemical composition were performed in order to investigate the Ti6Al4V-ZrO_2 interface reaction. Additionally, an interesting blackening phenomenon on ZrO_2 layer was described and discussed by means X-ray photoelectron spectroscopy (XPS) and thermal treatment. The results showed that chemical composition and mechanical properties are strongly dependent on sintering pressure.

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Mechanical properties of layered zirconia to zirconia-hydroxyapatite or zirconia-β-TCP composites for biomedical applications

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The selection of biomaterials is an essential aspect to promote a long-term success of dental implants, both to enhance osseointegration and maintain the necessary mechanical properties of these implants. In the last years, zirconia based implants have gained a lot of attention, and particularly 3Y-TZP (3 mol.% Yttria doped Zirconia Tetragonal Polycristals) have been presented as an excellent alternative to Ti6Al4V implants not only due to a good mechanical strength, excellent biocompatibility and osseointegration, but also by providing good esthetics due to their white-opaque color. However, zirconia-based implants are bioinert, meaning that when implanted in the human bone its interaction with the surrounding tissue is very weak. In this sense, several strategies have been developed to solve this problem, as by using coatings with bone growth “stimulating agents” like bioactive materials (hydroxyapatite and β-TCP) once their crystalline structure similar to the mineral phase of bone and their active surface provide biological bonding to bone. However, a major problem regarding coatings is their poor adhesion strength to the surface. In fact, during implantation the coatings adhesion strength may be surpassed, promoting the detachment of these coatings from the surface of the implant.

In this context, this work intends to develop a solution that can overcome the bioactive detachment problem by producing biocomposites of zirconia-hydroxyapatite and zirconia-β-TCP by cold pressing and sintering. The proposed design has a dual layer material, where the first layer is 3Y-TZP and the second one is a composite of 3Y-TZP reinforced with 10 % vol. of hydroxyapatite or βTCP. This second layer would be placed on the surface of the implant to stimulate osseointegration while preventing the bioactive delamination to occur. The first layer would guarantee the necessary mechanical properties of the implant bulk. These two layered materials (zirconia to zirconia-hydroxyapatite and zirconia to zirconia-β-TCP) are characterized regarding their mechanical properties, before and after an ageing treatment.

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Magnetic, electric, multiferroic, and plasmonic functional materials (A2)

Nanoscale modifications in Eu^{3+} doped sol-gel glasses by means of cw laser irradiation through µ-lens

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This study deals with the use of laser radiation focused by dielectric microspheres to modify surfaces of glasses. After conveniently illuminate a microsphere, a narrow beam can emerge with a waist that is under the Abbe diffraction limit, reaching dimensions ~ λ/3 or lower. This phenomenon receives the term of photonic nanojet. For this purpose, a glass of the SiO_2-TiO_2-P_2O_5 system doped with Eu^{3+} has been prepared by sol-gel and the Eu^{3+} luminescence was used to detect the temperature of the irradiated region. Combination of atomic force microscopy (AFM) and fluorescence measurements allows controlling the glass topography in the nanometer scale and of surface heterogeneity over large areas. The results presented in Fig.1A-B demonstrate the capabilities of these measurement techniques. Fig. 1A shows five regions that may be assessed by circular boundaries, which correspond to the places where the microspheres were deposited and irradiated with a diode laser 532 nm. In Fig. 2B is shown an enlargement of one of these limits (the framed region of A) and a circular hole located approximately at the center of the circle with a diameter of 450 nm. It is interesting to note that, due to propagation of heat appears a side damaged area around the irradiated zone, and therefore the resulting modified expected area is greater than that imposed by the diffraction limit. The formation of the hole under continuous wave radiation to the glass surface from a laser diode of 532 nm, can be considered as a demonstration of the accuracy of the use of dielectric microspheres as µ-lens.

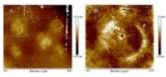

Fig. 1A-B - Image of the glass after treatment with a 532 nm laser focused with microspheres. In B detailed AFM image of the framed region in A.

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Broadband FMR in Mn-doped Li ferrite nanoparticles

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Spinel ferrites are widely used for electrotechnical equipment since their discovery in the forties. Nanoscale devices with engineered physical and magnetic properties result in substantial improvement in the quality of materials that are useful in a variety of applications. In the last years there is a strong interest in ferrite nanoparticles due to the fact that nanoscale materials possess properties that are comparable to or superior to those of bulk materials counterparts, as well as its potential applications in sensors or microwave devices. Lithium ferrites are well known materials due to its numerous technological applications especially in microwave devices, but also in magnetic recording, transformer cores and rod antennas, and Mn doping reduces porosity and grain size and improves their resistivity and Curie temperature.

Mn-doped lithium ferrite nanoparticles were prepared by sol-gel technique by means of Pechini method, and then annealed at different temperatures in 250-1000 ºC range. This route of preparation has revealed to be one efficient and cheap technique to obtain high quality ferrite nanosized powder. Sample particles sizes obtained with XRD data and Scherrer’s formula lie in 15 nm to 200 nm, with increased size with annealing temperature.

Magnetic field induced microwave absorption in nanoscale ferrites is a recent an active area of research, in order to characterize and explore potential novel applications. In the present work microwave magnetoabsorption data of the annealed lithium ferrite nanoparticles are presented. These data have been obtained with a system based on a network analyzer that operates in the frequency range 0 - 8.5 GHz. At fields up to 200 mT we can observe a broad absorption peak that shifts to higher frequencies with magnetic field according to ferromagnetic resonance theory. The amplitude of absorption, up to 85 %, together with the frequency width of about 4.5 GHz makes this material suitable as wave absorber. Samples annealed at higher temperatures show asymmetrical absorption peaks caused by a secondary process at high frequencies, over our upper range, similar to the behaviour observed in polycrystalline samples, thus suggesting its multidomain character.

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Adhesion of $Ge_2Sb_2Te_5$ Thin Films for Phase Change Memory Application

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Phase change memory (PCM) is considered to be one of the most perspective new types of memory devices. Today the best results for the PCM devices are obtained with using of the composition $Ge_2Sb_2Te_5$ (GST225). However, despite of the progress PCM technology must be sufficiently improved.

It is important to provide high adhesion of the different layers in the multilayered PCM cells. This problem is especially important for the programming layers, which must withstand multiple cycling with sharp change of the temperature. However, adhesion propertied of GST225 layers is low and is poorly studied. So, the aim of this study is investigation of the adhesion propertied of GST225 layers to the different materials and layers.

GST225 layers were prepared by thermal vacuum evaporation of the synthesized material. X-ray diffraction (D8 Advance Bruker, $CuK_{\alpha 1}$ radiation, 0.15418 nm) showed that as-deposited films were amorphous.

Elemental analysis by Rutherford backscattering (E_d=1.0 and E_α=2.7 MeV at 135° scattering angle) and Energy Dispersive X-Ray Analysis (CAMEBAX, Cameca) showed that deposited films had composition of GST225 with the accuracy of ±5%.

Electron energy analysis was carried on by XPS spectrums in Ultra High Vacuum (SPECS Phoibos 150 with delay-line detector and a monochromatic AlKα (1486.74 eV) X-ray source). High resolution spectra were recorded at normal emission take-off angle and with a pass-energy of 20 eV, which provides an overall instrumental peak broadening of 0.5 eV.

Adhesion propertied of GST225 layers were tested on Si and ceramics wafers, Si wafer with different sublayers (SiO_2, Al, Ti, Ag, TiN+W, NiCr).

According to atomic force microscopy (NT-MDT Solver Pro) the thicknesses for Al, Ti, TiN+W and NiCr layers were 300 nm, while for Ag layer was 60 nm.

The nanoindentation (nanoindentor B-J53) measurements were performed using a three-sided pyramidal Berkovich diamond indenter having a nominal edge radius of 20 nm (faces 65.3° from vertical axis) attached to a fully calibrated nanoindenter (TTX-NHT, CSM Instruments). Load displacement curves, hardness and Young's modulus were determined. Optical and AFM images after indentation were controlled. It was found that the sublayer significantly affects the mechanical properties of the films. The films with a sublayers of TiN and Ti have a much higher stability than film with Al and Ag sublayers.

So, adhesion propertied of GST225 layers to the different materials and thin films were investigated.

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Three component reaction: Green synthesis of 3,4-dihydropyrimidin-2-(1H)-ones using copper-based catalysts

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The three-component reaction known as the « Biginelli reaction » is one of the most important and useful multicomponent reactions, which has advantages to join two core units (a dihydropyrimidinone and an aromatic carbocyclic or heterocyclic) on the same structure leading to remarkable heterocyclic system. Variations in all three components led to a library of more than 700 000 products known as DHPMs which, most of them, display a fascinating array of therapeutic and pharmacological properties.

Our contribution bases on the synthesis of 3,4-dihydropyrimidinone and its derivatives according to the reaction Biginelli's three-component catalyzed by copper as described in scheme 1. In a first step, we used copper nitrate as catalyst which has proven highly effective in obtaining DHPMs products with very good yields (80%) in our reaction conditions optimized (benzaldehyde/ethylacetoacetate/urea/Cu^{2+} = 1/1/1.5/0.2 mmol at 80°C under solvent-free during one hour of reaction). In all cases the pure products were isolated by simple filtration and identified by comparing their spectral (FT-IR, ^1H NMR) and physical data with those reported in the literature. In the second step, we have described in the same conditions the synthesis of DHPM in presence of xCu/support (x = 5, 10 and 15 wt.% ; support = SiO_2 and Al_2O_3) prepared by impregnation method. The use of these catalysts proved less effective yield of DHPM (55%) compared with copper nitrate. However, this synthetic remains promising because it is possible to recycle the supported catalyst. The catalyst was easily separated from the reaction mixture by filtration.

Key words: Biginelli reaction, 3,4-dihydropyrimidinones, copper catalysts

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Multiferroic Nanofibers by Electrospinning

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Nanostructured composite multiferroics combining a magnetostrictive phase elastically coupled to a piezoelectric material have been the subject of great interest. By dispersing a magnetostrictive material inside a piezoelectric matrix the elastic interaction between both phases induces a coupling behavior, the so called magnetoelectric effect. The ability to couple to either the electric polarization, the magnetization or to their coupling offers additional degrees of freedom in device design. However, in the form of fibers composite multiferroics have been poorly explored. In this respect, nanofibers prepared by electrospinning present a high surface-to- volume ratio and unique structure. Electrospinning is based on the high voltage jet drawing of a polymer solution or melt through a capillary (needle) and has been shown to be a very convenient approach for nanofibers production of polar and magnetic materials.

In this work, we have studied the synthesis of composite multiferroic nanofibers by electrospinning, where the piezoelectric phase was composed by barium titanate (BTO). For the magnetic phase, either cobalt ferrite (CFO) or nickel ferrite (NFO) were used, due to their high magnetostriction. The BTO, CFO and NFO sol-gel precursor solutions were mixed and subsequently spun to form BTO-CFO and BTO-NFO nanofibers with different concentrations. A high temperature (1000ºC) annealing step was used for polymer vaporization and grain coalescence. The X-ray diffraction studies show that the fibers are polycrystalline with the tetragonal-BTO phase and the CFO and NFO cubic spinel structure. The Raman spectra presented the corresponding modes characteristic of the tetragonal-BaTiO3 structure, indicating the stabilization of the polar ferroelectric phase, along with the ones from the cobalt-ferrite. The dielectric properties show that the tetragonal (ferroelectric) transition of BTO is broadened and its temperature is reduced as the ferrite concentration increases, due to the nanoscopic grain sizes. The influence of the ferrite content in the prepared nanofibers, on their structural, electrical and magnetic properties will be presented.

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Al_2O_3-Ni composites with a gradient distribution of metallic phase obtained by novel centrifugal gelcasting method

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Functionally graded Al_2O_3-Ni composites were fabricated by a novel centrifugal gelcasting method. This technique is based on a combination of centrifugal force with gelcasting in which a consolidation of slurry proceeds through *in situ* polymerization reaction. The method allows to receive variable distribution of the metallic particles in a ceramic matrix. The final composite elements have been obtained in the form of a tube which precisely reproduced the shape of the die (possibility of obtaining elements of complicated shape). Samples have been characterized by ~~a~~ high mechanical strength and gradient distribution of the metallic phase. The slurries containing Al_2O_3 and Ni particles exhibited high stability at high solid content (50 vol.%) and thus green samples of high relative density (> 58 %) have been obtained. Rheological behavior of alumina-nickel suspensions containing organic monomer used in the centrifugal gelcasting process has been studied. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and stereological analysis were used to characterize the functionally graded composites. Microstructural characteristics were investigated from outer surface towards the inner side of the tube. The observations revealed that the outer surface of all composite~~s~~ samples consisted of the maximum volume fraction of nickel particles in contrast to the inner part of the tube which was devoid of the metal particles. Graded property of materials was investigated through hardness and fracture toughness measurements. The results of fracture toughness testing revealed that the maximum K_{IC} values were observed in the region at the outer edge of the tube due to the presence of nickel particles. The stereological analysis in this case allowed for a comprehensive description of the microstructure of obtained Al_2O_3-Ni composites.

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Modification of magnetic ordering through substrate strain in Lu substituted $EuMnO_3$ thin films

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This work aims to understand the alterations induced by film/substrate lattice mismatch concerning structure, lattice dynamics and magnetic response of $Eu_{1-x}Lu_xMnO_3$ thin films extended to $0 \leq x \leq 0.4$ with Orthorhombic symmetry, when compared to results reported for ceramics with analogous nominal composition [1]. Thin films deposited by chemical solution route onto $Pt/Ti/SiO_2/Si(100)$ oriented substrates exhibit noteworthy modifications in the magnetic ordering properties and contrarily to ceramics, do not show any sharp phase transition to the paramagnetic state, revealing instead a field induced ferromagnetic response stable up to 100 K. X-ray diffraction and Raman spectroscopy measurements enable to identify the mechanical compressive state induced by the substrate and Lu doping, allowing to interpret the behavior of these films phase on the basis of a magnetoelastic coupling effect, driven by alterations in electronic orbital overlapping and the associated antiferromagnetic superexchange interactions.

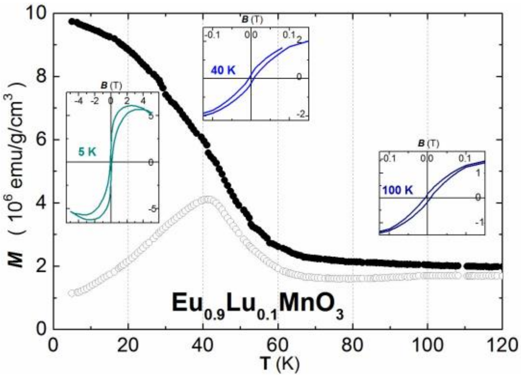

Fig.1: Magnetic measurements of x =0.1 thin film sample

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A detailed study of the physio-chemical properties of Fe doped $Pr_2O_2SO_4$

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Praseodymium oxy-sulfate, $Pr_2O_2SO_4$, has traditionally been suggested as oxygen storage materials due to their large oxygen storage capacity. Although there are various mechanisms suggested to be involved in the oxygen storage in $Pr_2O_2SO_4$, for example that the distortion of the oxygen sub-lattice generates some mobile oxide-ions and that the change in the oxidation states of Pr^{3+}/Pr^{4+} can catalyze oxygen exchange, it is the redox ability of sulfur that is mainly attributed for the high levels of oxygen storage capacity. Due to the ability of the Ln oxy-sulfates to store oxygen, they have been applied as catalysts for the high-temperature water–gas shift reaction, for anaerobic catalytic CO oxidation, for cathode material--combined with Ag or to $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ form a new composite electrode for intermediate temperature solid oxide fuel cells (SOFCs)[1]. However, the intrinsic properties of the $Pr_2O_2SO_4$ is still not satisfactory, such as total conductivity, ionic conduction contribution, oxygen partial pressure dependence and the slow reactions of $Pr_2O_2SO_4$ to Pr_2O_2S and backwards. In the present work, the physio-chemical properties of $Pr_2O_2SO_4$ as stated above are thoroughly improved by doping of Fe, and then studied by fundamental electrochemical tools, such as electrochemical impedance under different oxygen partial pressure with a series of temperature, electromotive force measurement (EMF), coulombic titration, along with XPS, FTIR, and Raman spectra for quenched $Pr_2O_2SO_4$ from 850°C to 25°C in ~10 mins, in oxygen, air and nitrogen, distinctively, to keep the high temperature original states.

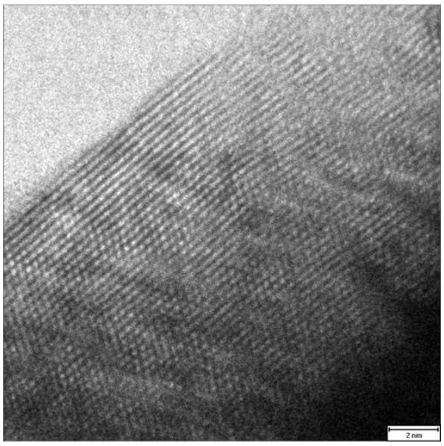

Fig. 1. TEM of $Pr_2O_2SO_4$, the bar is 2nm.

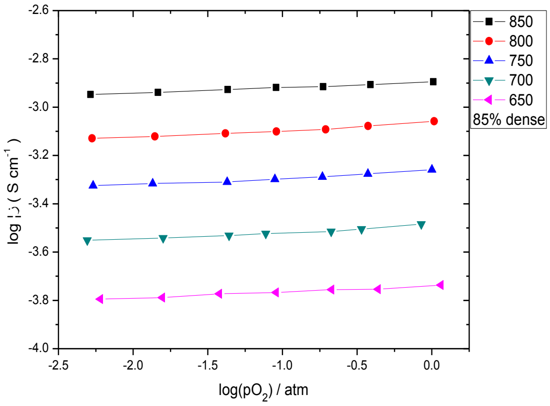

Fig. 2. Conductivity of $Pr_2O_2SO_4$ vs pO_2 from 650-850°C.

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Preparation and characterization of lead-free $K_{0.5}Na_{0.5}NbO_3$ piezoceramics obtained from mechanochemically activated powders

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The potassium sodium niobate solid solution, especially the composition $K_{0.5}Na_{0.5}NbO_3$ (KNN), is one of the most promising candidates for the replacement of lead-based piezoelectric materials, due to its high Curie temperature, high electromechanical coupling factor and moderately low dielectric permittivity. Such properties make KNN perfectly suited for the usage in the ultrasonic range. Medical applications of KNN piezoceramics can also be considered because this material is biocompatible.

Nevertheless, it is very difficult to obtain satisfactory performance of KNN ceramics prepared by conventional high-temperature solid-state method. The main problems arise from poor densification, abnormal grain growth and compositional inhomogeneity. In order to obtain dense, fine-grained ceramics with stoichiometric composition, it is necessary to modify processing route or to use the powders with higher sinterability. Mechanochemical activation of the starting powders is an effective way to increase their reactivity. As a result, the powders can be calcined at lower temperature. Then, as nanopowders have high specific surface area, it is possible to obtain better densified ceramics.

Starting powders of Na_2CO_3, K_2CO_3 and Nb_2O_5 in stoichiometric ratio were milled in SPEX 8000 Mixer Mill. The structural changes during the process were controlled by XRD. Powders milled for 35h and 80h were calcined at different temperatures (450-700°C) for 2h. The crystallization of the perovskite KNN phase has been completed after calcination at 550°C. Optimal calcination temperature was further confirmed by TG/DTA. KNN piezoceramics has been obtained from calcined powders by conventional sintering of the pellets at 1000°C/3h. Microstructure of the powders and ceramic samples has been investigated by SEM. Complex dielectric permittivity has been determined by dielectric spectroscopy in temperature range between RT and 550°C, in frequency range 1 kHz - 1MHz.

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Effect of In nanodroplet size on morphology of liquid metal-assisted electrochemical deposited Ge nanowires

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In the present time germanium nanowires shows great interest among the science community. Due to the excellent electrophysical properties such structures can be used in energy storage and generation applications and optoelectronics. However, the technological complexity of nanostructured Ge manufacturing process limits its production [1]. Recently in [2] a new method of preparing crystalline filamentary Ge nanostructures has been proposed. Described method based on electrochemical deposition of Ge from aqueous solutions at room temperature. In this case liquid metal nanodroplets that have low melting points, such as Hg and Ga, are used as an electrode.

In this paper, we demonstrate a simple method of Ge nanowires formation by electrochemical deposition from aqueous solutions at room temperature using In nanodroplets as a nucleation centers. Indium nanoparticle arrays are formed by vacuum thermal evaporation and condensation of evaporated material small batches using molybdenum vaporizer. This method allows controlling the density and size of In nanoparticles, which in turn makes possible to control the dimensions of the Ge nanowires.

This work presents results of particle size indium influence on the obtained Ge structures morphology. The morphology and composition of the samples were investigated by SEM and TEM with an energy dispersive X-ray (EDS) detector. The results show that the nanowire length and diameter depends on the In nanoparticle size. The lower In nanoparticle size, the lower diameter and maximum length are Ge nanowire will have after the deposition process. Thus the size of the In nanoparticle determines the maximum length and the initial diameter of the Ge nanowire. In order to fit the experimental data, we have proposed a simplified model and adapted it to our growth conditions.

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TiO_2 nanotubular layers formation with improved conductivity by specific thermal annealing procedure

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The self-ordered vertically aligned TiO_2 nanotubular (TNT) layers formed by electrochemical oxidation have an ideal electrode configuration for energy applications due to adjustable geometry (diameter, length), crystallinity, and direct contact to the Ti metal layer where they are grown. As a result, such TiO_2 nanotubular arrays have big perspectives for such applications as photovoltaics, Li-ion batteries, supercapacitors, photoelectrochemistry and biomedicine. Until now such layers have only a limited success, due to the comparably slow redox switching properties and high resistivity of the TiO_2. For now various modification techniques have been investigated to improve TiO_2 nanotubular layers electrical and physicochemical characteristics. These modification methods are based on TiO_2 nanotubes decorating or doping with various materials. However most of them are using high-temperature processing in an atmosphere of flammable gases, such as acetylene, and yet not allow obtaining a uniform doping along the tube depth.

In this work we introduce a facile procedure that allows obtaining anatase phase TNT layers with improved conductivity, excellent adhesion properties to the substrate and high hydrophilicity that is important feature for its subsequent modifications for further functional applications.

TiO_2 nanotubular arrays are formed by anodization in fluorine-containing non-aqueous ethylene glycol based electrolyte. Subsequent modification includes thermal annealing in vacuum chamber at 450 ºC during 1 hour followed by thermal annealing in air atmosphere at 300 ºC during 30 min.

By Differential scanning calorimetry, Auger spectroscopy and XRD analysis methods were used for optimization of multi-step thermal annealing parameters. Electrical properties of the samples were investigated by cyclic current-voltage characteristics measurements in the range of 0 to 2 volts. Obtained current-voltage characteristics were compared with the CVC's obtained on non-annealed and annealed in air at 450 ºC during 1 hour on identical TNT layers using the same measurement technique.

The obtained results showed that TNT layers modified by developed multistep thermal annealing procedure have increased conductivity values that in 4 order exceeding the values obtained for samples annealed in air.

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Observation of Positive and Negative Magnetodielectric Effects in Relaxor $PbCo_{1/3}Nb_{2/3}O_3$ Ceramic

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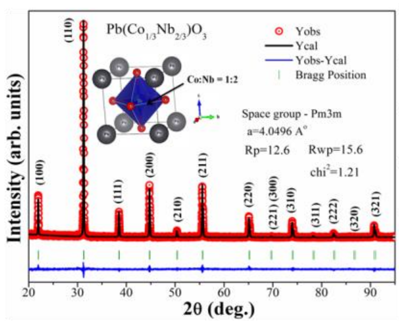
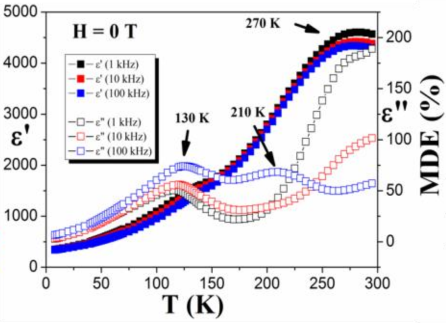
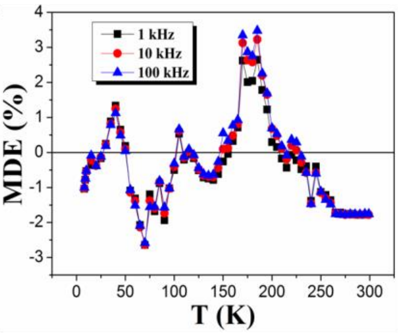
Lead cobalt niobate ($PbCo_{1/3}Nb_{2/3}O_3$: PCN) is a multifunctional electroceramic belongs to the class of relaxor ferroelectrics which are very popular due to their extraordinary properties and applications. To the best of our knowledge magnetoedielectric study of PCN ceramic has not been studied. With this motivation we performed magnetodielectric measurement on PCN ceramic synthesized by two step columbite precursor method using high purity chemicals: PbO (99.9%), CoO(99.99%), Nb_2O_5(99.9%). The room temperature crystal structure and microstructure is examined using x-ray diffraction (XRD) and scanning electron microscope (SEM) respectively and dielectric constant as a function of frequency as well as temperature is measured in 0T and 9T magnetic field using high performance frequency analyzer (NOVO-CONTROL). Microstructure images revealed closely packed grains with grain size ~8-10 μm. Room temperature X-ray diffraction (XRD) pattern suggests single phase pseudo cubic crystal structure having Pm3m symmetry, where Co and Nb randomly sitting at B-site with lattice constant ~4.0496(2) Å. Rietveld Refinement on XRD data yields larger value of thermal parameters, implying Pb and O are disordered along <111> and <110> directions respectively. The temperature dependent dielectric properties revealed re-entrant relaxor behaviour (T_m ~130 K and 210 K for 1 kHz) along with a high temperature diffused phase transition, T_c ~270 K. The low temperature frequency dependent dielectric maximum, $f(T_m)$ is analyzed using generalized glass model (also called critical slowing down model). The magnetodielectric effect (MDE(%)=(ε'(9T)-ε'(0T))/ε'(0T)*100) depicts positive and negative MDEs implying coupling between mangnetic and dielectric properties. Such positive and negative MDEs are also observed in disordred double perovskite Pr_2CoMnO_6 ceramic whereas single MDE peak is reported in B-site ordered phase. Therefore, it is believed that the re-entrant relaxor behaviour and multiple positive-negative megnetodielectric effects are associated with the quenched disorder as well as multiple heterogeneities present in PCN ceramics and details will be discussed.







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Ultrasonic irradiation as a tool for enhancing the catalytic performance of ZVI nanoparticles towards nitrate reduction

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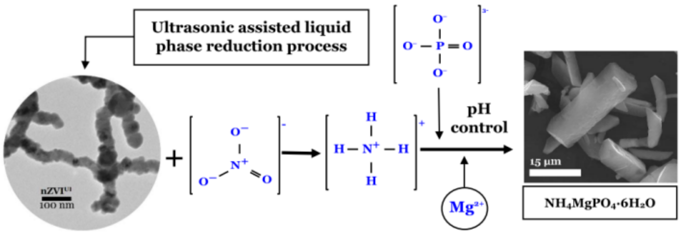

The successful removal of contaminants and recalcitrant compounds from contaminated effluents by particles with catalytic activity is highly dependent on the properties of the used particles including its crystallinity, particle morphology (size and shape) and specific surface area [1], [2]. Such characteristics when properly tailored may promote the catalytic performance of the catalyst. In the present study, a liquid-phase reduction (LPR) process is combined with ultrasonic irradiation (UI) aiming to enhance the key properties of zero valent iron nanosized particles (nZVI) for enhancing its performance when assisting the removal of nitrate from contaminated waters. Appropriate conditions including reagents concentration and injection rate, the ratio between the cation (Fe^{+3}) and the used reductant ($NaBH_4$) were selected for carrying out the chemical precipitation of nZVI, under or in absence of UI. The nZVI, synthesized with and without the utilization of UI, were subsequently tested in a process of nitrate removal from solution based on a Taguchi approach, in order to estimate the catalytic activity of the prepared nZVI. The produced particles were characterized by XRD, TEM, SEM, gas adsorption (BET) and Raman spectroscopy. Ion chromatography was employed for monitoring ammonium, nitrate and nitrite concentrations in the reaction media where the catalytic efficiency of nZVI as nitrate reductants was tested. The results showed that UI application resulted in a higher synthesis yield of nZVI with smaller size but a more crystalline structure as compared to nZVI synthesized in absence of UI. Also nZVI obtained under UI were seen to display a statistically higher catalytic activity towards the nitrate reduction, thus pointing out the effectiveness of coupling UI to the precipitation method, in terms of technical and economic points of view. The study of nitrate reduction mechanism confirmed ammonium ions to be the dominant end-product of the reactional process, and furthermore, as a precursor for the synthesis of struvite (NH4 MgPO4·6H2O), a valuable fertilizer.

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Synthesis and Characterization of Mg/Al- Carbonate Layered Double Hydroxides (Mg/Al-CO_3LDH 2:1) with high crystallinity

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Herein, we present a simple synthesis of Mg/Al-Carbonate Layered Double Hydroxides that has been studied. This latter is prepared by a co-precipitation method with the Mg^{2+}/Al^{3+} ratio of 2, at pH = 10. We have used solution (A) containing $MgCl_2.6H_2O$ and $AlCl_3$.9H2O and basic carbonate solution (B) prepared by dissolving appropriated amounts of Na_2CO_3 and NaOH.
The physicochemical techniques DGA/DTA, XRD, BET and IR were used to characterize the material.The x-ray diffraction analysis of the resulting product showed it to have a layered double hydroxide structure. The peak (00l) generally observed for the lamellar compounds. The FTIR spectra for the synthesized sample showed the presence absorption bands of CO_3 characteristic of the lamellar materials. The sample synthesized has a good cristanillity.

Keywords: Lamellar materials, Mg/Al-Layered Double Hydroxides (LDH), Co-precipitation

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Structural and luminescence characterization of heat-treated porous anodic alumina films formed in selenic acid solution

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Porous anodic aluminum oxide (AAO) is a widely used material for formation of the nanocomposites. These nanocomposites can be further implemented in different devices, for example, in the field of optoelectronics [1].

It is known that the choice of the electrolyte affects significantly the properties (geometrical, optical, mechanical) of the growing AAO. Thus, the development of the novel electrolytes for the AAO formation affords expanding the range of AAO applications. In this case, the investigation of the relationships between anodization and pre/posttreatment parameters, chemical composition and binding, and the resulting properties of AAO formed in such electrolytes is essential.

Recently, it has been shown that self-ordered AAO structures can be obtained in electrolyte, based on selenic acid [2]. The geometrical parameters of such structures are also promising: small pores (around 10 nm) together with the small porosity (around 3%). This nanoporous alumina has been already applied for formation of the metamaterials [3]. However, the optical properties of AAO formed in the selenic acid based electrolyte are still poorly investigated.

In the present work, Raman spectroscopy, thermal gravimetric analysis and photoluminescence spectral measurements were applied to study the chemical binding and luminescent properties of AAO samples prepared in selenic acid electrolyte, and the effect of thermal treatment (in the range of temperatures 200-500°C) on it. The luminescence spectra of the fabricated samples are compared with the spectra of AAO formed in the commonly used electrolytes (sulphuric, oxalic, phosphoric acids). The special features of the thermal behavior of the samples formed in the selenic acid electrolyte are considered, and the origin of the photoluminescence centers is discussed.

The work was supported by grant of the President of the Russian Federation (MK-9536.2016.3).

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High room temperature magnetodielectric response on flexible polymer based nanocomposites

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The magnetodielectric effect (MDE) is defined as the variation of the dielectric permittivity as a response to applied magnetic fields. Materials exhibiting large MDE are suitable for new devices including tunable filters, four-state memories, magnetic sensors, and spin-charge transducers. One of the most important issues in this field is how to achieve a large MDE near room temperature.
In this work, multiferroic composites consisting of ferromagnetic/magnetostrictive $CoFe_2O_4$ (CFO) and ferroelectric polyvinylidene fluoride (PVDF) have been investigated for high MDE coupling. Flexible particulate composites with general formula $[xCoFe_2O_4]/[(1 - x)$ (Polyvinylidene fluoride)] were prepared for x = 0, 3, 11, and 20 wt. %.

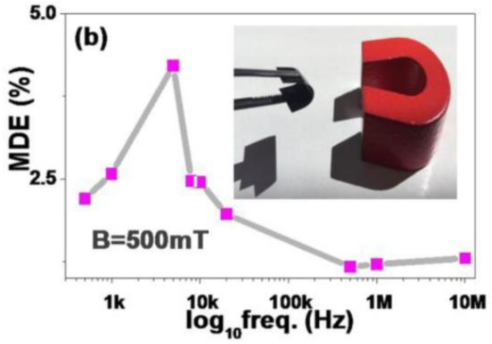

Figure 1 - MDE (%) as a function of the frequency.

It is shown that the dielectric constant, dielectric loss, and saturation magnetization of the composites increase with the increasing $CoFe_2O_4$ content, being 13, 0.13, and 13 emu g-1, respectively, for x = 20. The change in the dielectric response (magnetodielectric effect (%)) is the highest among all the reported polymer-based composites for the x = 20 sample (4.2%), and on the contrary, the highest value of the magnetodielectric coefficient (γ) is higher on the x = 3 sample (0.015 emu^{-2} g^2).

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Synthesis and characterization of ZnO:Al thin-films grown by DC-Sputtering

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Zinc Oxide thin films doped with Aluminum (AZO), have been used widely in the past years as transparent conductor oxide (TCO). These have been utilized as transparent electrodes (TE) in different applications also functioning as replacement of the tin oxide doped with Indium (ITO) because of toxicity and high cost. TCOs should possess low resistivity ($<1\text{x}10^{-3}\Omega$cm) and transparency at the visible region of the electromagnetic spectrum, greater than 80% of transmittance because they are used in different applications where the quantity of passing light has to be maximum. Doping ZnO with different elements (such as Al, Cu, Ti, Ga and In), grants the material superior properties than ZnO by itself. Most of the TCO are deposited as thin-films through different techniques such as: Pulsing laser deposition (PLD), Magnetron Sputtering (RF and DC (pulsed)), chemical vapor deposition (CVD), etc. In the following work, the deposition of the films was made employing Sputtering with a DC source, implementing a variation in the Oxygen partial pressure (PpO_2).

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CO sensors based on nanostructured SnO_2 thick films

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There is a current need for high sensitivity sensors at room temperature for toxic gases as CO. However, besides detecting the ability to detect low concentrations of CO there is also a current need for CO sensors to monitor the efficiency of gas combustion, for example in boil heaters. For these purposes CO concentration and working temperature are higher than in the former case. Tin oxide (SnO_2), due to its semiconductor behaviour with high chemical stability and good optical and electric properties, has been used for various devices among them gas sensors, and in particular CO gas sensors [1]. It is also known that the performance of a gas sensor is dependent of the morphology and microstructure of the sensing material. In adition enhanced sensing properties are expected from nanostructures due to their high surface area and energy and ability to be locally functionalised. Hence nanostructures are currently considered very promising for applications in gas sensors [2]. Within a project on going with BOSCH Thermoelectrics, in this work we are exploiting CO sensing properties of SnO_2 thick films prepared from two different nanostructures, nanoparticles and nanorods. SnO_2 nanopowders were synthesised by hydrothermal synthesis and the films were produced by electrophoretic deposition (EPD). The gas sensing behaviour was studied for concentrations of CO in the range of 2000 and 5000 ppm, and with operating temperatures of 150 °C. The sensor sensitivity ηs, calculated as ηs = (sensor resistivity in air) / (sensor resistivity in CO), is ~11.2 and ~2.5 for SnO_2 nanoparticles films for [CO] = 2000 ppm and for [CO] = 5000, respectively, at 150 ºC. Similar values have been reported in the literature and for lower CO concentration but for higher temperatures (T = 250 ºC [3]). Our results show a lower response time for the higher CO concentrations.

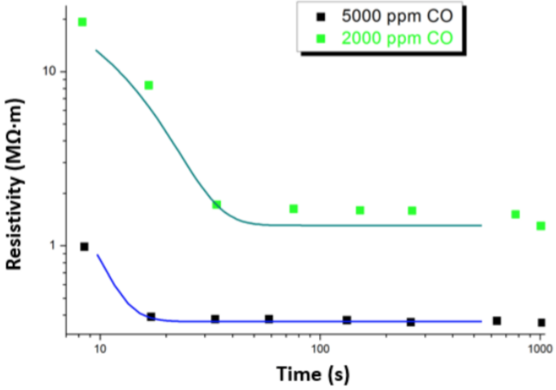

Figure 1: Gas sensing behavior of SnO_2 nanoparticles thick film for [CO] of 2000 and 5000 ppm at 150 °C and using a frequency of 68kHz.

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Relaxor to ferroelectric phase transition in $0.83PbMg_{1/3}Nb_{2/3}O_3$-$0.17PbTiO_3$ single crystal

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Lead based relaxor ferroelectrics are technologically important materials. The compositions consisting of canonical relaxor and normal ferroelectric exhibit morphotropic phase boundary (MPB). The compositions in the vicinity of MPB show superior piezoelectric and dielectric properties.

One of the most popular system is lead magnesium niobate – lead titanate ($PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ – PMN-PT) which besides excellent properties show very interesting crossover from purely relaxor behaviour to normal ferroelectric. The intermediary compositions have a spontaneous 1st order phase transition from relaxor to normal ferroelectric phase. These phase transitions are very interesting from the point of view of lattice dynamics.

This work is devoted to the study of dielectric properties of PMN-17PT single crystals in a broad frequency (20 Hz – 120 GHz) and temperature (100 ¬ 500 K) interval. These studies allowed us to thoroughly investigate the dynamics of this peculiar relaxor to ferroelectric phase transitions.

The 1st order phase transition was detected by the dielectric spectroscopy. It will be shown that PMN-17PT single crystal has a broad relaxor-like dispersion above 1 MHz frequency. The dielectric spectra were described by the empirical formulas and the temperature dependence of mean relaxation time was extracted from the approximations.

The thorough studies of temperature and frequency dependences revealed interesting features about dipole dynamics in PMN-17PT. The main scope of this work is to present the dynamics of this phase transition and reveal some controversies which were observed.

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Structural and magnetic characterization of nickel ferrite/zinc ferrite nanocomposites

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Several different nickel ferrite/zinc ferrite nanocomposites with core/shell structure have been synthesized by combining hydrothermal and co-precipitation methods. As-obtained and calcined nanopowders were characterized using XRD, TEM, Raman spectroscopy and VSM to elucidate their structural and magnetic properties. It is found that the synthesis procedure has a moderate impact on structural characteristics of as-synthesized powders both for pure nickel ferrite and for the composite. On the other hand, magnetic properties are drastically changed by addition of zinc ferrite layer on to the nickel ferrite core. By appropriate addition of zinc ferrite shell, the shape of VSM hysteresis is changed and saturation magnetization is increased. This indicates that the obtained core/shell nanocomposites are superparamagnetic.

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Microstructure studies of hot pressed ($K_{0.5}$ $Na_{0.5}$) NbO_3 samples

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Piezoelectric ceramics are technologically very important materials with applications in actuators, sensors, as components in microelectronics and biomedical devices; they are also used in transducers for ultrasonic imaging, positioning and energy harvesting [1-3]. For past few decades, materials based on lead (PZT) are used as building blocks in piezoelectric devices due to their excellent properties. However, lead is very well known as hazardous material for humans and environment, and recycling it is a tedious and expensive process, so it is of great concern. Therefore, scientific community is searching for a replacement of lead based piezoelectric materials by other environment friendly materials. Bismuth Sodium Titanate- Barium Titanate (BST-BT) and Potassium- Sodium based Niobates (KNN) are considered as potential candidates due to their competent piezoelectric properties. KNN has a perovskite structure and is one of the most promising lead free ferroelectric systems, with higher Curie temperature than PZT, and piezoelectric properties matching the order of magnitude of those of PZT. This makes it a highly sought material with applications in industry. Besides, KNN is highly chemically inert to human tissue, making it suitable for medical applications, and has other advantages over PZT, as the compositional independent morphotropic phase boundaries, MPB (between ferroelectric phases at ~200^{o}C and between ferroelectric and paraelectric phases at 400^{o}C).

There exist practical difficulties to produce high dense KNN materials with reproducible electrical properties through conventional solid state processing methods, because of the highly volatile nature of its alkaline constituents, compositional segregation and narrow sintering temperature range [4]. In this work, we prepared high dense ($K_{0.5}$ $Na_{0.5}$)NbO_3 samples using hot pressing technique and these samples were analyzed using SEM, TEM and impedance spectroscopy. The microstructure studies using SEM reveal that the sintering temperature influences the grain size distribution and the TEM analysis shows that hot pressing has created defects in ($K_{0.5}$ $Na_{0.5}$)NbO_3 which reflex on the electrical properties.

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Synthesis of Fayalite Fe_2SiO_4 as a Tar Removal Catalyst for Biomass Gasification

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The formation of tar is one of the main obstacles to gasification of biomass and recovery of the resulting gas commodities. Therefore, different catalysts have been proposed to promote the elimination of condensable organic compounds, including their reforming, with emphasis on catalysts based on Ni (Ni/Al_2O_3, Ni/$MgAl_2O_4$, ...) and low cost natural minerals such as olivines, (Fe,Mg)2SiO4 [1]. However, the mechanisms and influencing factors (compositional effects, thermal pre-treatments and their structural and microstructural effects) are still poorly understood [2].
The present work is focused on the development of a procedure for preparation of synthetic fayalite Fe_2SiO_4, the iron-rich end-member of the olivine solid-solution series, with intention of subsequent catalytic studies of conversion of tar, resulting from biomass gasification, in a pilot scale reactor.
Thermodynamic predictions were performed as guidelines for required conditions to promote formation of Fe_2SiO_4 and to minimize onset of secondary phases. Thermodynamic modelling was also used to assess prospects to utilize suitable gas redox pairs (H_2O/H_2 or CO_2/CO) to meet the required redox conditions.
Silicon carbide, hematite and iron nitrate were employed as starting reagent for synthetic procedure. In agreement with thermodynamic predictions, high-energy (600 rpm) milling of $SiC+Fe_2O_3$ or $SiC+Fe_2O_3+Fe(NO_3)_3$ did not result in formation of desired products. Further efforts were focused on thermal treatments of stoichiometric mixture of reagents, $Fe_2O_3:SiC = 1:1$, in controlled atmospheres at 1000-1100°C. Treatments in dry and humidified inert gas yielded phase mixtures containing metallic iron as one of the main phases, thus emphasizing a shortage of oxygen supply.
Thermogravimetric studies of precursors mixture on heating in dry CO_2 demonstrated multistep mechanism of overall reaction including (i) fast reaction between silicon carbide and hematite at ~920°C with substantial weight losses (due to release of gaseous products) and formation of metallic Fe. This is followed by (ii) formation of fayalite involving oxygen suppled in the form of CO_2 and competing with (iii) oxidation of iron to thermodynamically favorable magnetite. Comparative studies of reactivity in powdered and pelletized samples emphasized the importance of kinetic factor in formation of Fe2SiO4 while preventing further oxidation to Fe_3O_4 and SiO_2. Finally, the procedure was designed (2-step heating to 1100°C followed by fast cooling) for preparation of pelletized phase-pure fayalite catalyst.

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Printable cellulose-based sensors for paper electronics

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Conductive flexible hydrogel composites were printed on paper substrates using a functional ink designed and formulated for screen-printing (Fig. 1). The inks were prepared using abundant and eco-friendly materials by blending carbon fibers (CFs) into the matrix of a water-soluble cellulose derivative, carboxymethyl cellulose (CMC). For an optimal concentration of CFs (10 wt.%), the printed patterns exhibit a sheet resistance of around 300 Ω/sq without any post-printing annealing process. The resistance of the screen-printed hydrogel patterns is sensitive to variations on relative air humidity (RH%) through moisture adsorption and swelling of the cellulosic matrix surrounding the CFs. It was found that the sensitivity to temperature and humidity can be triggered by drying the printed patterns at 120 ºC (Fig. 2). A negative temperature coefficient thermistor with a sensitivity of 0.079 ºC^{-1} at 25 ºC and a hygristor, where a variation in the RH from 10 to 60 % increases the resistance by 15 times, were screen-printed on paper substrates using the formulated CMC/CFs based ink.

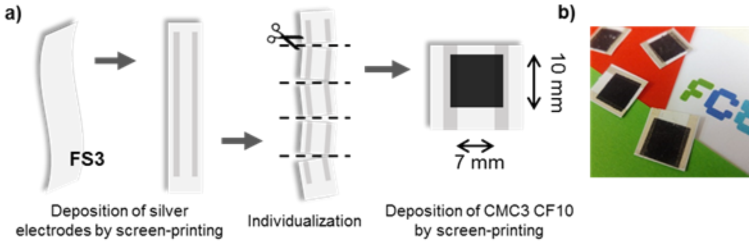

Fig. 1 – (a) Fabrication of fully printed sensors on paper; (b) Photo of the sensors.

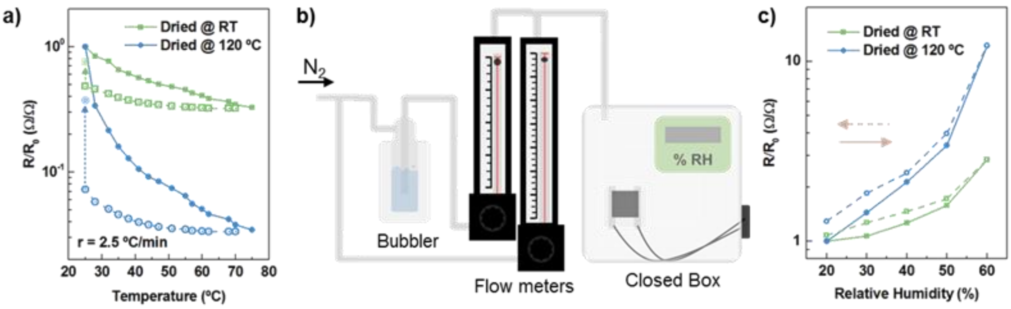

Fig. 2 – (a) Sensor response to temperature (b) schematic representation of the environmental chamber and (c) response to relative humidity (RH%) variation.

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Characterization of PVDF-Cu/Ni nanocomposites obtained via immersion precipitation

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Polymer nanocomposites with high dielectric constant and high thermal conductivity are highly attractive for use in various branches of applications such as electromagnetic shielding, electric stress control and higher storage capability of the electric energy. In this study, polyvinylidene fluoride (PVDF) films were prepared via an isothermal immersion precipitation method using water as antisolvent. Further, PVDF nanocomposites films containing copper and nickel as nanofillers were also prepared using the same method. The effects of the type and content of the nanofillers on the crystallization behaviour of PVDF were investigated. Thus the structure and microstructure of the prepared nanocomposites were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction techniques (XRD), Raman spectroscopy, Scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). The thermal and electrical behaviour were also studied. PVDF films exhibit a spherulitic crystal structure with the predominance of ß and γ phases. The spherulitic morphology of PVDF films is maintained in the PVDF nanocomposites but the degree of crystallinity and phase composition, namely the ratio of β to γ-phase, is affected by the addition of the nanofillers. The effect of the nanofillers on the thermal and electrical behaviour is also addressed.

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Evaluating the surface interaction of nanoplasmonic thin films with *Candida albicans*

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DC sputtered thin films, composed of noble metal nanoparticles (e.g. Au and Ag) dispersed in a dielectric matrix, exhibit specific optical properties, related to the distribution of these nanoparticles in the matrix. The Localized Surface Plasmon Resonance (LSPR) is unique for these plasmonic nanocomposites and the characteristics of the absorption bands can be tuned by the size, shape and distribution of the metal nanoparticles, as well as by the dielectric medium in which they are dispersed. To promote the growth and coalescence of nanoparticles, and microstructural changes in the dielectric matrix, a post-deposition thermal treatment is employed, resulting in changes of the LSPR absorption band.

The properties of nanoplasmonic thin films are considered promising for applications in sensing technology, namely in LSPR-(bio)sensors, where shifts in the plasmon peak are measured when molecules or biological agents, like macromolecules or even microorganisms, are present.

However, the structural modifications caused by the annealing also rule the overall biological response of the thin films. It has been demonstrated that Au/TiO_2 thin films induce significant alterations to cell membrane integrity of *Candida albicans*, reducing its cell viability.

In order to ascertain possibility of applying these thin films in biosensing platforms for the detection of microorganisms, it became necessary to first study their interaction with the plasmonic thin films. For this study, sets of Au/TiO_2, Au/Al_2O_3 and Ag/TiO_2 nanoplasmonic thin films were deposited by reactive DC magnetron sputtering. Their microstructure was modified, to obtain a LSPR band, using different annealing temperatures and these alterations were characterized. Afterwards, it was studied the growth of *C. albicans* in liquid culture, in direct contact with the films' surface, which allowed to correlate their structural properties with the biological response of the yeast to the presence of the thin film.

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Growth and structure of high Curie temperature ferroelectric crystals

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A detailed growth and structural study of perovskite systems $xBiInO_3$ - $(1\text{-}x)PbTiO_3$ single crystals with a high Cuire temperature around 555 °C were performed. We have undertaken the x-ray diffraction (XRD) study at different temperatures to obtain direct structural information about the phase transition from the ferroelectric to the paraelectric phase. With the help of differential scanning calorimetry (DSC) measurement, it showed “temperature hysteresis”, implying that the transition is of first order, with a coexistence of paraelectric and ferroelectric phases in a range of temperatures. Fourier transform infrared (FTIR) spectroscopy was used to characterize the lattice vibrational modes. Scanning electron microscopy (SEM) was used to observe the morphology of the grown crystals. The XRD rocking curves was used to study the crystal quality.

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Magnetic properties of Sodium Ferrite obtained by solid state reaction

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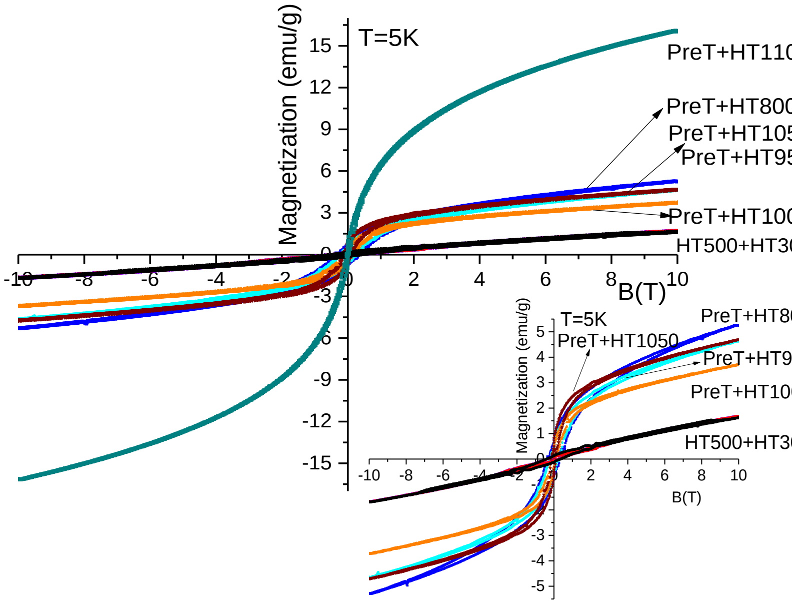
Ferrites are ceramic oxides which have been widely studied due to its interesting magnetic properties. Although ferrites can be obtained with several crystal structures the spinel is the most studied one. These materials are soft magnets with high resistivity and low coercivity leading to industrial applications in electronic and microwave devices, satellite communications, transformers and digital recorders.

Sodium ferrite exhibits remarkable magnetic properties and it is a potential candidate for these applications. This was firstly studied in the 1950s but has not in detail.

In this work, sodium ferrite ($NaFEO_2$) powders were synthetized using sodium acetate and iron nitrate as raw materials by solid state method and then heat treated between 300 and 1100 ºC, for 4 h.

X-ray diffraction was used to characterize the structure and scanning electron microscopy to analyze the morphology. For treatment temperatures below 800 ºC, Fe_2O_3, Na_2FeO_4 and $Na_2CO_3.H_2O$ crystal phases were predominant. For higher temperatures as the sodium carbonate phase was present with β-$NaFeO_2$, an extra pre-treatment (PreT) was performed (600 ºC, 12 h) and β-$NaFeO_2$ become the single phase.

The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM). The dc magnetic susceptibility was measured from 5 K to 300 K, cooling the sample under two regimes: in zero field (ZFC) and with the magnetic field applied (FC). Typical hysteresis curves were obtained at several temperatures. The magnetic results were related with the structure of the crystal phases.



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Highly Efficient Luminescent Lanthanide Complex-based Di-ureasils Derived from In-situ Sol-gel Process

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The photoluminescence properties of lanthanide trivalent cations (Ln^{3+}) such as Eu^{3+} and Tb^{3+} are always research focus due to the special f^n electron configuration shielded by out s and p orbital electrons. Therefore, the luminescence properties of Ln^{3+} possesses some peculiar characteristics, e.g. large stokes shift, long lifetime and line-like emission bands in visible region. However, the transition between states of f^n configuration is strictly parity forbidden leading to low UV-visible light excitation probability. Fortunately, when the suitable organic groups coordinate with Ln^{3+} ion center, the lanthanide complex can have large luminescence efficiency. Comparing with conventional silica gel hosts, the organic-inorganic hybrids have mechanical stability with certain flexibility. Simultaneously, the amorphous and transparent organic-inorganic hybrid can create a comfortable environment for improving complex thermal, chemical and photo stabilities.The carboxylates lanthanide complex has gradually demonstrated the researching value in this field.

In this work, the Eu complexes with 4,4-oxybis(benzoic acid) (Oba) and 1,10-phenanthroline (Phen) as "antenna ligands" were successfully in-situ synthesized in di-ureasil (d-U(600)) processing at ambient environment without heating and high-pressure requirements. The samples were prepared by doping 6 mol% of Eu(Oba)x(Phen)y (x=1,2,3 and y=1,1.5) into d-U(600) hybrids. The obtained hybrids with lanthanide complex were structurally characterized by Infrared spectra, X-ray diffraction patterns, NMR and TG analysis. The photoluminescence properties of synthesized materials were also studied throughly, and the results show that the luminescent hybrid materials are highly efficient with 47–50% of quantum efficiency and 32–46% of quantum yield.

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BCZT-ferrite composites, effect of magnetostriction of the magnetic phase on the magnetoelectric effect

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We report the influence of the magnetic phase on the magnetoelectric response of particulate magnetoelectric composites. The composites constituted by (Ba, Ca)(Zr. Ti)O_3 (BCZT) as piezoelectric phase and $CoFe_2O_4$ (CFO) or $NiFe_2O_4$ (NFO) as magnetic phases and were prepared through the conventional solid state method in the 50/50 volume ratio. The phase and crystalline quality has been verified with the help of –ray diffraction while surface morphology with the help of scanning electron microscopy. Piezoforce response microscopy (PFM) has been utilized for microscopic piezoelectricity while local magnetism through magneto-force microscopy. We demonstrate that the increase in the magnetic coercive field for composites composed BCZT-CFO in comparison to the BCZT-NFO. The value of magnetic coercive field for CFO based composite is 200 Oe while that for NFO based composite is 120 Oe. Also, the ME properties has been attributed to the mechanically mediated effect, in which the ME values are strongly dependent to the piezoelectric and elastic properties of the ferroelectric phases and the maximization of ME coefficient was obtained when ferromagnetic phase has the higher piezomagnetic coefficient. It is worth mentioning here that maximum ME for BCZT-NFO is 4 mV/Oe·cm while for that of BCZT-CFO is around 1 mV/Oe.cm for the same volume content of ferrite phases.

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Luminescencent properties of Alexandrite ($BeAl_2O_4$:Cr^{3+}) - brazilian mineral.

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Alexandrite is a variety of chrysoberyl crystal that contains chromium: $BeAl_2O_4$: Cr^{3+}, and rare and precious mineral that changes color according to the light incident on it. Moreover, in the synthetic form it is used technologically as active medium for laser with properties superior to its main competitors, ruby and Nd: YAG. The investigation of optical properties of this material in synthetic and natural form is presented in this work. Data are obtained through the techniques of Optical Absorption (OA), Photoluminescence (PL), Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL). In order to investigate optical properties of alexandrite, the present work deals with the influence of thermal annealing on optical absorption and luminescence spectra of natural samples. This feature may be used to control the optical properties of natural alexandrite, which can be associated to the observed laser emission effect. Results of photoluminescence measurements for natural and synthetic alexandrite are presented, where the samples are excited by the 488 nm line of an Ar^+ laser, at different temperatures. Results indicate anomalous behavior of Cr^{3+} transition depending on the measurement temperature. A simple model to explain the phenomena is suggested. In addition, thermoluminescence investigations of natural alexandrite are performed to understand the effects of ionizing radiation and heat treatment on these crystals. OSL measurements were also carried out to complement the characterization of TL through the studies of the traps for optical stimulation. Luminescence was stimulated with blue LEDs (470 nm) provided by an automatic reader. Irradiation was performed with a $^{90}Sr/^{90}Y$ beta source, and the emitted light was measured with a photomultiplier tube, protected with suitable optical filters. Measurements were performed with the same equipment, Risø TL/OSL-DA-15 reader, to evaluate the thermal and optical stability of the defects related to OSL and TL. Preliminary measurements show that alexandrite samples from the same block of mineral exhibit TL peaks at the same temperatures, and that grow with the radiation dose. Probably Cr^{3+} ions have an important part in the process.

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Dielectric Properties of $Ba_{1-x}Bi_xTi_{1-x}(Mg_{2/3}Nb_{1/3})_xO_3$ ceramics

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Capacitors are the most widely used components in modern electronic devices. Large number of MLCCs (multi-layer ceramic capacitors) are manufactured annually. For these applications, $BaTiO_3$ is the base material for MLCCs, also referred to as the cornerstone of the electroceramic market [1]. In the present study, $Ba_{1-x}Bi_xTi_{1-x}(Mg_{2/3}Nb_{1/3})_xO_3$ (x = 0-0.6) were processed through conventional solid state route. The XRD patterns at $x = 0$ (i.e. $BaTiO_3$) showed tetragonal ($P4mm$) $BaTiO_3$ phase. However, at $x \geq 0.05$, the formation of pseudo-cubic or cubic structures was observed. No secondary phase was observed within the detection limit of the in-house XRD facility. According to the principles of crystal chemistry and ion radii rule, Bi^{3+} is expected to sit on A-site with Ba^{2+} and ($Mg^{2+}Nb^{5+}$) will occupy the B-site with Ti^{4+} of the host lattice (equation 1).

$$\mathrm{Bi(Mg_{2/3}Nb_{1/3})O_3} \xrightarrow{\text{in BaTiO}_3\text{ matrix}} \mathrm{Bi}^{\bullet}_{\mathrm{Ba}} + 3^{\mathrm{x}}_{\mathrm{O}} + 2/3\mathrm{Mg}''_{\mathrm{Ti}} + 1/3\mathrm{Nb}^{\bullet}_{\mathrm{Ti}} \rightarrow (1)$$

Temperature dependence of relative permittivity and dielectric loss for samples with $0.4 \leq x \leq 0.6$ showed a temperature independent plateau in permittivity (□$_r$). The sample $x = 0$, revealed a sharp T_c (Curie point) near ~126°C. The peak broadening increased with increase in x from 0.05 to 0.1 along with a shift in T_c to below room temperature. Long range temperature stable dielectric properties were observed for sample $x = 0.5$ which exhibited □$_r$ ~ 940±15% (~ 34-550°C) with a loss tangent < 0.025 (74-455°C).

Impedance spectroscopy of the samples was carried out to investigate the electrical microstructure of ceramics [2]. Activation energies of the samples were calculated from the slope of log(□ versus 1000/T (Arrhenius plot). Some samples showed that oxygen ion conduction take place while for large values of x, an intrinsic conduction mechanism was observed, based on impedance spectroscopy. The dielectric characteristics of the samples ($0.4 \leq x \leq 0.6$) indicates that these materials could be ideal base materials for high temperature ceramic capacitors [3] due to their high dielectric stability over a wide temperature range.

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Dielectric properties of Ni-Doped Barium Hexagonal Ferrites ($BaFe_{12}O_{19}$)

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Hexagonal ferrites (hexaferrites) have gained tremendous attention both technologically and commercially owing to their variety of applications including magnetic recording, ferrite cores and sensors, permanent magnets for power generation, loud speakers and small DC motors, microwave absorbers for microwave darkrooms and anti-electromagnetic interference coatings and in the fabrication of transistors, switch mode supplies and capacitors. Magnetic properties of BaM like saturation magnetization, remanent magnetization and coercivity can be modified/improved by several means including the substitution of Fe^{3+} ions at crystallographic positions, using different synthesis route and by altering grain size and grain morphology. An organized study of high-temperature dielectric properties and practice of CIS is still infrequent for BaM ceramics. Electrical properties are influenced by structural inhomogeneities like grain boundaries, grain, oxygen vacancies, and alkaline vacancies in materials. Since polycrystalline ceramics are processed at high temperatures, these defects are unavoidable. These defects can affect the electrical properties of BaM by interacting with domains and domain walls. By understanding the character and etiquettes of these defects, electrical characteristics of BaM ceramics can be tailored In the present study, the effect of Ni^{2+} on the structural and electrical properties of bulk and nanocrystalline BaM has been studied. Bulk and nanocrystalline BaM ceramics with the composition $BaFe_{12-x}Ni_xO_{19}$ were synthesized by conventional solid state and solgel method respectively. Samples were characterized using x-ray diffraction (XRD) and their electrical properties were measured using precision impedance analyzer.

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Mesoporous silica nanoparticles diameter and morphology control through template supramolecular assembly

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Mesoporous silica nanoparticles (MSNs) have received considerable attention due to their excellent biocompatibility, high surface areas, large pore volumes, high loading capacity, uniform and tunable pore sizes, and versatile surface functionalization.[1]

The most common processes to synthesize MSNs use either ammonium bases and co-solvents, or hydroxide base in aqueous media, leading to diameters that are usually larger than 100 nm.[2] For MSNs with diameter under 100 nm, only a few works can be found, usually by changing the silica source/surfactant ratio, temperature, or by introducing silicate hydrolysis retardant agents – essentially with a low degree of control over the properties of the obtained MSNs.[2]

Here we developed a new exclusively aqueous method for the preparation of MSNs with controllable sizes under 100 nm, with low size dispersity, through the fine control of the aggregation number of the supramolecular assembly of the template cylindrical micelles.[3,4,5] The synthesis is performed using a sol-gel method, in an aqueous medium, with TEOS as silica source, a cationic surfactant as template, without ammonium bases or co-solvents, at constant temperature. We are able to control the particle diameters from 15 to 80 nm with low size dispersity, by varying the pH and/or the ionic strength. The MSN diameters obtained are directly proportional to the increase of the pH and/or ionic strength, due to the neutralization of the micelle surface charges from the charge screening process. This leads to a reduction of the colloidal stability of the individual cylindrical micelle and consequent aggregation to reduce the interaction with water, increasing the supramolecular aggregation number. Additionally, the morphology (spheres vs. rods) of the particles is tuned by varying the reaction temperature or the pH. These new methods open a new path for the use of MSNs.

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Stimuli-Responsive Hybrid Nanoparticles for Smart Delivery

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Mesoporous silica nanoparticles (MSNs) are excellent nanocarriers, featuring very high cargo capacity because of their large surface areas and pore volumes. Their size and pore dimensions can be accurately tuned, and they allow versatile functionalization.[1] By incorporating fluorescent molecules into their inorganic network, we obtain MSNs with excellent optical properties for imaging or sensing, since a large amount of dyes can be incorporated with no self-quenching effects.[2,3] The external particle surface can be further selectively modified with biomolecules for targeting, such as folate,[4] and stimuli-responsive polymers for delivery control.[5]

By combining controlled delivery and traceability functionalities (a large cargo capacity, fluorescent beacons for imaging, a smart release control mechanism and targeting capabilities), these hybrid MSNs provide an ideal vehicle for delivery on demand, to a desired location.

In this communication we will show how a temperature-responsive polymer shell can act as a precise gate keeper to control cargo release from the MSN pore system. The polymer shell was obtained by RAFT, offering low size dispersity and well-defined end-groups for convenient anchorage to the nanoparticles. Controlled release of the cargo was achieved by a “pumping” mechanism: below a critical transition temperature the polymer shell is hydrophilic and expanded opposing cargo diffusion out of the shell, but above this temperature the polymer network becomes more hydrophobic and collapses onto the silica surface, “squeezing out” the cargo.

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Effect of subgrain textures on magnetic anisotropy of (Co,Ni)O/soft magnetic alloy bilayers and multilayers

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Coupling of magnetic moments across the interfaces between ferromagnetic ordered (FM) and antiferromagnetic ordered (AFM) lattices yield anisotropy to magnetization/magnetic field hysteresis cycles where the difference of coercivity field on decreasing and increasing the magnetic field sets the value of the exchange bias magnetic field, H_{EB}. The theory of interface mediated exchange bias has produced sound interpretations for major dependences of H_{EB} early reported in the CoO/Co core-shell particles and extensively studied latter, namely in the CoO/permalloy and $Ni_{0.5}Co_{0.5}O$/permalloy multilayer systems. Main outcomes from models and recent refining in the analysis of exchange bias are re-accessed in short. The observation that field cooled (FC) magnetic susceptibility of AFM hexagonal RMnO3 multiferroic materials showed the main features observed in the temperature dependence of thermoremanent moment (T_{RM}) and (H_{EB}) of (Co,Ni)O/permalloy bilayers and multilayers enlarged the interest of studies of H_{EB} to the multiferroics. In the present topic review the complexity of AFM/FM interfaces emerged as the major limit to the understanding of (T_{RM}) and (H_{EB}) properties and in giving expression to their dependence on uncompensated spin (UCS) density. Approaches that introduce particle size effects on spin-flop coupling are discussed. The effect crystallite sizes on USC density in the AFM surface has been described by interfacial spin models giving no clue or details on the contribute of subgrain boundaries. It is established here by the analysis of dependences (H_{EB}), subgrain size, texture and film surface roughness on layer thickness that both T_{RM} and H_{EB} are interface properties. The boundaries of columnar sub-grains of AFM layers work as nucleating points for spin orientation transition and set the dimensional scale of the energy barrier for magnetization reversals. Differences in the dependence of T_{RM} and H_{EB} on subgrain sizes of the AFM layer remain subtle, only H_{EB} showing a definitive link to the dimension scale of the traces of columnar subgrain boundaries in the AFM/FM interface. Such association between H_{EB} and the scale of subgrain imparts a specific and unique role to the subgrain boundaries. Grain boundaries as may happen with other defects being places where the AFM exchange can be partly frustrated, the interaction with the FM layer can stabilize one specific spin configuration resulting in exchange bias.

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The electrical properties of Au/ZnPc/p-Si/Al and Au/AlPc/p-Si/Al organic heterostructures for solar cell applications

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The electrical properties of Au/ZnPc/p-Si/Al and Au/AlPc/p-Si/Al organic heterostructures in dark condition are investigated. For this purpose, we measure the current-voltage (I-V) characteristics at room temperature under dark conditions for both organic zinc and aluminum phthalocyanine materials. The electronic parameters of the organic heterojunctions under dark including ideality factor n, barrier height (Φ_b), series resistance (R_S) are extracted using the Cheung-Ceung and Norde methods respectively. These parameters are found to be 4.9 and 2.3, 0.69 eV and 0.74 eV, 8 kΩ and 10 kΩ respectively for ZnPc/p-Si and AlPc/pSi contacts.

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Synthesis by sol-gel of pure and alumina doped nano crystalline powders of zinc oxide. Structural and optical properties study

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Pure and alumina doped nano crystalline powders of zinc oxide were synthesized by a simple and inexpensive method of sol-gel type with the atomic concentration of aluminum ([Al]/ [Zn]) being between 0.1 and 20 percent.
The structural and optical properties of the synthesized powders were analyzed by X-ray diffraction, Infra red absorption and S.E.M observation.
For the zinc oxide powders doped with alumina, a decrease in the size of crystallites is observed. This effect is noticeable especially in the case of doping at 750 °C compared to powders doped at 450°C.
We have observed a new phase attributed to the spinel $ZnAl_2O_4$ which appears at high doping concentration as three specific peaks in the X-ray diffraction spectra.
Similar results were obtained in the infra red absorption spectra.
The results are discussed in light of a specific growth model of alumina doped ZnO crystal.

Key words: ZnO, Al_20_3, DRX, Infra Red, Sol-gel, SEM, $ZnAl_2O_4$, nano composite ZnO/PMMA.

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Structural effects on the optical properties of zinc blende cubic from hexagonal wurzite prepared by the modified colloidal method

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In this work we present the structural transformation of zinc blende cubic (ZnO_2) from hexagonal wurzite structure (ZnO) and their effects on the optical properties. Derived from ultraviolet-visible spectroscopy and the photoluminescence spectroscopy. The ZnO and ZnO_2 were prepared by the modified colloidal method using low temperatures with a simple variation of the dispersing medium, for ZnO was used ethanol and methanol was used for ZnO_2 these materials were characterized by X-ray diffraction patterns (XRD) and the Rietveld refinement analysis using Fullprof were performed in order to confirm the crystal structure, Raman and UV-Vis spectroscopy. For ZnO_2, XRD results suggest a cubic symmetry with Pa-3 space group, in comparison with ZnO that shows a hexagonal symmetry with P63mc space group. Raman spectroscopy confirms the XRD results for each structure. Fourier electron density contour maps were obtained in order to elucidate the bond type. ZnO_2 shows a covalent character in comparison with ZnO that shows an ionic character. The particle size and shape distribution was monitored by transmission electron microscopy and the size is analyzed for Scherrer equation too. The optical band gap energy E_g is determine by reflectance diffuse ultraviolet-visible spectroscopy, this results shows for ZnO_2 ~4.5 eV and for ZnO was around 3.3 eV. The thermogravimetric analysis shows the evolution of ZnO_2 to ZnO, transformation occurs around 150°C. Violet (350 nm) high intensity was observed by Photoluminescence (PL) for ZnO2 in comparison with blue (450 nm) intense emission for ZnO. Our results suggest that both compositions show the presence of quantum confinement by the particle size reduction and blue shift present in the UV-Vis and FL spectrum. These results open the possibility to apply these materials in photovoltaic or optoelectronic applications.

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Red / NIR emission of $ZnGa_2O_4$:Cr^{3+} nanoparticles produced by pulsed laser ablation in water for bio applications

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Imaging techniques are present in everyday diagnosis and study of biological processes. The spectroscopic methods, such as fluorescence, are some of the most promising for bioimaging. The most common luminescent biological markers used nowadays are the ones based in Stokes emission process in which ultraviolet (UV)/ visible excitation is needed, such as organic dyes or lanthanide chelates. However, besides the low chemical, thermal and photostability associated to these materials, their excitation in the UV region presents also a limitation for *in vivo* analysis. Excitation *in vivo* with UV light is commonly associated with low penetration depth, autofluorescence and damages of biological tissues. Persistent luminescent nanoparticles (NPs) that can be excited before their incorporation in biological systems emerge as viable alternatives to overcome these problems, allowing increased sensitivity in the detection. A material that has appropriate optical properties for this purpose is zinc gallate, $ZnGa_2O_4$, doped with trivalent chromium, Cr^{3+}. The reported persistent luminescence of this material in the spectral region of red/near infrared, within the optical biological window, is of particular interest for biological imaging. In this sense several physical and chemical techniques have been explored for the production of this material at the nanoscale.

In this work, the pulsed laser ablation technique in liquid (PLAL) was successfully used as an alternative technique for the production of $ZnGa_2O_4$:Cr^{3+} nanoparticles. Comparatively to the most common chemical routes PLAL allows the fast production of high purity NPs, using a simple setup. For the ablation, $ZnGa_2O_4$:Cr^{3+} pellets produced by solid state reaction, used as targets, were immersed in distilled water.

Nanoparticles present the same crystalline phases as the precursor targets with a majority phase of cubic zinc gallate, in the form of polyhedral particles as well as reduced size nanoparticles, and a minority phase of β-gallium oxide in the form of needles.

The luminescence study revealed similar behaviour in nanoparticles and targets with an intense red emission, visible at room temperature and characteristic of the trivalent chromium, which is preferentially observed under ultraviolet excitation. Time resolved luminescence studies allowed to see that the luminescence persists for at least two hours and forty-four minutes after removing the excitation light. The results prove to be very promising for the application of the PLAL produced luminescent nanoparticles as biomarkers. Furthermore, a red shift of the emission lines with increasing temperature offers the possibility to use these nanoparticles in thermometers, allowing monitoring the temperature at cellular scale and showing the potential of these nanoparticles multifunctionality.

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Transparent Molybdenum Oxide Thin Films Obtained by Reactive Magnetron Sputtering

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In the last years, relevant investments have been done to promote the implementation of electrochromic (EC) materials in displays or light modulation systems. Transition metal oxides (TMOs) deposited in the form of a thin-film, are promising materials for this purpose. Among TMOs, molybdenum oxide (Mo_xO_y) presents unique combination of chemical and environmental stability along with very interesting electrical and optical properties, which potentiate their use for EC based devices. Mo_xO_y is already used in other applications such as gas sensors, capacitors, batteries, etc. The diversity of these applications can be attributed to the wide range of molybdenum oxidation states (+2, +3, +4, +5 or +6) and the easy manipulation of those states via oxidation or reduction processes. Of particular interest is the Mo_xO_y system for electrochromic applications where structure, electrical and optical performances play an important role.

In this work Mo_xO_y films were deposited by magnetron sputtering in a reactive environment at room temperature. Argon was the working gas introduced using a fixed flow, and the reactive gas was oxygen (O_2) with variable flows in order to prepare a set of films with different Mo oxidation states (from Mo-MoO_3). The resulting films were characterized by X-ray diffraction (XRD), energy dispersive X ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), profilometry, Raman, UV-VIS optical spectroscopy and electrical measurements.

It was found the existence of a structural threshold, from a crystalline to amorphous nature, between 8 and 16 sccm of oxygen flow. This structural modification is responsible for an opaque to transparent transition. Optical measurements showed transmission around 98% for the samples with oxygen flow higher than 14 sccm, which are fully stoichiometric MoO_3. All transparent films in the range of interest for application in EC materials present a thickness below 500 nm and a compact/dense and featureless morphology. The electrical resistivity of the films increases with the increase of oxygen flow, which is compatible with the transition from metallic to oxide films.

The overall set of characterization results for the Mo_xO_y films are promising, and currently the obtained films are being characterized from the electrochromic point of view: coloration efficiency and coloration/bleaching time.

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Laser Floating Zone synthesis and characterization of Erbium and Molybdenum co-doped Ytterbium Aluminum Garnet (YbAG:Er:Mo) for optical thermometry

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A kind of optical thermometry method is the fluorescence intensity ratio technique (FIR), based on the measurement of fluorescence intensities ratios from two thermally coupled excited levels that, being independent of spectrum losses and fluctuations in the excitation intensity, leads to a high accuracy of the material temperature measurement. Just some materials, mainly triply ionized RE ions imbibed in an appropriate host, obey the needed requirements to act as a thermal sensor being Erbium-doped ytterbium aluminum garnet (YbAG:Er) one of them [1]. However, up-conversion emission from YbAG:Er, when excited in the Near Infrared spectral Region (NIR), is not very efficient, so high intensity excitation is needed reducing the temperature range of applicability of this material as a FIR temperature sensor. To overcome this drawback YbAG:Er can be co-doped with transition metals in order to enhance the emission efficiency.

We report the synthesis of YbAG:Er and YbAG:Er:Mo fibers by the Laser Floating Zone (LFZ) grow technique. To the best of our knowledge this is the first work were LFZ grow of YbAG:Er:Mo has been achieved. The structure of the prepared materials was confirmed and characterized by X-ray powder diffraction (XRD), Raman spectroscopy and Surface Electron Microscopy (SEM/EDS). The relevant optical properties were characterized by reflectance and photoluminescence (PL). XRD results show that the fibers are single phase YbAG without other phases present. Raman spectroscopy corroborates these results. Room temperature PL results confirm the introduction of the $Er3+$ ion in the host lattice and its optical activation and the existence of up-conversion mechanisms with emission in the expected violet, green and red spectral range depending on the excitation power, when excited with a 980 nm diode laser. The co-doping with Mo result in an enhancement of the up-conversion efficiency and the temperature dependence of up conversion emission was studied under low power excitation revealing the good properties of the YbAG:Er:Mo as a temperature sensor material.

[1] Bin Dong, Baosheng Cao, Yangyang He, Zhuang Liu, Zhipeng Li, Zhiqing Feng, Adv. Mater. 2012, 24, 1987–1993.

Keyword(s): YbAG:Er:Mo, Laser Floating Zone, Up-conversion, FIR

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Adsorption of tannic acid on aluminum oxide (α-Al_2O_3) particles

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Colloidal processing is based on the manipulation of interparticle interactions in order to control the stability of suspensions. A stable suspension with well dispersed particles is only achieved when repulsive interparticle forces predominate. One way to provide such forces is through the use of organic compounds which work like surfactants. Currently, there is an effort to replace synthetic dispersants by natural ones obtained from renewable sources. Tannins are water-soluble, biomolecular polyphenolic compounds containing oxygenated functional groups and complex chemical structures. Tannic acid (TA), one of the hydrolysable tannins best known, is generated by organic matter into soils and can be found in surface and groundwater. Aluminum oxide is considered a model surface for metallic oxides and its reactivity is determined by the number and type of surface sites. Dissociative chemisorption of water on α-Al_2O_3 produce surface hydroxyls, which can be singly (Al-OH), doubly (Al_2OH) or triply (Al_3OH) coordinated. Adsorption of organic molecules on such sites can take place mainly through exchange reaction, hydrogen bond or electrostatic interactions. In this work adsorption of different contents of tannic acid (1701 g/mol) on α-Al_2O_3 particles (9,72 m²/g) has been performed. The experimental data from the TA interaction on α-Al_2O_3 particles surface follows the Sips and the Redlich-Petterson-type adsorption isotherm models. The maximum TA monolayer adsorption capacity of α-Al_2O_3 was 13 mg/g (6.5 µmol/m²) at 20 °C. According to the DRIFTS analyzes, irrespective of the adsorbed content, TA adsorption on α-Al_2O_3 particles surface preferentially took place on Al_3-OH hydroxyls through electrostatic interactions and hydrogen bonds with its phenolic groups.

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The electrical conductivity of $BiFeO_3$ nanocrystalline ceramics

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The results of $BiFeO_3$ ceramics electrical conductivity research obtained by the spark plasma sintering of nanopowders synthesized by the organic nitrate precursors combustion are presented. The original nanosized powder was calcined at the temperature of 600^0 C. The average size of particle estimated from the diffractograms are ~ 50 nm. The ac - conductivity measurements were conducted in 1kHz - 10 MHz frequency range over a temperature range of 25 - 500^0 C.

It is shown that $\sigma_{ac} (\omega)$ obeys a power law of ω^s, where s <1. At temperatures > 350^0 C and frequencies of > 1MHz conductivity passes through a maximum, and with increasing frequency the conductivity maximum temperature T* is shifted to lower temperatures. In the frequency range 1 - 10 MHz $\Delta T^* = 25^0$C, the average temperature T * ~ 480^0C.

The conductivity has the thermally activated character. In the investigated temperature range the three overlapping processes are involved in the relaxation conductivity: i) in the temperature range 25 - 150°C with Ea = 0.46 - 0.042 eV; ii) in a temperature range of 150 - 350^0C with E_a = 0,65-0,11eV and iii) at temperatures> 350^0C with E_a = 0,96 - 0,76 eV. The activation energy E_a decreases with increasing frequency.

The low-frequency conductivity is identified with the dc conductivity (σ_{dc}). At frequencies > 100 kHz conductivity behavior can be interpreted in the representation of the model correlated barrier hopping (CBH) charge carriers. It is assumed that the hopping mechanism implemented in ceramic grains between the ions Fe^{2+} and Fe^{3+}. The role of oxygen vacancies in the conductivity are also discussed.

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Study of the degradation of inorganic coatings by commercial detergents

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The application of coatings on various substrates for either decorative or functional purposes has been an area under constant evolution. Coatings such as TiCN and TiC can enhance the characteristics of the material on which they are deposited. However, when subjected to washing processes in dishwasher machines, degradation of the coating can occur.

In this study, simulations of a dishwasher washing were carried out, using the main components of two commercial detergents which have distinct effects on the degradation of the coating.

Electrical conductivity and pH of the solutions were analyzed over time to monitor degradation of the plates as well as visual inspections.

The coated plates were characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), complemented with the measurement of the CIELAB coordinates. Due to the higher porosity of the TiCN film, oxygen penetration is facilitated resulting in significant degradation of the coating [1], which can be observed in the figure 1. This effect is enhanced when a combination of the bleaching agent (H_2O_2) and an adjuvant agent ($Na_5P_3O_{10}$) is used, resulting in a decrease of 99% in the titanium content on the surface of the sample.

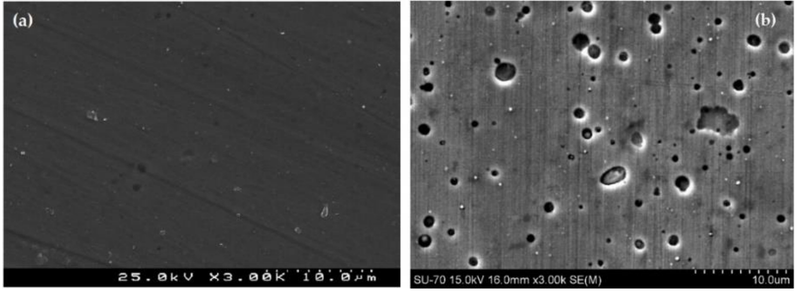

Figure 1. SEM analysis performed on plates coated with TiCN: untreated (a) and after washing with a combination of compounds present in the commercial detergent formulation (b).

From this work, the components of the commercials detergents responsible for the degradation of the coatings have been clearly identified. The results obtained showed that the impact of detergents on the TiCN film is much more extensive than on the TiC film. In order to achieve a chemical resistant coating, some modifications on the coating process should be made.

[1] Monteverde, F., Bellosi, A. Oxidation behavior of titanium carbonitride based materials. *Corros. Sci.* **44,** 1967–1982 (2002).

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Materials for energy, environment and sustainable materials (A3)

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Gd-doped $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$ mixed conducting materials: structural, thermal and electrical properties

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Doping and co-doping strategies of the basic material $SrTiO_3$ by different acceptor, isovalent or donor impurities allows one to vary widely its functional properties. In the present work, the influence of substitution of Gd for Sr in the concentration range of x = 0–0.4 on the structural, thermomechanical, electrical and electrochemical properties of $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$ was investigated.

Samples of $Sr_{1-x}Gd_xTi_{0.5}Fe_{0.5}O_{3-\delta}$ (x = 0–0.4) were synthesized by a solid state reaction method. According to XRD data the materials were single-phase at $0 \le x \le 0.15$, whereas an impurity pyrochlore-like phase was formed at a higher concentration of gadolinium. Conductivity of $Sr_{1-x}Gd_xTi_{0.5}Fe_{0.5}O_{3-\delta}$ decreased with increasing x. For example, the total conductivity of the samples with x = 0, 0.05, 0.1 and 0.15 was equal 0.476, 0.167, 0.107, 0.132 S cm^{-1} ($pO_2 = 10^{-16}$ atm, 900 °C), respectively. Regardless of the negative impact of donor doping on the electrical properties of $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$, the oxygen permeability of Gd-containing ceramic membranes reaches significantly high values which are comparable with those of some lanthanum nikelates or barium ferrites (Figure).

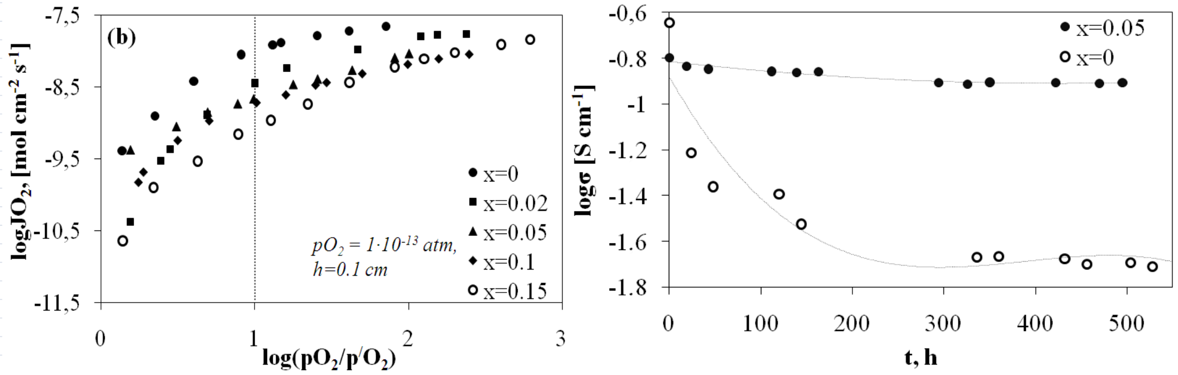

Figure: Oxygen permeability of $Sr_{1-x}Gd_xTi_{0.5}Fe_{0.5}O_{3-\delta}$ and conductivity long-term testing

Additionally, the introduction of gadolinium resulted in increased long-term stability of the materials. For Gd-free sample the conductivity drop was equal to one order of magnitude, however the conductivity of $Sr_{0.95}Gd_{0.05}Ti_{0.5}Fe_{0.5}O_{3-\delta}$ lowered by about 22% of its initial value. The Gd-doping significantly reduced the average TEC values in both low- and high- temperature intervals which might have a pronounced effect on the mechanical properties of these materials in the processes of the electrochemical cell's formation and operation.

The present work was supported by the Russian Science Foundation (project no. 16-19-00104).

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Sintering, microstructure and transport properties of $BaCe_{0.5}Zr_{0.3}Ln_{0.2}O_{3-\delta}$ (Ln =Y, Dy, Gd, Sm and Nd) materials

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Mixed systems based on $BaCeO_3$–$BaZrO_3$ are considered as promising and perspective electrolytes for solid oxide fuel cells due to their good chemical stability and acceptable ionic conductivity. It is well known that the nature and concentration of dopants strongly affect the target properties of such materials. For example, the stability can be achieved mainly by the variation of Zr/Ce ratio in $BaCeO_3$–$BaZrO_3$ systems, whereas ionic conductivity depends on the type and concentration of acceptor dopant(s). The present work aims at identifying the influence of acceptor dopant on the crystal structure, microstructure and electrical properties of $BaCe_{0.5}Zr_{0.3}Ln_{0.2}O_{3-\delta}$ (BCZLn, Ln =Y, Dy, Gd, Sm and Nd).

The BCZLn powders are prepared by a modified version of citrate-nitrate combustion method followed by synthesis at 1100 °C for 5 h. The resulting mixture is ball milled and pressed into pellets at 250 MPa in hydraulic press. The pressed pellets are sintered at 1450 and 1600 °C for 5 h in air in order to understand the role of sintering temperature on the phase formation and microstructure. The relative density of the as-obtained ceramics is higher than 95%. The phase composition and microstructure of the samples are studied by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM), respectively. The total conductivity of BCZLn are measured by impedance spectroscopy (200–500 °C) and four-probe dc method (500–900 °C) in air, wet air and wet hydrogen atmospheres.

According to XRD data, all the ceramic samples are single-phase and belong to the perovskite structure. However, their cell volume decreases with increasing sintering temperature, which can explained in terms of increasing barium deficiency. For example, chemical analysis clearly shows that BaO evaporates from the surface of the sintered pellets at 1600 °C. SEM analysis shows the well-developed structures of the materials and the absence of impurity phases, although the surface morphology of sintered ceramic samples substantially changes depending on the sintering temperature. The correlations between chemical composition, sintering procedure~~s~~ and transport properties are revealed. It was found that Y^{3+} and Dy^{3+} can be considered as the most suitable dopants for the mixed $BaCeO_3$–$BaZrO_3$ system.

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Study of the degradation of ibuprofen by photocatalysts type $M_XTi_{1-X}O_2$ / (M = Fe, W…)

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Aquatic environments are impacted by numerous pressures, both quantitative (agricultural, industrial and urban), and qualitative (changes in physico-chemical parameters of water and hydromorphology). Today, among the multiple sources of pollution that are exerted on these media, the contamination by drug residues is proven. These residues are classified as "micropollutants" because they are often detected in very small quantities, ranging from micrograms to nanograms per liter. Despite their presence in small quantities, their potential effects on the environment must not be overlooked, because they are molecules designed to act on living organisms and, on the other hand, their presence remains constant, since their rejection is relatively continuous. The presence of these residues in the environment is a recent concern. In the future, the current situation is likely to increase following the increase in drug consumption. Ibuprofen (2- (4-isobutylphenyl) propionic acid) is the most widely consumed drug in the world, although it can be degraded biologically, the environmental risk of its presence in water remains high due to The formation of the intermediate products generated during biological degradation, it is for this reason that more and more attention is being paid to a means of eliminating this molecule, such as photocatalysis, a process for treating water because The use of solar energy is an economical and adequate solution.
Indeed, our study concerns the degradation of ibuprofen by photocatalysts $M_xTi_{1-X}O_2$ (M = Fe, W ...). The photocatalysts were prepared by the sol-gel method and characterized by different techniques: DRX, Raman, UV-vis, ATG-ATD... The rate of degradation was assessed by UV-visible spectroscopy. The results obtained show that the photocatalysts show a good degradation of the ibuprofen in the visible range with respect to pure TiO_2.

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Computational optimization of bio-adsorbents for the removal of pharmaceutical compounds from water

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Pharmaceutical active ingredients are amongst the most persistent wastewater contaminants and pose serious threats to non-target organisms and the environment. Thus, several tertiary treatments to be applied in waste water treatment plants have been proposed in order to mitigate this problem. In this context, adsorption by activated carbons is one of the most promising methodologies due to its versatility and high removal efficiency. However, activated carbons are traditionally expensive and therefore not widely applied. The development of low-cost alternative materials is imperative in order to unlock the activated carbon potential in the pharmaceutical removal from contaminated wastewaters. Primary sludge from paper mills has been previously appointed as a potential source of carbon for activated carbon production by pyrolysis. Nearly 20 million tons of this waste are produced annually, constituting a major issue for the mills due to economic and environmental concerns. The exploitation of this waste as feedstock for a new added-value product is therefore advantageous in the scope of circular economy.

Despite the large amount of studies, there are still aspects of the molecular adsorption mechanisms of organic pollutants into activated carbons that are unknown. Computational chemistry may help shed some light by studying molecular properties based on a validated activated carbon model. In this work, primary sludge was used in the production of (non)activated carbons, from simple pyrolysis to K_2CO_3 activation. The different materials were characterized by a battery of techniques such as zero charge point, functional group determination by Boehm's titration, FTIR, TEM, SEM, EDS, organic and inorganic carbon, elemental analysis, specific surface area (BET) and proximate analysis and adsorption kinetics/capacity of carbamazepine. The gathered data was then used in the formulation of a validated model of the proposed activated carbons. This model was used to gather pertinent information regarding the possibility of improving the starting activated carbon.

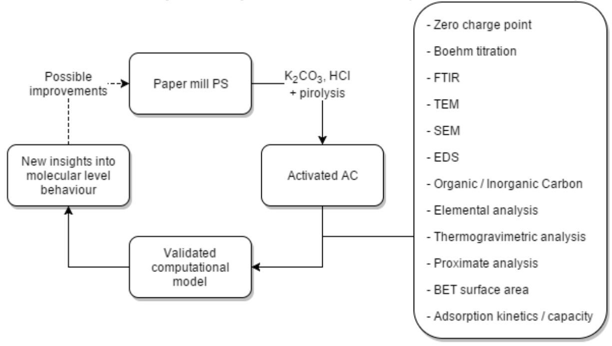

Fig 1. Schematic representation of the work

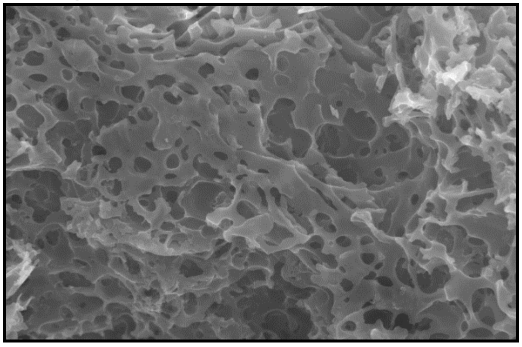

Fig 2. SEM micrograph of AC-K_2CO_3 at 10000×

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Production of activated carbons from raw and bleached pulp to remove drugs from water

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The production of activated carbons from alternative raw materials fits within the concept of sustainable economy, where value-added materials are produced from cheap substrates. In this work, two types of pulps, derived from the paper production process, were used as precursors for production of carbons to be applied for the removal of pharmaceutical drugs from contaminated waters. For this purpose, raw and bleached pulp were impregnated with two chemical activation agents (K_2CO_3 or H_3PO_4) and then pyrolysed and washed with acid. The precursors were also pyrolysed without any chemical activation procedure. After production, the materials were physically and chemically characterized by proximate analysis; determination of total organic carbon (TOC) and inorganic carbon (IC); elemental analysis; the Brunauer–Emmett–Teller (BET) specific surface area; point of zero charge (PZC); Boehm's titration for functional groups determination; Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The physico-chemical characterization showed that activated carbons reveal better properties for the adsorption process, such as the amount of micropores and the higher specific surface area. In Fig. 1 is depicted a SEM image of raw pulp (a) and another of a carbon produced from raw pulp, which was activated with K_2CO_3, pyrolysed at 800ºC and washed with HCl (RP800-K_2CO_3-HCl) (b). The developed porosity is notorious due to the effect of the activating agent; the pyrolysis also resulted in the increase of the surface area and the acid washing removed the inorganic material and ashes originated during pyrolysis, unblocking pores. These characteristics make these carbons interesting materials to treat contaminated waters, namely, with pharmaceutical drugs. To test these activated carbons as adsorbents, batch adsorption tests were performed using the anti-epileptic carbamazepine (CBZ). The results showed a complete adsorption of CBZ from the contaminated water at very low adsorbent dose, indicating the potentialities of the produced materials to be applied in wastewater treatment.

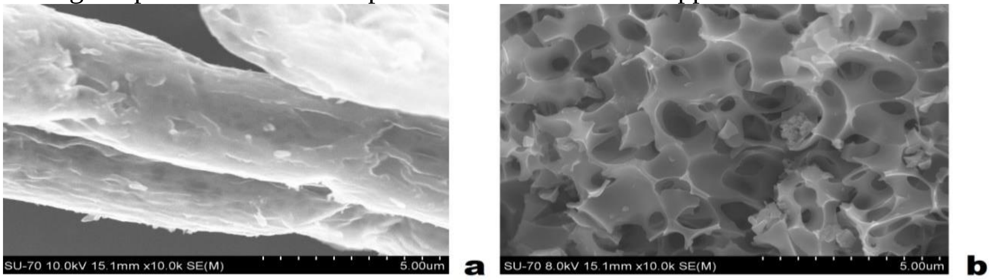

Fig. 1. SEM micrograph of RP (a) and RP800-K_2CO_3-HCl (b) at 10 000×

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Microstructure and electrochemical assessment of Cu-CGO cermet anodes

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CuO-$Ce_{0.9}Gd_{0.1}O_{1.95}$ (CuO-CGO) nanocomposite powders obtained by in situ one-step synthesis were used to prepare Cu-CGO cermet anodes for solid oxide fuel cells (SOFCs). The effects of the CuO content (varying from 40 to 60 wt.%) on the lattice parameter and crystallite size of CuO and CGO phases were investigated by X-ray diffraction (XRD) with Rietveld refinement of the XRD data. CuO-CGO composites were screen-printed on both faces of ceria-based substrates, fired at 1150 °C, reduced to Cu-CGO cermets, and electrochemically characterized by impedance spectroscopy in hydrogen and synthetic biogas atmospheres. One-step Cu-CGO anodes with 40 wt.% CuO showed area specific resistances of 0.15 ohm.cm^2 (in hydrogen) and 2.30 ohm.cm^2 (in biogas) at 800 °C. The anode performance is deteriorated by increasing the CuO content to 60 wt.%.

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The electrochemical properties of the cathodes based on doped lanthanum nickelate for proton-conducting electrolytes

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The aim of this work is the development of electrochemically active and stable electrodes for a high temperature proton-conducting electrolyte for intermediate temperature solid oxide fuel cells (SOFC). Study of the electrochemical properties of the composite electrodes based on $La_{1.7}M_{0.3}NiO_{4+\delta}$ (M = Ca, Sr, Ba) with a proton-conductive ceramic component $BaCe_{0.89}Gd_{0.1}Cu_{0.01}O_3$ in contact with the proton-conducting electrolyte $BaCe_{0.89}Gd_{0.1}Cu_{0.01}O_3$ was performed by impedance spectroscopy in wet air during 1500 hours. The composites are used as functional layers in bilayered electrodes with current collector layers made of 99.4 wt. % $La_{0.6}Sr_{0.4}MnO_3$ + 0.6 wt.% CuO. The best characteristics (low values of the polarization and serial resistances) were found for the electrode with $La_{1.7}Ba_{0.3}NiO_{4+\delta}$ - $BaCe_{0.89}Gd_{0.1}Cu_{0.01}O_3$ functional layer (0.63 $\Omega\cdot cm^2$ and 73.69 $\Omega\cdot cm$ at 700°C, respectively). After 1500 h of high temperature testing and 2 thermocycles the polarization resistance of the above electrode reduced to 0.30 $\Omega\cdot cm^2$. The obtained electrode was tested on other proton-conducting electrolytes, namely $BaCe_{0.89}Y_{0.1}Cu_{0.01}O_3$ and $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_3$ + 1 wt.% CuO and may be considered as the most promising for SOFC with a proton-conducting electrolytes.

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Structural, thermal, electrical and electrochemical properties of Ca-substituted $Nd_{2-x}Ca_xNiO_{4+\delta}$ (x=0-0.3) cathode materials

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Production of economically competitive solid oxide fuel cell (SOFC) systems requires, in particular, development of the electrochemically active and stable cathode materials to decrease resistance to the oxygen reduction reaction (ORR) at the cathode and prolong the life time of the devices. $Nd_2NiO_{4+\delta}$ and $Nd_{2-x}NiO_{4+\delta}$ have attracted much attention as promising cathode material for the intermediate temperature SOFCs based on oxygen ion- and proton-conducting materials as far as they possess sufficiently low ASR values. Previously, it was shown that Sr-doping in amount up to x=0.4 decrease polarization resistance of the $Nd_{2-x}Sr_xNiO_4$ cathodes [1]. Despite of some efforts made on study the structural, electrical, magnetic properties of Ca-substituted neodymium nickelates and oxygen over-stoichiometry and diffusion [2, 3] there are a few works on the electrochemical performance of $Nd_{2-x}Ca_xNiO_{4+\delta}$-based electrodes.

In this work Ca-substituted layered nickelates with general $Nd_{2-x}Ca_yNiO_{4+\delta}$ (x=0, 0.05; y=0-0.3) composition were prepared by the solution-assisted solid state reaction method and their structural and physico-chemical properties were investigated in order to select the most optimal materials, which can be used as cathodes for solid oxide fuel cells. With an increase in Ca content in $Nd_{2-x}Ca_yNiO_{4+\delta}$ the following tendencies were observed: i) a decrease in the unit cell parameters and volume, ii) stabilization of the tetragonal structure, iii) a decrease of the thermal expansion coefficients, and iv) enhancement of thermodynamic stability and compatibility with selected oxygen- and proton-conducting electrolytes. The comporative study of the electrochemical performance of the electrodes with $Ln_{2-x}Ca_xNiO_{4+\delta}$-based (x=0 and 0.3; Ln=La, Pr, Nd) functional layers was performed in contact with $Ce_{0.8}Sm_{0.2}O_{1.9}$ and $BaCe_{0.89}Gd_{0.1}Cu_{0.01}O_{3-\delta}$ electrolytes.

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Thermophysical and heating properties of a composite rubber membrane with energy harvesting purposes

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The use of unconventional technologies of solar energy can reduce the high levels of pollution caused by fossil fuels. In this context, recycled rubber membranes from End of Life Tyres (ELTs) can be used with this purpose, due to their high capacity to absorb solar radiation. However, the rubber has low thermal conductivity compared to metallic materials, commonly used in solar collectors with energy harvesting purposes. Therefore, the use of metallic fibres can improve the thermophysical properties of the membranes, although it is not well known its effect on rubber membranes exposed to solar radiation. The main objective of this study is to evaluate the thermal behavior of rubber membranes reinforced with steel wool fibres and their potential use as solar radiation absorbing material. With this aim, four different membranes have been studied using the same rubber particles gradation, but with four different contents of steel wool fibres. Thermophysical and heating properties have been evaluated. Additionally, the thermal behavior of a solar collector prototype manufactured with these membranes was also evaluated, see Figure.

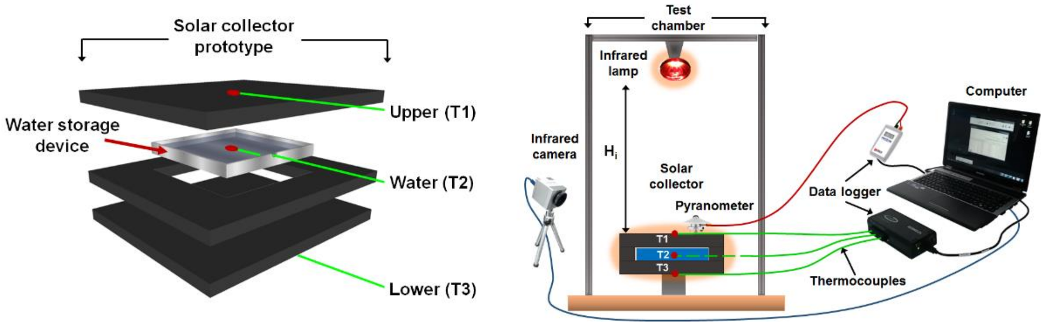

Figure. (Left) schematic representation of solar collector prototype with thermocouples and (right) heating test in solar collector prototype via infrared radiation.

The main results of this study show that the addition of steel wool fibres can increase the amount of heat absorbed, thus increasing the amount of heat transferred to low energy areas and also increasing the heating rate in the membranes, in relation to a membrane without fibers. However, fibres addition over 0.5%/v. do not contribute to an increase in the temperature reached by the membranes when exposed to infrared radiation. Finally, the development of a solar collector prototype fabricated with rubber membranes with 0.5%/v of fibres can transmit the heat absorbed by the membrane to the water, reaching a temperature of 45°C under the maximum irradiance studied demonstrating that it can be used as new sustainable construction materials for energy harvesting applications.

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Ionic Liquid-Poly(lactic) Acid Blends towards Proton Conductive Polymer Electrolyte Membranes for Fuel Cells

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Proton-exchange membrane fuel cells (PEMFCs) are considered to be a promising technology for clean and efficient power generation. Recently, there is much research on developing environmentally benign membranes with better performance and lower cost as alternative proton exchange membrane (PEM) materials [1,2]. One approach towards achieving this goal is mixing a biopolymer with ionic liquids aiming at improved transport properties of the polymer electrolytes with high concentration of highly mobile ionic moieties [3]. The objective of this work is to develop electrolytes consisting of biopolymer/ionic liquid mixtures for H_2/O_2 proton exchange membrane fuel cell applications. For this purpose poly(lactic acid) (PLA) and 1-butyl-3-methylimidazolium based ionic liquids (ILs) were mixed to form flexible, transparent and free-standing films. The PLA provides the necessary mechanical and hydrolytic stability and the IL protonic conductivity. The analysis of PLA/IL blends by SEM indicates the existence of dispersed phase domains which are spherical in shape. TGA and DSC showed that the electrolytes are stable at temperatures higher than 200 ºC. The highest electrical conductivity of these membranes measured by impedance spectroscopy is in the range 10^{-4}–10^{-2} Scm^{-1} at 98% RH, for ionic liquids based on the $[PF_6]$ and $[BF_4]$ anions, respectively. Although PLA based membranes do not offer significant advantages over traditional Nafion membrane as far as proton conductivity is concerned, the distinct set of advantageous biological and physico-chemical characteristics of these blend materials can be widely exploited in the near future in environmentally benign membrane based applications for energy devices.

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Hydrogen evolution reaction at rGO-supported PdAu and PdFe alloys

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As energy demands are constantly increasing, finding clean and renewable fuels is highly important. This can be achieved by using hydrogen as an energy carrier in what has been named as the hydrogen economy. The development of efficient electrocatalysts is required to overcome most of the technical and economic issues associated with hydrogen production via water electrolysis.

In this regard, palladium (Pd)-based electrocatalysts seem a promising alternative for water electrolysis because Pd has a lower cost than Pt, while retaining some of the qualities that make Pt such an efficient electrocatalyst for hydrogen evolution reaction (HER), such as similar exchange current density or hydrogen binding energy (HBE).

Pd-based alloy nanoparticles, namely PdAu and PdFe, assembled on reduced graphene oxide (rGO) are investigated as cathode electrocatalysts for HER in alkaline water electrolysis. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) are used to carry out the structural and morphological characterisation of the as-prepared rGO-PdAu and rGO-PdFe nanocomposites and their electrocatalytic activity and stability is studied by voltammetry and chronoamperometry.

Polarisation curves allowed definition of the Tafel regions, from where it was possible to calculate several kinetic parameters that characterise the HER at the two nanocomposites. The evaluation of the Tafel slopes, anodic charge transfer coefficients, exchange current densities, as well as the HER onset potentials, demonstrated the superior performance of the rGO-PdAu electrocatalysts in comparison to rGO-PdFe. The behaviour of the alloys is consistent with the Sabatier principle and in agreement with the volcano-type relation between the exchange current density and the HBE.

The overall lower price of the rGO-PdAu electrocatalyst, when compared to commonly used Pt-based electrodes, together with its good stability and promising results, show that rGO-PdAu nanocomposites are good candidates for application as novel electrocatalysts for the HER in alkaline media.

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Luminescent electrochromic devices incorporating ionogels

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Nowadays, around 30–40% of the primary energy worldwide is spent in buildings, most of that energy being used for heating, cooling and lighting. Reducing building energy consumption can have a vast impact in climate change by reducing CO_2 levels in atmosphere since most of the energy derives from coal, oil and gas. Fenestration products play an important role in energy saving, since up to 60 % of the total energy loss of a building comes from its windows [1,2]. Electrochromic devices (ECDs) have emerged as a “green” technology and have a high potential when applied to windows by changing properties, such as the solar factor and the visible transmission of radiation of the solar spectrum in response to an electric voltage. This allows to reduce the request for electric lighting, as well as cooling and heating loads, resulting in a drastic decrease of energy consumption in glazed-buildings [2]. In cold climate regions, smart windows with uninterrupted near-infrared (NIR) light transmission are the ultimate request for energy-efficient buildings. Ionic liquids (ILs) are molten salts with melting point below 100 ºC and interesting properties, such as thermal stability, low volatility high ionic conductivity and wide electrochemical stability window. Because of these properties they have been explored as high performance electrolytes. Trivalent lanthanide (e.g., Eu^{3+} and Er^{3+}) complexes usually exhibit attractive photoluminescence features, but poor mechanical properties and low thermal stability. The incorporation of ILs with lanthanide complexes in a sol-gel [3]-derived silica matrix can result in a luminescent ionogel, a multifunctional material displaying high ionic conductivity, high thermal stability, wide electrochemical stability and high quantum efficiency [3]. In the present work, novel luminescent ionogels emitting in the visible-NIR will be synthesized, characterized and tested aiming the fabrication of luminescent ECDs

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Photocatalytic degradation of Rhodamine B dye using SiO_2-TiO_2nano supported in HY zeolite on the cotton textiles

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The TiO_2 photocatalytic properties have been widely applied for the purpose of degrading organic pollutants such as antibiotics, dyes and pesticides, which reach the aquatic environment and considerably reduce the quality of water. Several works seek associates it with other materials / atoms / molecules in order to decrease its band gap energy offering the possibility of its use for water treatment utilizing solar radiation as a source of power. By other hand, since the degradation process of the pollutants takes place on the surface of the photocatalytic material, considerable efforts have been spent on improving its surface properties. In this sense, SiO_2 has showed be an excellent material to combine to the TiO_2. Some benefits of these materials compared to TiO_2: larger surface area, small percentage of the rutile phase formation and better thermal stability. In addition, zeolites also have been applied to enhanced the photocatalytic properties of the various semiconductors. These aluminosilicate materials can to act as acceptor of the photogenerated electron-hole pairs in the semiconductors decreasing its recombination, to provide active sites bringing the molecules pollutants closer to the surface of the catalyst or even to increase the acidity caused by the presence of Brönsted acid sites. In this work, it was produced by sol-gel method composites based on the SiO_2, TiO_2 nanoparticles and HY zeolite, which posteriorly were immobilized on cotton textile substrates and verified its activities by degradation of Rhodamine B (RhB) dye in aqueous solution under similar solar irradiation. It was investigated the influence of different amounts of HY zeolite in composites and also the initial pH value of the dye solution. To this end, the experimental setup for degradation of RhB dye was composed by a recirculation photocatalytic homemade reactor, which consisted of a slanted plate. The RhB dye solution in the reservoir was maintained under agitation (in the dark) during the entire operation time and was continuously circulated in the system by a peristaltic pump at a constant flow rate, enabling optimal distribution of the liquid over the catalytic support. A lamp, placed above from the surface of the reactor plate, supplied the artificial irradiation. The photocatalytic activity of coated samples was evaluated based on the ratio of C/C_0 calculated from the absorbance measurements. Double ring mode vibration in the FTIR spectra suggests that the composite preparation did not change the HY zeolite structure. The silicon/Aluminum ratios in the unit cell of the HY zeolite were also obtained by X-ray diffraction using the Breck and Flanigen equation, in good agreement with FTIR results. Data from UV-vis diffuse reflectance spectra shows that the presence of HY zeolite in the composites increased the band gap values. In addition, all composites with HY zeolite (SiO_2-TiO_2nano-HY) exhibited a substantially higher photocatalytic performance than the composite without HY zeolite (SiO_2-TiO_2nano). Potential zeta measurements indicated always negative values for both SiO_2-TiO_2nano and SiO_2-TiO_2nano-HY in the pH range of 2.5–10, although SiO_2-TiO_2nano presented lower suspension stability and, therefore, this can be a plausible explanation for its low efficiency. Finally, it was found that in acidic medium the degradation rates of RhB were much larger than in basic medium suggesting that excess of OH^- may have neutralized the dye charge impairing its adsorption on the catalyst.

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Exploiting a Taguchi based strategy for optimizing the surface area and crystallinity of iron nanoparticles

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For various applications, especially when requiring stability and high surface reactivity, it is crucial that engineered nanoparticles (NPs) might combine both well-developed crystalline structure and high specific surface area (SSA) [1], [2]. Therefore, the investment on optimization studies aiming to adequate NPs synthesis methods to these requirements is welcome. Within this context, iron-based NPs as attractive candidates for various purposes including biomedical applications and also environmental purposes (agents of contaminants removal), are the target of the present study. In this work, a two-step strategy was undertaken in order to enhance the crystallinity and SSA of zero valent iron NPs. In a first step, a L-9 Taguchi experimental design was adopted to evaluate the impact of specific synthesis conditions on the characteristics of iron based particles synthesized by chemical precipitation and using sodium boron hydride as reductant. In the second step, the application of ultrasonic irradiation during the synthesis process was carried out aiming at enhancing further both the crystallinity and SSA of the particles produced under particular conditions. Transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis, gas adsorption (BET isotherm) and thermo-gravimetric analysis (TG) were the used techniques to characterize the prepared NPs. According to the results, the (reductant/metal cation) ratio, R/C, and the cation (Fe^{3+}) concentration were identified as the two main factors influencing the specific surface area (BET) of the materials. Also, no significant effect of the reductant addition rate on the SSA of the products was observed. Ultrasonic irradiation was also demonstrated to have a substantial enhancing effect on both crystallinity and SSA of the metal powders prepared under selected synthesis conditions. The obtained results are discussed within the framework of NPs nucleation and growth phenomena.

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Chemical Stability of Perovskites-Type Oxide Electrodes for the ORR and HPRR in Alkaline Media

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In Solid Alkaline Fuel Cells (SAFC), the alkaline media offers improved electrode kinetics and may allow the use of low cost materials in replacement of the expensive platinum based ones. Layered oxides with the Ruddlesden-Popper structure, La_2MO_4 (where M is a transition metal), present oxygen mobility and allow the adjustment of the electrocatalytic characteristics of the material by suitable doping. Namely, substitution of trivalent La^{3+} with divalent Sr^{2+} (Sr'_{La}) it stimulates the creation of electron holes and changes the e_g orbital occupation of the transition metal [1]. Here we try to assess the potential of $La_2M_{1-x}D_xO_{4\pm\delta}$ materials, where M is Ni or Cu and D is Ce, Sr and Pr as alternative electrodes for SAFCs. Single phase lanthanum cuprates and nickelates (with the exception of the Ce-doped materials) could be obtained by a combination of high energy milling of the precursors and subsequent treatment at 1000 ºC for 10 min. Stability tests in strong alkaline media (pH>14) revealed that Sr and Cu cations readily leach out of the surface. Ni also tends to pass into solution, but with slow kinetics. Pourbaix diagrams computed for perovskites of analogous chemical composition confirmed the poor stability of cuprates and nickelates, enhanced by Sr, but also revealed that Mn-based materials such as $LaMnO_3$ were more likely to be stable in alkaline conditions within the tested potential window. This was confirmed by a study of perovskite-type oxides $LaCoO_3$, $La_{0.84}Sr_{0.16}CoO_3$, $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$ and $La_{0.7}Sr_{0.3}MnO_3$ as catalysts for the oxygen (O_2) reduction reaction (ORR) and for the hydrogen peroxide (H_2O_2) reduction reaction (HPRR). Of these materials, $La_{0.7}Sr_{0.3}MnO_3$ exhibited the highest activity for H_2O_2 reduction, with the cyclic voltammogram displaying a current density of about 2 mA cm^{-2} at -0.6 V, about one order of magnitude higher than that observed for the Ruddlesden-Popper phases. The effect of the transition metal cations on the catalytic behavior could be rationalized in light of the electronic structure of the *d* orbitals.

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Rare earth doped $LiMn_{1.5-x}Ni_{0.5}RE_xO_4$ based cathodes for high improved lithium-ion batteries

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The development of efficient electrical energy storage systems is essential for applications such as electric vehicles (EV), hybrid electric vehicles (HEV) and portable devices.

One of the most used energy storage systems are lithium-ion batteries and they are composed by electrodes (anode and cathode) and separator. The cathode is responsible for the cell capacity and cycle life where the active material is the lithium reservoir in the electrode

The spinel cathode $LiMn_{1.5}Ni_{0.5}O_4$ is an active material that has received increasing interest due to its advantages as high operating voltage of ~ 4.7 V, high energy density of 650 $Wh.kg^{-1}$ and theoretical capacity of 146.7 $mAh.g^{-1}$.

Cathode electrodes produced with this spinel structure show capacity fade resulting from an aggressive side reaction with the electrolyte that occurs at high-voltage operation.

To reduce this effect, in this work, LiMn1.5Ni0.5O4 doped with rare earth is synthetized and electrochemically characterized.

Different rare earth elements, neodymium (Nd), Gadolinium (Gd) and Dysprosium (Dy) were used in order to evaluate the effects of both the rare earth element and content, the latter being performed for Gd.

It was observed that the inclusion of rare-earth element preserves the cubic spinel structure, leads to smaller particle size and improves the cyclic performance of the produced batteries.

The $LiMn_{1.48}Ni_{0.5}Gd_{0.02}O_4$ sample is the one with the best battery performance to act as active material for cathodes in rechargeable lithium-ion batteries

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Activated carbon production from Teak wood wastes by physical activation and their application in the removal of pesticides from the liquid phase

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Pesticides are used world over to protect crops. Despite the advantages provided via the usage of pesticides, their residues in the environment, enhance the latent risk of hazard to the ecosystems and human life. To minimise the threat, several treatment processes are available for the removal of such compounds from water and wastewaters. Among the wide range of processes, adsorption onto activated carbons (ACs) is the most widespread technology used to deal with the treatment of water contaminated by pesticides.

The use of biomass in the ACs production allows to, reduce their price, and converts unwanted matter, surplus waste, of which billions of kilograms are produced annually, to useful valuable adsorbents. Moreover, the valorisation of wood wastes, like from Tectona grandis, by the production of added value materials is one of the possible strategies to expand the income sources and increase the economic activity. This type of approaches is very important in particular for the developing countries of the world, like East Timor.

There are a quite number of studies regarding the preparation of ACs from a diversity of precursors. However, there is scarce information concerning the use of teak sawdust [1,2]. In this work the wood wastes of Tectona grandis tree (from East Timor) were used as a precursor for the production of ACs, by physical activation with carbon dioxide at different temperatures and different activation times.

A systematic study and analysis of the structural and chemical characteristics of those carbon adsorbents, like apparent surface area, pore volume, mean pore with, and chemical surface groups, and others parameters like the degree of burn-off, allows us to predict future applications. The ACs with a high burn-off exhibited a well-developed porous volume and high apparent surface. Selected ACs were tested on the pesticides removals from the liquid phase and the preliminary results are very promising, allowing to expect good performance of theses adsorbents on the removal of a broad range of pollutants. The results obtained in this study suggest that teak sawdust is a suitable precursor for high microporous ACs production.

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Temperature influence on pesticides removals from aqueous solutions on activated carbons prepared from synthetic polymers blends

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Pollution of surface and ground waters causes risk to human health because of the potential health hazards of their contents of inorganic and organic compounds. In particular, the toxicity of pesticides and their degradation products is making these chemical substances a potential hazard. However, the application of pesticides is growing around the world, in particular in the developing countries, like East Timor.

The removal of pesticides from waters is one of the major environmental concerns. Among a variety of methods available to this end, adsorption is one of the well-known methods used in the removal of such hazardous compounds. Activated carbon (ACs) is the most widely used adsorbent material for this purpose due to its efficiency and economic feasibility. The adsorption process is a complex phenomenon, which depend on the adsorptive, adsorbent properties and equilibrium temperature. Since adsorption is a spontaneous process, a decrease in uptake is expected when the temperature increases. However, experiments conducted by Gimeno et al. revealed that, MCPA adsorption was an exothermic process for three of the four adsorbents studied and almost constant on the fourth [1]. The adsorption process was also reported as endothermic for diuron but exothermic for amitrole [2].

In this work, the influence of the temperature on the MCPA and 2,4-D removals was evaluated by adsorbing the MCPA and 2,4-D, on different ACs, at five constant temperatures, 283, 298, 303, 313 and 323 K. The adsorption of MCPA seems almost independent on temperature or increase slightly indicating an apparently endothermic adsorption process. However, it could also be due to the enhanced mobility of MCPA ions from the bulk solution towards the adsorbent surface and extent of penetration within adsorbent structure overcoming the activation energy barrier and enhancing the rate of intra particle diffusion.

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Polyacrylonitrile as Template in Preparation of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ Nanofiber and the Enhanced High-rate Performance for Lithium Ion Batteries

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Lithium-ion batteries (LIBs) have been the most popular energy storage devices for portable electronic products and electric vehicles (EVs) because of the high energy density and power density. Recently, layered Li–Ni–Mn–Co–O compositions have been widely suggested as potential alternatives with lower cost and low toxicity.

To obtain lower cobalt contained in cathode materials, $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ (LNMC) as one of them has been studied and become one of the most interesting candidates for the next generation cathode material because it is relatively lower cost and lower toxicity. The crystal structure of LNCM has been intensively studied by a number of experimental techniques, because the relative electrochemical properties concurrently change with the long-range and short-range crystal structure.

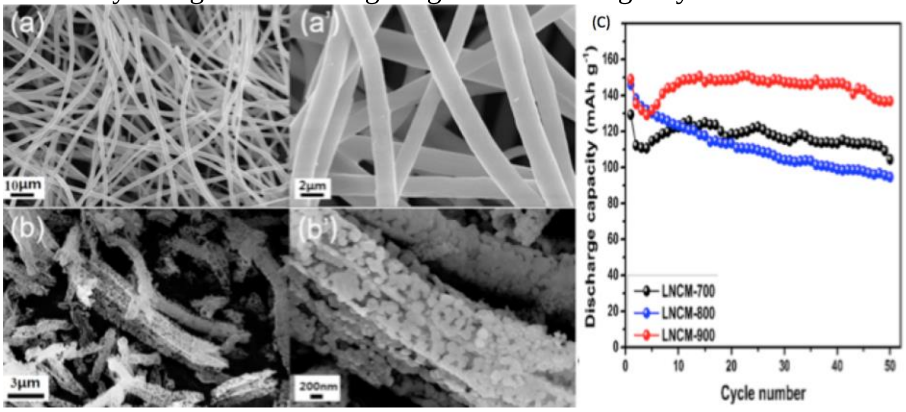

Fig. 1 SEM images of the precursor PAN nanofiber (a, a') and LNMC (b, b'); cyclic performance of LNMC samples.

In this abstract, nanofiber-like LNMC are produced as cathode material by electrospinning and calcination. Polyacrylonitrile (PAN) as template is helpful to produce LNMC nanoparticles with ordered one-dimensional crystal structure. The crystal structure and electrochemical properties of LNMC nanofibers are studied by X-ray diffraction, field emission−scanning electron microscopy (FE-SEM), Brunauer-Emmett-Teller (BET) measurements, and galvanostatic charge/discharge tests. In the interface of PAN and metal salts, LNMC are grown accompanying with the decomposition of PAN, the crystal morphologies of LNMC are quite dependent on the diameters and length of PAN/LNMC nanofibers. During the heat-treatment, the morphologies of PAN fibers control the removal of small molecules and the crystal morphologies of LNMC. The charge/discharge results indicate that LNMC with the tubular structure synthesized at 900 °C deliver the capacity of 149 mAh g^{-1}. Benefitting from a unique hollow and nanocrystalline architecture, it also exhibits good rate and cycling performance.

Guidelines for controlled design of $NiAl_2O_4$ cellular monoliths towards potential catalytic applications

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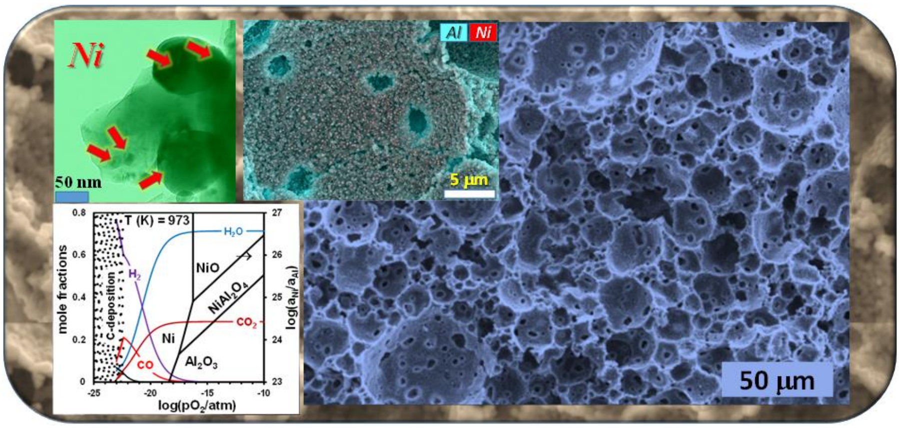

Rational design of systems for heterogeneous catalysis, involving active nanoparticles on a supporting substrate, is crucial for efficient industrial-scale chemical processing. Nickel aluminate, $NiAl_2O_4$, is one of the most important aluminates, being assessed for numerous applications as catalysts, with particular attention gained in steam and dry methane reforming. This work focuses on designing highly-porous cellular $NiAl_2O_4$-based spinel ceramics through combined suspension emulsification/reactive sintering and further decoration of the pore surfaces by Ni nanoparticles. Due to kinetic limitations and specific porous structure, the reduction occurs without affecting the integrity of the cellular monoliths. The reaction mechanism, assessed by XRD and TEM/EDS, includes both partial decomposition and reduction, resulting in the formation of $NiAl_{32}O_{49}$ and metallic Ni phases, respectively. The results suggest that the cellular bulk framework can be decorated with Ni catalyst in a controlled way, by proper selection of the initial cation stoichiometry of the $NiAl_2O_4$ spinel and appropriate reduction conditions. In selected conditions the reduction results in Ni nanoparticles of various dimension scales, finely-dispersed at the pore surfaces, with a significant fraction below 50 nm, as confirmed by TEM/EDS. The results of thermodynamic analysis emphasize that the redox tolerance of the spinel phase is dependent on the Ni:Al activity ratio, suggesting the prospects for tuning the catalytic activity and stability by designing the initial composition and resulting content of metallic Ni and Ni- and Al-containing metastable phases.

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Modification of thermoelectric properties of Nb doped $SrTiO_3$ ceramics by reduced graphene oxide

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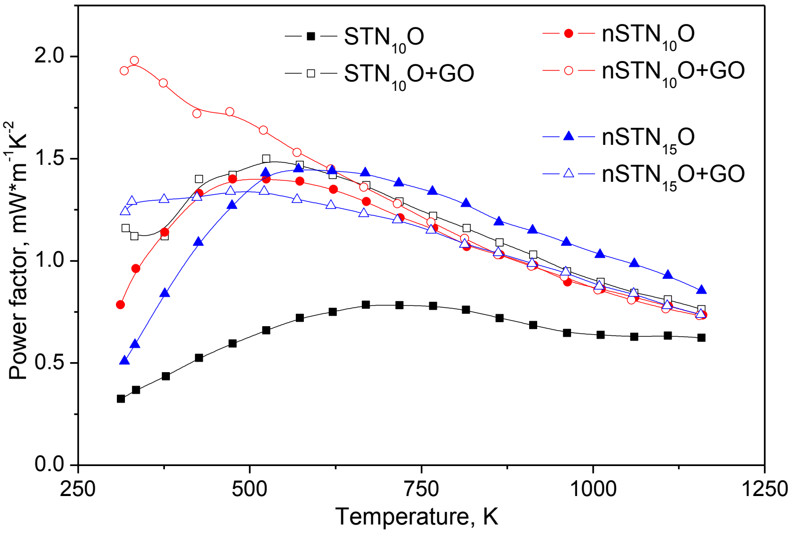
Thermoelectric materials are able to directly convert heat to electrical energy via the Seebeck effect, in which an electromotive force develops when the materials are located in a temperature gradient. The applications of strontium titanium oxide based thermoelectric materials are currently limited by their high operating temperatures.
In this work, Nb-doped $SrTiO_3$ with Nb content x = 0.10 and 0.15 as well as Sr/(Nb+Ti) ratio of 1 (STN_xO) and 0.98 ($nSTN_xO$) obtained by the conventional method was mixed with graphene oxide (GO) prepared by Hummer-based method. This composite was sintered at high temperature in atmosphere of 90% N_2 and 10% H_2 to reduce both Nb-doped $SrTiO_3$ and graphene oxide. Thermoelectrical properties of the obtained dense composite ceramics were studied in wide temperature range and compared to those without addition of GO. The electrical conductivity σ and Seebeck coefficient S of composite ceramics was significantly improved and, as result, the power factor $PF = S^2 \times \sigma$ increased, particularly below 500 K. Moreover, addition of GO has slight decreasing impact on the thermal diffusivity. Thus, higher thermoelectric figure of merit ZT values with addition of GO to the Nb-doped $SrTiO_3$ ceramics are expected.



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Anodic stripping voltammetric measurement of trace cadmium at lead-coated titanium electrode

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Heavy metals, as cadmium, attract a rising attention in environmental studies due to their increasing release by human activities, and acute toxicity, so the development of precise and convenient analytical methods for cadmium determination at trace level is extremely essential. The modified titanium electrode with lead film was used for determination of trace levels of cadmium using square wave anodic stripping voltammetry. The electroanalytical performance for the determination of Cd (II) on the lead-coated titanium electrode (PbTiE) was better than that bare titanium electrode. The measurement of cadmium on the PbTiE has the best reply under the following conditions: 10^{-3} mol L^{-1} Pb^{2+} in HCl (pH=1.0), deposition potential of -1.40V vs. Ag/AgCl/ KCl_{sat} and deposition time of 300s. The PbTiE reveals highly linear behavior in the concentration range 5 10^{-8} to 10^{-6} mol L^{-1}, with a limit of detection of 2 10^{-9} mol L^{-1} (Fig.1).

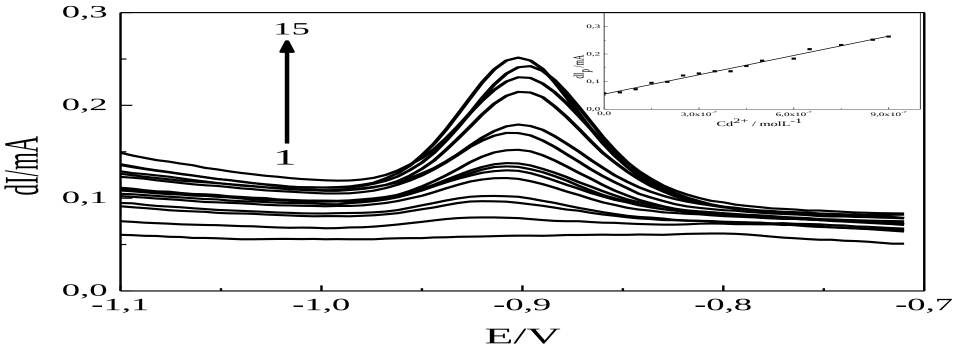

Fig.1: SWASV of Cd (II) at PbF-TiE under optimum conditions: Pb (II) :10^{-3} M, pH:1.0;deposition potential:-1.4V;deposition time:300 s; quiet time :30 s: pulse amplitude: 50mV; step increment: 6mV.Frequency: 50 Hz.

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Plasma nitriding surface as passivation layer for silicon cathode used in photo-electrochemical water splitting

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Photoelectrochemical (PEC) water splitting is becoming available and important method for solar energy conversion in the form of hydrogen fuels. A complete PEC cell requires two electrodes where one of them is photo-absorber (either a photocathode or photoanode) and the other electrode is called counter electrode. Silicon (Si) as a semiconducting photo-absorber for PEC water splitting has received a growing interest due to the natural abundance of Si, its high light absorbing ability, excellent electronic properties and low cost processing. However, its light absorbing ability suffering deeply with corrosion in aqueous electrolytes hinders its use in PEC applications.

To protect Si absorber for PEC applications against corrosion, plasma nitriding process was introduced to develop protection layer in this work. The plasma nitriding treatment on N-type silicon wafer was carried out in a capacitively coupled plasma system using nitrogen at pressure of 4.0 Torr, power of 100 W and time of 80 minutes. The nitriding layer was about 12 nm which was measured by ellipsometer. The performance of plasma nitriding treated Si photo cathode was characterized with voltammetry and impedance, and compared with oxygen plasma treated surface or untreated surface. It was found that the stability of Si photocathodes is improved by plasma nitriding for over 7 days compared to 2 hours without any treatment and 4 hours by oxygen plasma treatment.

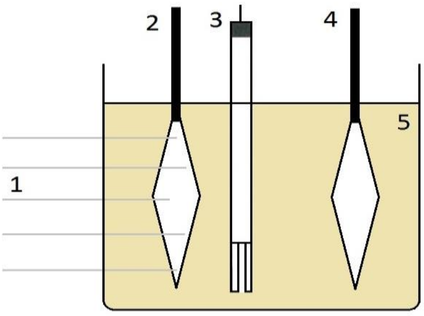

Fig.1. Schematic of photo-electrochemical cell set-up: 1) light emitting diode (LED) white light; 2) silicon electrode (work electrode); 3) reference electrode (Ag/AgCl in saturated KCl aqueous solution); 4) counter electrode (platinum or graphite plate); and 5) aqueous solution.

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Carrageenan hybrid siliceous materials for the uptake of metoprolol from water

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Emerging chemical pollutants such as antibiotics and other pharmaceuticals are frequently found in surface waters, which indicate that these compounds are not totally removed by conventional water treatment procedures. To overcome this problem alternative treatment methods are needed.
Adsorption is an attractive alternative process in view of its simplicity of implementation and low cost. Nanoparticles (NP), owing to small size and high surface to volume ratio are very promising sorbents. Enhanced adsorption and selectivity of the NP toward target pollutants can be achieved by surface modification with biopolymers containing proper functional groups. In addition, magnetic features can be imparted to the sorbents if using magnetic NP, which is convenient for magnetically assisted removal of pollutants from water. In the present work, new carrageenan hybrid siliceous nanomaterials were prepared and then tested as sorbents for the uptake of metoprolol (MTP), which is a beta-blocker prescribed for treatment of hypertension, arrhythmia and heart failure [1]. MTP is one of the most frequently detected beta-blocker in surface waters, with potential harmful effects on aquatic organisms and human health.
The sorbent materials were synthesized via sol-gel process of a mixture of TEOS with an alkoxysilane containing the biopolymer κ-carrageenan (SiCRG). Magnetic nanosorbents were also prepared using a similar procedure carried out in the presence of magnetite (Fe_3O_4) NPs (Figure 1). The materials were characterized using electron microscopy (TEM/SEM), infrared spectroscopy, elemental analysis and zeta potential measurements. Adsorption experiments were performed at different pH and variable MTP initial concentration. The maximum adsorption capacity was 447 mg/g for magnetic hybrids which represents an improvement of 300% compared to most efficient MTP sorbents reported in the literature. Magnetic hybrids were easily regenerated in mild conditions, and exhibited good reusability for at least 3 cycles. Overall the results showed that these materials can be used as environmental friendly sorbents for the removal of pharmaceuticals by using magnetic separation technologies.

Figure1: Schematic representation of synthesis of magnetic hybrid materials.

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Magnetic biohybrid nanosorbents with tunable surface chemistry for the removal of cationic and anionic herbicides from water

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Herbicides have a critical role in the modern agriculture, delivering a very efficient way to control weeds that proliferate in non-desired areas. Nevertheless, the uncontrolled application of widely used herbicides, e.g. glyphosate and paraquat, resulted in their environmental accumulation and in the contamination of life resources (*e.g.* food, soil and water)[1]. The detection of such herbicides in drinking water sources raised serious concerns due to the negative impact on human health and therefore, parallel to preventive measures, there has been interest to implement efficient processes for their removal from water. Herein, the synthesis of four magnetic nanosorbents of hybrid nature is reported. These materials have been successfully prepared through the encapsulation of a uniform iron oxide magnetic core with a siliceous shell containing the biopolymers κ-carrageenan, chitosan, starch (rice) and a quarternized chitosan (HTCC). Because these nano bio-hybrids possess variable surface chemistries, they offer the ability to remove cationic or anionic herbicides from water by the judicious selection of the adsorption conditions. As such, these materials have been investigated in the uptake of herbicides from water using variable operational conditions, namely at distinct pH, variable herbicide concentration, contact time and temperature. Our results show that in certain conditions, the hybrid particles containing κ-carrageenan and HTCC are efficient for the removal of paraquat and glyphosate from water through adsorption and magnetic separation. Additionally, these hybrid materials exhibit good regeneration capacity delivering a simple, low-cost and environmentally friendly approach for water remediation purposes.

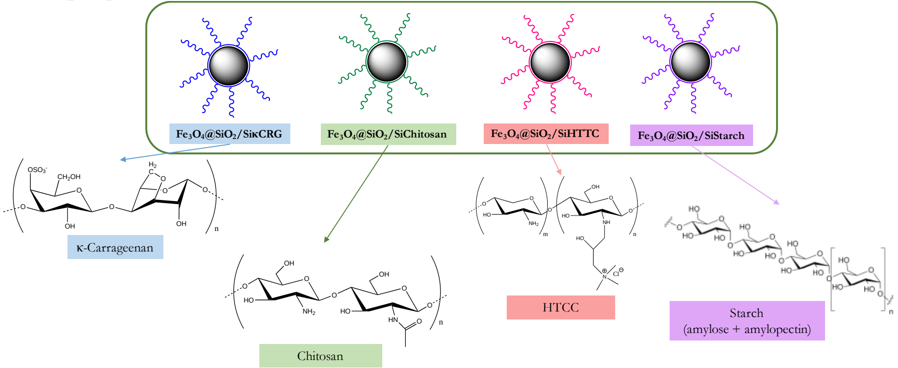

Figure 1 – The magnetic nanosorbents used in this work for the removal of herbicides from water.

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Magnetic nanoparticles for trace mercury preconcentration and quantification in waters

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The Water Framework Directive (WFD) (200/60/EC) classifies mercury (Hg) compounds as priority hazardous substances and imposes maximum levels in water, which enforces the need for regular monitoring. Several analytical techniques have been used for its determination, however a broad variation of mercury levels has been reported in the literature.

Mercury determination in natural waters is not a trivial task. The complexity of the environmental matrices, the inadequate use of analytical techniques and the transport and pre-treatment of water samples may increase the risk of sample contamination or loss of analyte. In addition, the ultra-trace concentration of analyte is also a limitation that makes the reliable determination of Hg a major analytical challenge.

Thus, the development of reliable methods for the accurate quantification of low concentrations of Hg in natural waters has been a challenge for the scientific community. Mercury concentrations in natural waters are usually too low and Hg determination at trace levels usually requires a preliminary separation and preconcentration step in order to achieved quantifiable level. Also in the most of cases, before analysis the application of adequate reagents for analyte desorption from the sorbent is required. These steps are the principal source of contamination or loss of analyte.

The aim of this investigation is to develop a reliable method for the determination of trace Hg in water. The process is based on the use of silica coated magnetite nanoparticles functionalized with dithiocarbamate groups that work as sorbent for the extraction and preconcentration of Hg. Compared with traditional sorbents, a distinct advantage of the tested material is that the magnetic sorbents can be easily separated from aqueous solution by the application of a magnetic gradient. After sorption, the mercury retained on the sorbent material is directly determined using a simple technique based on the thermal decomposition of the sample.

The results shows that magnetite nanoparticles functionalized with dithiocarbamate groups is an efficient sorbent for Hg preconcentration in different matrices and the proposed method allows to quantify with trueness the Hg in waters, at low levels such as 20 ng/L.

Influence of wettability on the anti-scaling performance of heat transfer surfaces

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This communication presents low energy surfaces with different roughness values to prevent the deposition of calcium carbonate on heated surfaces that are in contact with water. Most devices used to heat water (e.g. heat exchangers) have problems originated from the deposition of calcium carbonate on the heated surfaces that are in contact with water. The inorganic layers formed on thermally conductive surfaces lead to the reduction in efficiency of the heat transfer process and ultimately cause the failure of the devices.

To decrease this problem, substrates with modified interfaces exhibiting low surface energy can be used, but the effect of some properties like the wettability of these surfaces on the rate of calcium carbonate deposition is yet to be understood.

In this work the problem was approached through the application of different pre-treatments and coating layers to reduce the surface energy of copper substrates with three different roughness values. This resulted in samples with a wide range of wettability values towards water, as inferred from water contact angle measurements. Calcium carbonate deposition tests, both in static conditions and with water flow, were carried out and the amount of calcium carbonate deposited was measured. The results show that under static conditions there is a correlation between hydrophobicity and low deposition of calcium carbonate.

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Surfaces modified by bio-inspired molecules for molecular oxygen reduction catalysis

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The oxygen reduction reaction (ORR) is a sluggish reaction over any metal substrate, limiting the kinetics of the electrochemical devices using the molecular oxygen as oxidising agent. The pursuit of new reliable substitutes of the conventional catalysts will lead to the preparation of materials with increased electrocatalytic activity and economically interesting in order to push forward the market of such electrochemical devices.

The purpose of this work is to develop a high performance cathodic catalyst for the ORR based on bio-inspired molecules (synthetic metalloporphyrins and Vitamin B12), which display a high intrinsic catalytic potential, as widely recognized by the scientific community. To achieve this goal, porphyrin moieties were electrochemically immobilized on electrode surfaces. Cyclic voltammetry was employed to understand the electrochemical behaviour of the metal complexes in solutions over different substrates as well as that of the matrices assembled on the electrode surfaces. The electrodes were modified using two different approaches: a) by continuous potential cycling of the substrate in solutions containing the coordination compound and b) by incorporation of the catalyst into a conducting polymer matrix during its synthesis. For the second method were used the electrochemical techniques of cyclic voltammetry, chronoamperometry and double impulse chronoamperometry, and studied the more important parameters of each technique in order to optimize the catalytic activity of the films for ORR. The caracterization of the modified electrodes for the RRO's catalytic activity was made using cyclic voltammetry. The XPS technique was used to identify quantitatively the presence of porphyrins on the polymers surface. Finally, were performed in-situ ellipsometry tests to the potentiostatic growths in the presence of porphyrins with the purpose of determining the optical parameters and the polymer thickness.

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Sustainable Design: Development of new products from pine resin and flax fiber

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Natural fiber composites, often referred to as biocomposites, represent viable and ecologically advantageous alternatives to conventional composites. Flax fiber has been introduced in the industry to replace the use of fiberglass, saving about 10 times energy expenditure during processing. Rosin, on the other hand, is a resource that is not currently used in the composite industry, but which exists in abundance in Portugal and has a high potential for use in complex products.

The main objective of this study is to describe the formulation of a new composite material, based on these two resources, and to present Design proposals that validate its applicability and demonstrate the hidden potential that may presently be underexploited.

Solid-state rosin presents very fragile characteristics. In order to give more resistance and flexibility to the matrix, the use of additives such as EVA (Ethylene Vinyl Acetate) was considered, and flexural tests were performed on both materials, reinforced and not reinforced with flax fibers, to measure its properties.

The obtained samples showed good visual characteristics and some ductility, where a content of 10% of fibers, increases about 3 times the strength and rigidity of the non-reinforced matrix.

The present study shows that there is potential for Portuguese resin and flax to integrate new products, especially in the furniture and lighting industry. In this sense, prototypes of a modular bench and a luminaire were developed to validate the applicability of the material.

Keywords: Biocomposites; Industrial Design; Sustainable development; Flax fiber; Pine resin.

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Deposition of silver-doped TiO_2 (TiO_2:Ag) coatings by PVD for footwear industry

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Ecologic and health effects on applying materials with advanced functions for leather surface finishing are priorities for the European leather industry and contribute to the increase of added value and durability of leather and fur articles. The innovative properties of Ag/TiO_2 on leather surface are due to their antimicrobial, self-cleaning and flame retardant characteristics. Furthermore, it allows the reduction of the chemicals with high pollutant potential.

TiO_2 and Ag/TiO_2 thin films were deposited on leathers by magnetron sputtering. X-ray diffraction (XRD), as well as, Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS), were performed in order to monitor the crystalline structure and the composition of the different thin films. Reflectance measurements were made to calculate the band gap using the Kubelka e Munk equation. In order to study the photocatalytic performance of the films, an organic dye (methylene blue) will be used as a typical pollutant in a concentration of $\approx 1\text{x}10^{-5}$ M. The thin films will be immersed in this solution in an open-top quartz cell, with the irradiation perpendicular to the surface. No oxygen will be artificially introduced in the solution during the irradiation experiments. The concentration of the dye will be monitored as a function of time by the Beer–Lambert's law. A LED with irradiance of 2 mW / cm^2 was used to simulate the solar UV and visible light radiation sources.

As principal results, all samples doped with Ag presented a lower band gap compared to non-doped (TiO_2), decreasing from 2.88 eV (TiO_2) to 1.94 eV (Ag/TiO_2), respectively. Also, the doped samples (Ag/TiO_2) had a better photocatalytic efficiency, with a kinetic constant of degradation of k $=10.87\text{x}10^{-2}$ than the non-doped (TiO_2) sample, k = $0.62\text{x}10^{-2}$, as predicted because its band gap was lower.

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Magnetised Mn_3O_4 nanocomposite for water decontamination

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The development of new materials and methods for the treatment of contaminated aqueous solutions is increasing due to the higher demand for water supply for human consumption and industrial development, combined with more stringent environmental legislation. A nanocomposite with magnetic properties has been successfully synthesized by means of the co-precipitation of manganese oxide, Mn_3O_4, by using air (an eco-friendly oxidant), onto magnetite particles. The nanomaterial was characterized by XRD with Rietveld method, TEM and N_2 adsorption (BET) techniques. Magnetic nanocomposites can be conveniently recovered by magnetic separation, avoiding the filtration steps, which currently still represent a barrier to the application of high performance advanced materials in environmental remediation processes and treatment of great volumes of aqueous solutions. The resulting nanocomposite has a surface area of ~40$m^2.g^{-1}$ and a particle size of ~30nm. The application of the magnetic nanocomposite in the removal of Cd(II) from aqueous medium was evaluated. The adsorption isotherm for Cd(II) is fitted using the Langmuir-Freundlich model and the estimated maximum adsorption capacities at pH 6 and 7 are similar (0.28±0.02 and 0.31±0.02 $mg.m^{-2}$, respectively). The kinetic results show that the studied system follows the pseudo-second-order model, indicating that cadmium is probably being adsorbed in a specific mechanism by the manganese oxide in the composite. Turbidity tests showed that the magnetic sedimentation was efficient and promising for wastewater treatment in large scale. In previous work of our group, this material had demonstrated high affinity for As(III) and also for dyes degradation. The present work simplifies the synthesis of a manganese oxide composite to be applied in environmental systems as both an oxidant and an adsorbent.

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Advanced Photocatalytic Heterostructered Materials for the Controlled Release of Active Compounds upon Solar Activation

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Titanium dioxide-based materials have attracted a lot of interest in recent years due to its chemical stability, non-toxicity, low cost and mainly due to its photocatalytic properties. Therefore, TiO_2 materials have been used in worldwide of applications such as for self-cleaning, photocatalysts for environmental purification and also as antibacterial agents. The main objective of this work is to monitor the controlled release of active compounds (e.g., insecticides, pesticides, fragrances, etc.) from microcapsules functionalized on the surface with photocatalytic TiO_2 films or nanoparticles. The encapsulation process of the active compound was achieved by a polymeric coating and the resulting microcapsules have sizes ranging from 150-350 µm (Figure 1).

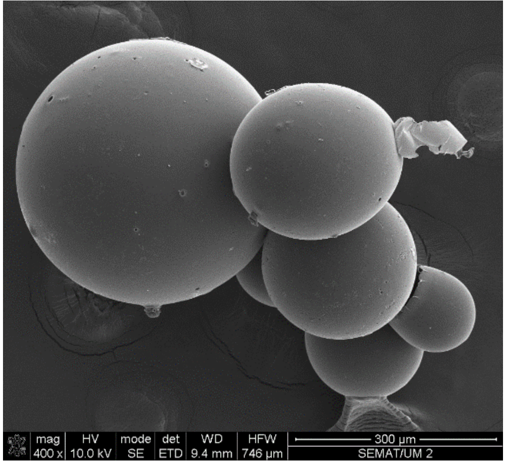

Figure 1. Scanning electron microscopy of PMMA microcapsules chemically functionalized with photocatalytic TiO_2 nanoparticles

Under ultraviolet radiation TiO_2 develops redox processes that initiate the rupture of chemical bonds on the wall of the microcapsules and thus dissociates the polymeric capsule, releasing the encapsulated compound. This study focuses on monitoring the amount of active compound released under UV irradiation and in the presence of photocatalytic TiO_2-based materials. Thermal and doping treatments were endured in order to study the influence on the optical properties, crystallinity, domain size and surface area of TiO_2 nanomaterials. These properties were correlated with the release of active compound from the microcapsules and also with photocatalytic effect of TiO_2.

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Influence of Li_2S content in a Solid Glass Li^+ Electrolyte

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Glass Li^+ electrolytes that plate/strip a lithium anode reversibly for over 1200 cycles are doped with Li_2S electric dipoles. The magnitude of the dielectric constant is optimized with respect to the Li_2S content. The following measurements with respect to Li_2S will be reported:
- X-ray diffraction (XRD);
- Differential Scanning Calorimetry and Thermogravimetry (DSC/TGA);
- Electrochemical Impedance Spectroscopy (EIS);
- Chronopotentiometry.

We have made the comparison of the performances of full cells with and without Li_2S.

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Carbon based materials (A4)

Local Effects of Graphene and Graphene Oxide on the Ferroelectric Properties of P(VDF-TrFE)

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Ferroelectric polarization can be used to assemble various organic and inorganic species and to create nanostructures with controlled properties. Now tremendous research activity is going on ferroelectric /carbon nanotubes, ferroelectric/graphene and ferroelectric/graphene oxide, which are very promising due to their multifunctionality and possible use in self-assembled “green” (free of lead or any hazardous material) nanoelectronic devices for sensing, actuation, acoustic detection, energy harvesting etc. In particular, copolymers of poly (vinylidene fluoride) and poly trifluoroethylene wiz. P(VDF-TrFE) is a promising material for these composite microstructures. This paper describes composite films of copolymer P(VDF-TrFE) with varying concentration of graphene oxide (GO). Experimental and theoretical investigations were done to understand the effect of the GO concentration on polarization and mechanical behaviors of bulk composites and composite microstructures. The obtained films were investigated locally using piezoresponse force microscopy (PFM). The switching behavior, charge states, piezoelectric response, self-polarization and dielectric permittivity of the films were found to depend on the concentration of GO. For understanding the mechanism of piezoresponse evolution of the composite we used models of PVDF chain, its behavior in electrical field and computed the data for piezoelectric coefficients using HyperChem. Experimental results qualitatively correlate with obtained in the calculations.

This work was financed by the Russian Science Foundation (Grant 16-19-10112).

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Decoration of carbon nanostructures using silver sulfide nanocrystals

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Semiconductor nanocrystals have been extensively explored due to their unique size dependent optical and electronic properties, which are of interest in a number of applications including sensors, solar cells, catalysts and optoelectronic devices. [1] Graphene based materials have emerged as promising materials in many technologies due to their structure-dependent physical and chemical properties. [2] The implementation of technologies combining these two types of materials opens new routes for the development of innovative materials. For example, silver sulfide Ag_2S (Eg= 1.08 eV) has been reported to harvest photons efficiently in the visible spectral region, which makes this semiconductor an interesting material to be explored in visible light photocatalysis. Following previous work on the use of single-molecule precursors [3,4] for the functionalization of several materials, we present here the functionalization of carbon nanomaterials, such as graphene oxide and graphite oxide, with Ag_2S nanocrystals. These hybrid nanostructures were obtained by the thermal degradation of a Ag(I) dialkyldithiocarbamate complex and growth of semiconductor nanophases in the presence of the carbon substrate. [4] Several reaction parameters have been investigated in order to optimize the experimental conditions for obtaining morphological uniform hybrid nanomaterials. The hybrid nanostructures were characterized for their morphological features using SEM and TEM. Additionally, Raman spectroscopic methods have been applied to monitor the surface nature of carbon substrates due to its influence on the nucleation and growth of the metal sulfide nanophases.

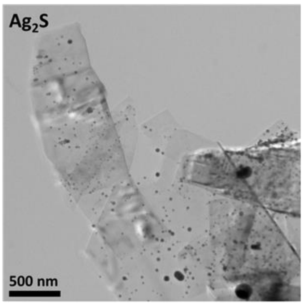

Fig 1. TEM images of graphite oxide with Ag_2S nanocrystals.

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Synthesis and characterization of magnetic graphene based nanocomposites for the recovery of rare earth elements

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Rare earth elements (REEs) are defined by the IUPAC nomenclature, as the 15 lanthanides together with yttrium and scandium. Because of their electrochemical, luminescent and magnetic properties, REEs can be widely used in many applications including catalysts, metal alloys, electronics, glass, magnets, ceramics, new materials and some other high-technology products. The demand for REEs is continually growing, but mining and processing these elements is difficult and expensive. The conventional rare earth extraction consists in grinding large volumes of hard rock and removing REEs through acid extraction and subsequent purification. This process is very energy intensive, disturbs large areas of pristine land, and generates large volumes of toxic tailing. Although still little explored, a friendly alternative to this process is the recovery of REEs from effluents by adsorption (and/or ion exchange). This technique is very versatile, efficient, has simple design and wide adaptability.

In recent years, two-dimensional graphene, the newest type of carbon nanostructures has been extensively explored in a wide range of fields. However, its usage in environmental applications has been less investigated. On the other hand, magnetic materials are of considerable interests in material chemistry because of their unique physical properties and outstanding surface chemistry properties. Taking advantage of the combined benefits of graphene and magnetic nanoparticles, here we report a simple strategy for preparing Fe_3O_4/graphene based nanocomposites through electrostatic self-assembly. The nanocomposites were then used as sorbents for the recovery of Lanthanum (La), Europium (Eu) and Terbium (Tb), three of the most important REEs.

Before their practical application, the magnetic nanocomposites were fully characterized by appropriate techniques. As example, TEM images confirms the successful deposition of Fe_3O_4 nanoparticles on graphene sheets, showing the Fe_3O_4 nanoparticles as dark dots on a lighter shaded substrate corresponding to the graphene sheets.

The efficiency of the nanocomposites to recover La, Eu and Tb from water was then evaluated by carrying out batch experiments. Results show that the La, Eu and Tb uptake is strongly dependent on the solution pH. For pH values around 7 the Lanthanides (La, Eu and Tb) recovery was superior to 90%.

In the whole, the prepared Fe_3O_4/graphene based nanocomposites exhibit excellent adsorption efficiency and rapid separation from the matrix by an external magnetic field, contributing to significant advantages in separation science.

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Graphene biosensor

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Recent advances in interdisciplinary research in molecular diagnostics have a quickly development of different classes of biosensors with increasingly better sensor characteristics. In addition, the development in engineering and nanotechnology areas has been of fundamental importance for miniaturization and technological multifunctionality of biosensors. Molecular diagnosis facilitates the primary detection of diseases with greater specificity and sensitivity, but they require time and are costly. Biosensors have emerged as a cheap, easy-to-handle, portable alternative with high sensitivity and specificity. Graphene is a two-dimensional nanomaterial with a thick carbon atom, the carbon atoms has sp2 hybridized and packaged in a crystalline lattice. Recently graphene has received special attention as an emerging material because of the potential applications due to their electrical, mechanical, optical and biological properties. It is estimated that at least 2.5% of the Brazilian population and about 200 million people worldwide carry the hepatitis C virus, the largest human epidemic today, higher than HIV/AIDS five times.
Methodology & Theoretical Orientation: To obtain the graphene nanoparticles were utilized the chemical synthesis then this material was deposit by electrochemical deposition in a special substrate. The graphene nanoparticles was characterized morphological and the biosensor performance for the detection of diseases such as, hepatitis C will be assessed for sensitivity, selectivity, stability, and repeatability by electrical measurements such as cyclic voltammetry.
The chemical synthesis and the electrodeposition techniques were very efficient to develop a biosensor device. The biosensor show great stability compared with the commercial sensors. So this device could be a great to detect infection diseases such as hepatitis C.

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New high-pressure C_{70} structures

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Two new C_{70} phases were synthesized at 9GPa and 270ºC (1D phase) and at 7Gpa and 600ºC (2D phase), employing a Paris-Edinburgh press equipped with WC or sintered diamond anvils. Their structures, both monoclinic, were determined by combining powder x-ray diffraction and density functional calculations (DFT). DFT calculations were performed by constraining the lattice parameters and symmetry to the experimental ones and gave the relaxed atomic positions for both structures, shown in the figure below. The structure of the 1D phase consists of zigzag polymerized C_{70} molecules, shown in the left panel of the figure, while the 2D phase consists of layered polymerized C_{70} molecules arranged in puckered hexagons, in which each molecule is bonded to three neighboring molecules (right panel of the figure). Such extended C_{70} structures have never been observed previously.

The present study also demonstrates the role played by the layer displacements on the phase transformations of C_{70} at high-pressure. Antiparallel displacements of the compact layers lead to short interfullerene distances and promote covalent bonding between the molecules. The present work definitely establishes C_{70} molecules as very efficient building blocks, in opposite to initial claims, to create novel nanostructured carbon phases. Mapping the reaction pressure-temperature diagram for C_{70}, as it was thoroughly carried out for C_{60}, should lead to the discovery of other new fullerene network structures.

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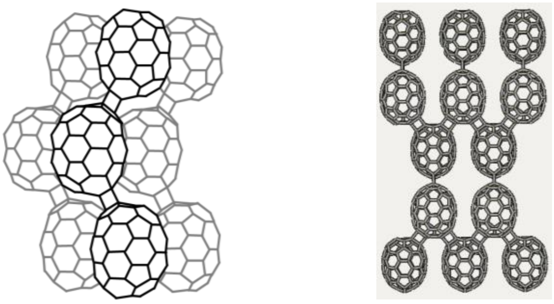

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Effect of annealing temperature and addition of carbon nanotubes on power factor of reduced graphene oxide freestanding paper

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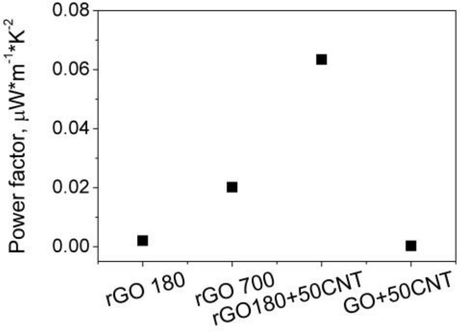
Thermoelectric (TE) energy conversion has an advantage to harvest widely distributed waste heat, and is also proved as an alternative route to convert solar energy into electric power economically. However, the dimensionless figure of merit (ZT) of the TE materials has been limited to the benchmark value of ZT = 1 for a long time. ZT is defined as $ZT = (S^2 \times \sigma/k)T$, where S, σ, k and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Efficient TE energy conversion, therefore, requires materials that have an enhanced power factor $PF = S^2 \times \sigma$ and reduced k.

Graphene is a material, which exhibits unique properties, including high mechanical stiffness and strength, coupled with high electrical and thermal conductivity. These properties make graphene an exciting prospect for a host of future applications in nanoelectronics, thermal management and energy storage devices. At the same time reduced graphene oxide (rGO), possessing many properties of graphene with advantages of larger scale and free standing abilities, can be easyly obtained by thermal or chemical reduction of graphene oxide (GO).

In the presented work we prepared reduced graphene oxide freestanding paper with thicknes ~20 µm, determined its PF and established how the PF can be modified by annealing in vacuum at temperature from 180 °C (rGO180) to 700 °C (rGO700). The effect of addition of up to 50% of carbon nanotubes (CNT) on the TE properties of the freestanding papers annealed at 180 °C (rGO180+50CNT) and without heat treatment (GO+50CNT) was studied as well.



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Symposium B - Structural Materials

Advances in ceramics, concrete, building materials (B1)

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Cost-Efficient and Eco-Efficient Mortars based on Fly Ash and Waste Glass

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Waste reuse is crucial in a context of a circular economy and zero waste program for Europe. Some wastes like fly ash and waste soda lime silicate glass deserve a special attention because they generated in high amount and have very low reuse rate. This paper reports mechanical results on 72 mortar mixes regarding the joint effect of the replacement percentage of fly ash by waste soda lime silicate glass, activator/binder ratio and admixture type. Results on cost efficiency of those mixtures are reported. Results regarding the global warming potential are also reported.

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Characterization of Concrete with Incorporation of Slag From Blast Furnace

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This work has focused on studying the possibility of the incorporation of crystallized slag from blast furnace in concrete to use in the filling of short steel columns. The natural sand was totally or partially replaced by the crystallized sand slag in the composition of concrete. The characterization of these concretes was made based on their physical properties (apparent and specific densities, porosity, and fineness modulus), mechanical properties (compressive and tensile strengths) and durability (capillary and absorption of water, and shrinkage). The experimental results show that the percentages of crystallized sand slag on the concrete composition have an important effect on the enhancement of the mechanical proprieties of concrete. The comparison of the different characteristics with conventional concrete shows the benefits of the use of crystallized sand slag from blast furnace in the production of concrete.

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Cost and property optimisation of concretes containing fly ash using mathematical and statistical strategies

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An integrated optimisation methodology has been used to optimise the material cost as well as the fresh and hardened properties of concretes containing fly ash as an active replacement for Portland cement. In the present investigation, the amount of fly ash is optimised to minimise material concrete cost under the fresh bulk density and consistency index constraints, and the hardened bulk density and 28-day compressive strength constraints, which are important characteristics of application, workability and durability of concretes. Locally- sourced fly ash was milled and sieved to produce a powder (particles below 45 µm) containing amorphous and crystalline phases. Simultaneous 3^{3-1} fractional factorial design of experiments and mathematical programming were used to optimise several qualities of the concretes (physical and mechanical properties and cost). This required mathematical models for the qualities, although it was challenging to model some of the different characteristics of a property. One approach used empirical models based on data from fractional factorial design coupled with the response surface methodology. Concrete mixtures were prepared using fly ash as replacement for 10, 20 and 30 wt. % Portland cement, with water-to-cement ratios of 0.38, 0.46 and 0.50, and aggregate-to-cement ratios of 3.20, 3.91 and 4.40. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were also used to complement the numerical and statistical approaches. Characterization results were used to calculate statistically significant and valid regression equations, relating fresh and hardened properties with the factor levels. The regression models were then used to delimit simultaneously the combinations of those three factors most adequate to produce a concrete mixture with specified properties and lower cost. It was possible to simultaneously specify good workability, low bulk density, high 28-day compressive strength and minimum cost for concretes over a range of fly ash from 15 to 20 %.

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Evaluation of ceramic propping agents applied for global shale gas exploration under extreme conditions

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Since shale gas revolution has launched in the past decade new advanced methods for effective hydrocarbons, release from low permeable rocks determine the global gas market. In spite of current American domination, there is a huge demand for this resource even at severe geological conditions, especially in Europe and China.

Hydraulic fracturing (rock stimulation), enables fractures creation in shale deposits. Taking into consideration presence of any geomechanical barriers, that prevent fracture propagation beyond shale formations, it is an important to propp the rock and allow gas flow to a borehole. It can be optimized by propping agents commonly applied as quartz sands only for shallow reservoirs and fissile shales (USA). Whereas, ceramic proppants are designed to meet rigorous downhole conditions on the high depths to increase output by 30 - 50%. In comparison to other proppants, ceramic ones predominate with the highest mechanical strength and roundness coefficient, lower solubility in acids and uniform size.

The aim of this research was examination of the ceramic propping agents produced from natural resources (kaolin, bauxite) and mixed with polymers applied as a binder. The proppants were produced by mechanical granulation and sintering at high temperatures. Utility of the raw materials was determined on basis of the TGA and BET measurements and bulk density. Particle size distribution was estimated due to laser diffraction technique and compared with visual evaluation (morphology and shape) by SEM. XRF and EDS enabled chemical analysis of the raw materials. Quality of the sintered granules was proved by roundness coefficient and bulk density outcomes. The µCT was a key investigation of proppants shape and pore size and distribution inside material. Moreover, 3D models enabled prediction of proppants settlement in the fissure. SEM with EDS studies enabled characterization of their microstructure, morphology and chemical composition. Moreover, turbidity and proppants solubility in acids were measured to predict a risk of decay in the well. Resistivity to high stress, which influences the integrity of created fractures, was established by proppants subjection to crush tests.

The obtained results reveal utility of the ceramic propping agents for enhanced unconventional gas output in high pressure, temperature and low permeable shale rocks. Moreover, it is an opportunity to develop European gas market and thus become more independent.

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Nanostructured mineral materials for controlled release of corrosion inhibitors in reinforced concrete

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The corrosion of steel rebars is one of the major causes of deterioration and limited service life of reinforced concrete structures. In fact, concrete provides the ideal environment for protecting embedded steel because of its alkalinity. However, carbonation and chloride ingress lead to corrosion of the steel rebars producing voluminous corrosion products which induce internal stresses leading to concrete cracking and spalling.

A way to circumvent this problem is the use of corrosion inhibitors added to the cement mixture. The direct addition might change the concrete properties reason why encapsulation of inhibitors in micro- or nano-containers for later release is an attractive solution.

In this work several corrosion inhibitors were loaded in mineral nanomaterials – layered double hydroxides – and their efficiency in controlling the corrosion of steel in simulated pore solution was investigated by electrochemical techniques. The characterization of the structure and morphology of the new material and the release kinetics of the inhibitors from the containers complements this study.

Intangible assets of iron ore tailings in building materials

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In today's age of intangible assets, the technological improvement of processes and products and the mitigation of socio-environmental impacts, together with the feeling of pleasure, well-being and satisfaction provided by any given product, are regarded as strategic for companies to maintain and devise new market opportunities. For the mineral extraction industry, the multidisciplinar and transversal character of strategic design might contribute to the development of such intangible values. The increase in ore tailings and solid waste generated by the industry, as well as its inadequate disposal, has awakened concerns over the sustainability of its processes and products, mainly due to the underlying social, environmental and economic issues, and consequently is affecting the market business. A critical review of the literature was carried out to ascertain the technological and environmental potential of the iron ore reject (IOR) and showed that the incorporation of IOR in building products, similar to conventional concrete blocks, might contribute to add value to the mineral extraction industry.

The IOR was first evaluated against river sand (RS), the aggregate commonly used in concrete blocks, through physical, chemical and morphological characterisation, as well as leaching and dissolution tests, as specified by the relevant Brazilian standards. Test results showed that the IOR contained fine, crystalline and dense particles, with no toxicity, thus demonstrating the feasibility of its technical use as filler or aggregate. Subsequently, physical and mechanical properties of pavers and structural blocks produced with 10% IOR in partial replacement of RS were investigated and compared with those of conventional products. The blocks produced with IOR were found to be comparatively stable in terms of dimensional changes and absorb less water (less porous) than the conventional concrete blocks, which suggests greater durability. Also, IOR blocks present the mechanical strength required by the Brazilian standards. Thus, with the incorporation of IOR the final product acquires a new intangibility and becomes cheaper and more attractive, hence, more competitive, while promoting the industry's efficient and effective introduction of innovation through the new found use for IOR.

Key Words: iron ore tailings; tailing dams; recycling; strategic design; synthetic aggregate.

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Physical and mechanical properties of cement mortars with direct incorporation of phase change materials

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The rapid world economic growth has led to an increase in the energy consumption. The fossil fuels dominate the world energy market. However, the fossil fuels are running out and present high costs. On the other hand, its use is related with the emission of harmful gases into the environment. Thus, the energy efficient use and the possibility of the use of renewable sources of energy are becoming increasingly important.

The energy efficiency of buildings is now one of the main objectives of regional, national and international energy policy, since this are one of the leading sectors in energy consumption in developed countries. The construction solutions based into the use of renewable energy contribute to increase the energy efficiency, to decrease the use of fossil fuel reserves and to reduce the pollutant emissions into the atmosphere. The use of renewable energy sources is a key factor to reduce the energy dependence of the buildings. Therefore, the heat storage possible with phase change materials (PCM) is a strategy to obtain buildings with high energy performance. The phase change materialshave the ability to reduce the temperature variation, due to their capability in absorbing and releasing energy to the environment.

The PCM can be incorporated into building materials using different methods, such as encapsulation, shape-establization, direct incorporation and absorption. The most common form of this material utilization is the encapsulation. Currently, there are still high production costs for the PCM encapsulation. Thus, it becomes urgent the development of new construction materials based in techniques and raw materials, with high thermal performance at low cost. These solutions become extremely competitive compared with traditional solutions with low contribution to energy efficiency. It is imperative the development of mortars for interior coating with PCM incorporation based on inexpensive raw materials (non-encapsulated PCM), contradicting the production costs of materials based on macro or microencapsulated PCM.

During the last years, several studies of construction materials with incorporation of encapsulated PCM have been published. The incorporation of PCM microcapsules in gypsum plaster boards, concrete, mortars, blocks and bricks was covered by these studies. The main objective of this work was the study of the influence of incorporation of phase change materials in cement mortars, evaluating their physical and mechanical properties. Based on the obtained results, it can be concluded that the addition of these materials caused some changes in the cement mortars properties in fresh and hardened states.

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Influence of heating rate on the microstructure and mechanical properties of porous fluorapatite ceramic developed from clay and natural phosphate

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Fluorapatite porous ceramic has been developed by solid state process from clay and natural phosphate mixture sintered at 1100 for 2 h with both heating rate of 5°C/min and 10°C/min. The phase, microstructural and thermal characterizations of the samples were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM) and thermal analysis (TG/DTA). Brazilian and three-point bending tests were performed to evaluate the mechanical properties. XRD results showed a significant improvement in the fluorapatite apparition at 1100 °C. The SEM observation showed that the sample sintered at 1100 °C using heating rate 10°C/min was relatively dense. As a result of this densification, the flexural and tensile strengths at 1100 °C with heating rate 10°C/min (16.96 and 9.62 MPa, respectively) were significantly enhanced with heating rate 5 °C/min (17.5 MPa and 10.97 respectively).

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Analysis of self compacting concrete production and addition of recycled poly ethylene terephthalate powder

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Use and reuse of waste in construction complement the sustainable development of the sector. Poly ethylene terephthalate (PET) is the second most polymer found in landfills in Brazil. This research is about the incorporation of PET powder in the production of self-compacting concrete (SCC) and the study of fresh state in its three main features: cohesion, fluidity and resistance to segregation. In the hardened state the compressive and tensile strength were observed. Initially it was performed chemical characterization of PET laboratory tests credited by INMETRO and after been found that the residue was analyzed within safe limits this use was incorporated into the concrete. To meet the characteristics of a SCC is necessary that the stroke be rich in fines. Thus, mixtures were made with additions mass, relative to mass of the fine aggregate by 1%, 2%, 3%, 4%, 5%, 7% and 10%. SCC properties in the fresh state were verified by scattering tests by Abrams cone method, funnel V and L. In case hardened state tests were conducted to analyze the compressive strength, tensile and Scanning Electron Microscopy method (SEM). Although all the features have shown compression and tensile strength reduction, the additions of 1%, 2%, 3% and 4% met the minimum limits of SCC Brazilian Standard fresh state. SEM method made possible to observe the lack of interaction and involvement of PET powder with the cement paste, which contributed to resistance reduction. Regarding statistical analysis by ANOVA method, the resistance measures, all additions showed variations between them. Therefore, it can be concluded that for concrete recipes with residue levels above 4%, the minimum requirements specified by the Brazilian recommendations for self-compacting structural concrete have not been met.

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Advances in metals and alloys (B2)

Superplastic Forming and Friction Stir Welding Technology for Manufacturing of AA2195 Vessel

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Aluminum alloy 2195 is used in aerospace applications since it has a unique combination of high modulus and strength with relatively low density. Furthermore, it can provide a high strength with superior properties in cryogenic environment after heat treatment so they have been used for cryogenic fuel tank of space launch vehicles. In the present study, superplastic forming (SPF) and friction stir welding (FSW) were conducted on AA2195 sheets to manufacture a lightweight pressure vessel. This provides superior formability and more saving of materials in final products than conventional forming processes do. The dome section of the tank was manufactured by superplastic forming and cylinder sections were welded with friction stir welding. Electron beam welding (EBW) is also used to weld an inlet boss to the cylinder and to join the final parts together. The results indicates that the optimum condition for superplastic forming of this alloy is a combination of strain rate of 10^{-4}/sec and strain rate sensitivity of 0.44. It is shown that the highest strength was obtained from the friction stir welded specimen with rotation rate of 600 rpm and traveling speed of 240 mm/min for this alloy.

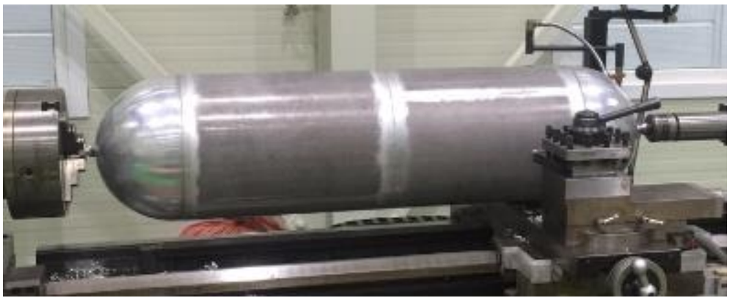

Figure. Photograph of a cylindrical vessel welded with FSW technology and the dome with superplastic forming technology

Correlation between the microstructure, thermal and electrical properties of $Cu_xAs_{50}Se_{50-x}$ chalcogenide glasses by using DSC and AC impedance spectroscopy

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Investigations on thermal properties of $Cu_xAs_{50}Se_{50-x}$ chalcogenide glasses prepared by the conventional melt quenching method were carried out using a differential scanning calorimeter (DSC). The measurements were performed in non-isothermal regime at different heating rates. It was established that copper introduction into As-Se amorphous matrix reflects on complexity of structural network. This was indicated by double crystallization process phenomenon accompanied with multiple melting endotherms observed in the DSC thermograms of the compound $Cu_{15}As_{50}Se_{35}$. These effects have been assigned to Cu_2Se and As_2Se_3 as a products of fragmentary crystallization of the basical structural phase Cu_3AsSe_4 in this sample. It was also noticed that the maximum of crystallization processes shift to higher temperatures with increase of the heating rate. The increament of peak areas as a function of heat treatment speed was explained as a consequence of the crystallization rate increase with increasing heating rate. The complexity of structural network caused by copper doping also reflects on electric properties measured on device Source Meter Keithley 2410. Impedance spectra of $Cu_{15}As_{50}Se_{35}$ showed two semicircles already on room temperature, indicating the phenomenon of phase separation and existence of two polarization procceses in a different frequency ranges. Dispersion curve of the real part of dielectric permittivity also contains two slopes. Switching effect was examined by recording the I-V characteristics on which the transition from low-resistance to high-resistance state was clearly noticed.

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Correlation of electrical and structural properties of semiconducting glassy chalcogenide alloys Ag–$As_{40}S_{30}Se_{30}$

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Bulk samples of chalcogenide glasses from the system $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$ for x = 5, 10 and 15 at. % Ag were synthesized with the melt–quenching technique. Their electrical properties were investigated by impedance spectroscopy in a frequency range of 100 Hz to 1 MHz at different temperatures. A preliminary structural analysis of prepared glassy alloys by X–ray diffraction technique and scanning electron microscope confirmed the amorphous nature for the sample with x = 5 at.% Ag, the amorphous phase separation for the sample with x = 10 at.% Ag, and the coexistence of two phases (amorphous + crystalline) for the sample with x = 15 at.% Ag. Therefore, a detailed analysis of impedance spectra by means of equivalent circuit models was used to establish correlation between the distinct microstructures and electrical properties of these compounds. The observed changes in electrical conductivity with Ag concentration could, inter alia, be ascribed to the modification of microstructure of prepared chalcogenide glasses. Additionally, the nature of variation of AC conductivity spectra is found to obey Jonscher's universal power law. Moreover, the complex impedance data of all samples revealed the presence of temperature dependent electrical relaxation phenomenon as well as their negative temperature coefficient of resistance behavior usually shown by semiconductors.

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Investigation of the stored energy in Cu-Ni-Si alloy after high-pressure torsion

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During the last decades, Equal Channel Angular Pressing (ECAP) has been successfully used to produce Bulk Ultrafine-Grained (UFG) materials [1]. The combination of a very small grain size coupled with the defect structure introduce during processing results in high yield strength and excellent mechanical properties. It well known that the stored energy in deformed microstructures, mostly in the form of their dislocation substructures, plays a significant role in controlling recrystallization nucleation which will affect the mechanical anisotropy of materials. The estimation of the stored energy can be carried out by several techniques. For example, bulk stored energy can be measured by Differential Scanning Calorimetry (DSC) and local stored energy can be estimated by microhardness, Transmission Electron Microscopy (TEM), diffraction line broadening analysis by X-rays or by Electron Back-Scatter Diffraction (EBSD). Detailed analyses on the stored energy of conventionally deformed coarse-grained materials can be found in the literature [2]. However, limited studies were devoted to estimate the stored energy in SPD-deformed materials [3].
The aim of the present work is to evaluate the evolution of stored energy in a commercial Cu–Ni–Si alloy after HPT processing at room temperature up 10 turns. First, the evolution of bulk stored energy was investigated by DSC. Afterwards, the local stored energy was measured using microhardness and EBSD.

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A DSC analysis of phase transformations in Mg-Ce alloy after severe plastic deformation

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Mg-based in general and Mg-Rare Earth alloys are gaining increasing interest in research and industry areas because of their good mechanical properties and weight saving [1]. Beside conventional techniques to produce these alloys, new methods were developed these last decades and are categorized as « severe plastic deformation ». Among these techniques that were applied to Mg-based alloys are Equal Channel Angular Pressing (ECAP) [2], High Pressure Torsion (HPT) [3] and Accumulative Roll Bonding (ARB) [4]. Such metal forming processes result in a strong grain refinement accompanied by a drastic strengthening effect. In addition to the « mechanical aspects », it is quite fundamental to consider the phase transformations that can occur during or after SPD processing. It has been well established that SPD processing influence considerably the occurrence, morphology as well as the kinetics of these solid-solid reactions [5]. Even if there is a strong lack of such studies in the literature, DSC technique was demonstrated as powerful and decisive technique in such studies [6]. The aim of this work is to study some aspects of the evolution of the precipitation and dissolution of intermetallic phases in a Mg-Ce using DSC technique. The main aspects are the sequence and the kinetics of these transformations.

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Prediction of gas content in aluminum melt alloys

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Hypoeutectic Al-Si alloys are the most common cast alloys of this family, with some minor elements such has Cu, or Mg, to improve mechanical properties after heat treatment. They are most used in the automotive and aeronautical industry. Hydrogen is in practice the only gas soluble in molten aluminum and is the main factor involved in the one of major problems associated with aluminum castings alloys: the porosity. Before pouring these molten metals into moulds, typical treatments are done, including, degassing with different possible techniques, to remove excess dissolved gas. This defect impacts on the reduction of the mechanical properties, loss of pressure tightness and poor surface integrity in castings.

Cooling curve analysis has been used in commercial applications for characterization of suitability of the melt to produce good components, for example, the level of silicon modification and the level of grain refinement, among others parameters.

The present work aims to compare the gas content, density index, cooling curve analysis and the validation technique image analysis, in a common Al7Si0,6Mg alloy.

Density index was determined with the density values from the reduced pressure test samples (RPT) and cooling curves were collected and mathematical treated to identify critical points, from molten state up to below solidification temperature, using treatment stations and suitable cartridge samples. Metallographic techniques were used to quantify the porosity in microstructure of samples.

The practical work carried out exhibited a correspondence between the amount of porosity in the microstructure, the specimen's density index value and some of its cooling curve parameters, such as the eutectic nucleation temperature and the eutectic growth temperature for the Al7Si0.6Mg alloy.

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Optimization via iterative processing of the grain boundary characteristics and its consequences on mechanical properties of nickel base superalloy 718

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The superalloy 718 (UNS N07718) is a fcc, age hardened nickel-base superalloy, commonly used for structural components that work under temperatures up to 650˚C and harsh environments, making this alloy widely used for airspace, offshore and nuclear components. The hardening effect comes mainly from the metastable phases γ" (Ni_3Nb-bct) and γ' ($Ni_3(Al, Ti)$-fcc). Other phases are present in a wrought microstructure as the (Nb,Ti)C and the δ phase (Ni_3Nb-orthorhombic). The thermomechanical processing route chosen for the alloy has a strong influence on its microstructural development. As the alloy presents low stacking fault energy (SFE), it is prone to the formation and multiplication of annealing twins. In this regard, iterative processing routes have been developed in order to manipulate the grain boundary distribution and increase the proportion of "special" low-energy boundaries ($\Sigma \leq 29$), with specific values of coincident site lattice (CSL). In addition of being low energy boundaries themselves, the annealing twins also take a role on the multiplication of the "special" boundaries, in particular $\Sigma3^n$ (Σ3, Σ9 and Σ27). It has been shown that a profuse network of such boundaries has beneficial effects on the properties of the alloy. The processing involves one or more steps of cold rolling followed by annealing heat treatments. However, this processing is accompanied by grain boundary movement and consequent grain growth. This can be a limiting factor for applications where a small grain size is a prime requisite.
The aim of this work is to investigate the effect of four thermomechanical processing routes, relating different degrees of cold deformation followed by annealing treatments where the δ phase was induced to control grain size, with a concomitant increase in the fraction of $\Sigma3^n$ boundaries. The characterization of the grain boundary character distribution and microtexture was performed via Electron Backscattering Diffraction (EBSD) analysis. The microstructural development of the alloy, especially the δ phase precipitation was observed by scanning electron microscopy. Tensile tests were performed in order to evaluate the influence of the microstructure on mechanical properties. The results show that a high proportion of $\Sigma3^n$ boundaries (> 60%) was achieved while maintaining a refined microstructure, via controlled precipitation of δ phase during processing. Regarding the mechanical properties, a positive relation of ductility with the amount of special boundaries was observed.

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Microstructural analysis of an AA 1070 aluminum alloy deformed by ECAP and cold rolling

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The use of severe plastic deformity (SPD) has shown a lot of interest in technological and industrial areas. Through this technique it is possible to produce ultrafine grains and/or nanocrystals in policrystals with coarse microstructure or also in monocrystals. After the process of severe plastic deformity the metal can present an improvement in their mechanical properties, mainly, an increase in tensile stregth. The severe plastic deformation (SPD) by equal channel angular pressing, has as main advantage the preservation of the transversal section of the sample after the SPD process. This technique occur at the insertion of the billet into an array along two channels with equal cross section. In this work, a microstructural evolution of an aluminium alloy AA1070 was investigated after the combined deformity process by ECAP route C and posteriorly cold rolling. An alloy AA 1070 has an initial coarse microstructure partially dynamically recovered, due to a process of hot rolling. For microstructural characterization of the samples was used an scanning electron microscope (SEM) using the electron backscatter diffraction technique (EBSD). The microtexture and the macrotexture were obtained through the electron backscatter diffraction(EBSD) using the scanning electron microscope with the lanthanum hexaboride (LaB_6) cathode and the *field emission gun scanning electron microscope* (*FEG* SEM). During the deformation was possible to obtain a microstructure with intense refinement of the grains obtaining ultrafine grains after the fourth pass of deformation by ECAP route C and cold rolling with reduction of 80%.

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Intergranular corrosion behavior of ZAMAK 3 in wet environments

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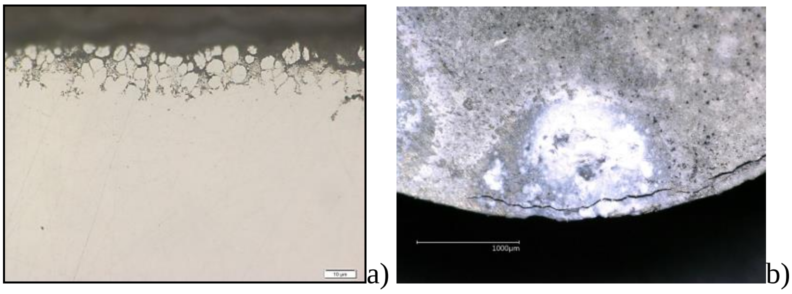
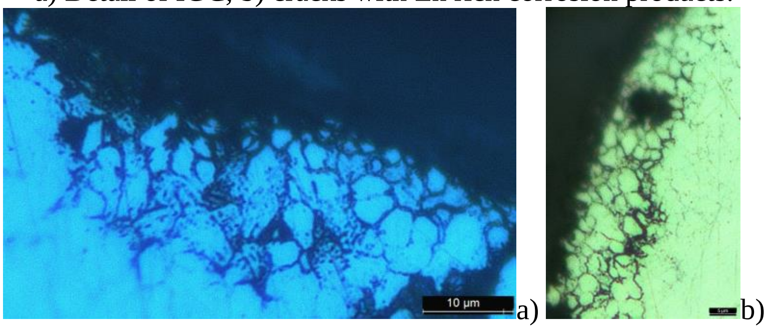
ZAMAK alloys are zinc based alloys widely employed in many applications such as automotive, buildings, clothing, toys, sports and electronic devices. They have a low melting point that allows a cheap and easy processing, and they can also count on high strength and wear resistance. However, ZAMAK alloys are prone to corrosion particularly in aqueous environments at elevated temperatures. In this study, tests have been carried out in order to analyse the behaviour of ZAMAK 3, Zn-4%Al, under wet conditions at different pH, temperature, and exposition time with respect to susceptibility to intergranular corrosion (IGC). Selective corrosion along grain boundaries was observed, see Figures 1 and 2. A high dependence of this corrosion phenomenon on pH and the microstructure from die casting was noticed.



a) b)

Fig. 1. Cross section of Zamak 3 after immersion in tap water (pH 7) at 95 °C for 2.5 days.
a) Detail of IGC, b) cracks with Zn rich corrosion products.



a) b)

Fig. 2. Cross section of Zamak 3 exposed to humid environments.
a) pH 2.8, during 3 days, b) pH 5 during 5 days. Details of IGC and cracks.

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Al-Mn-Ni ternary system: die cast microstructure and corrosion behavior

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Al-Mn-Ni ternary system with presence of minor chemical elements belongs to a particular die casting Al based alloys, UNI 6253, G-$AlNi_2Mn_2Ti$ (Fe0.5) F or Pyral classification. It is mainly used in applications wherein specific strength value is relevant, such as the transport industry and high corrosion or aesthetic properties are demanding. There is a lack of information related to microstructural characterization, particularly, attending the degree and distribution of cast defects and the relationship with specimens studied direction. This study has been looking for the strong relation between cast microstructure and defects concentration, such as microporosity and shrinkages. It has been used chemical attack with 0.05HF solution during 10 seconds, resulting the main microstructure formed by Al rich phase, as dendrites such as globular morphologies, and intermetallic phases rich in Fe, Mn, and Ni mainly, Furthermore, since Al base alloys leads to suffer localized corrosion, has been analyse their susceptibility against intergranular corrosion using different pH, time and temperature tests. The strong relation between microstructure and defects such as corrosion type playing with different media, from acidic to caustic pH environments, have been the main analysis done at this paper. Figure 1 shows heterogeneous cast microstructure, resalting microporosity at grain boundaries of Al rich phase dentrites.

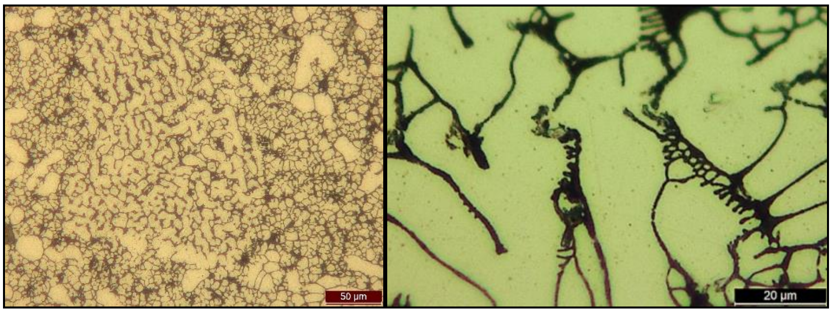

Figure 1. Die cast microstructure of Al-M-Ni system

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Advances in polymers (B3)

Influence of self-organized fluid flows on secondary and tertiary structure of bio-macromolecular system

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Spatial arrangement of bio-macromolecular systems affects their function and role in physiological processes, as is generally known. The modification of the secondary and tertiary structure of the given system occurs due to the changes of temperature, pH, ionic strength, shear forces, etc.
In this work is presented a new approach enabling initiation the changes of secondary and tertiary structure of the macromolecular system in the solution without modification the pH or ionic strength of the system. For this purpose is used the self-organized fluid flow in the form of Bénard-Marangoni convective instability. The result of continuously repeating the uneven shear strain of macromolecules in organized flowing solution is the change of mean coil size, its thermal stability and self-organizing capabilities, manifested through the changes in the surface activity at the interfaces or during the formation of self-supporting polymeric film. These changes can have significant implications, for example in producing smooth thin foils for medicinal application.

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Poly(1,4-cyclohexylene 2,5-furandicarboxylate): using 1,4-cyclohexanediol to enhance the thermal properties of FDCA-based polyesters

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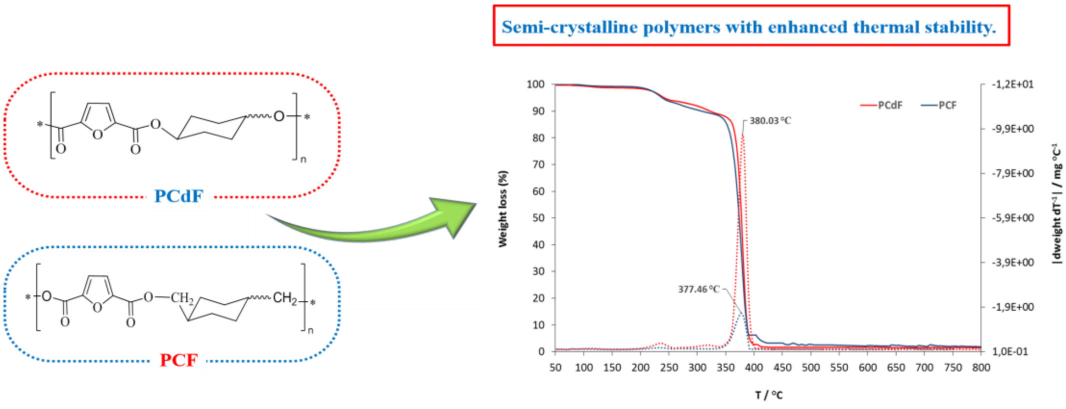
In the context of a sustainable economy, the search for new materials from renewable origin is leading to a revolutionary change in polymer science. In fact, in the last decades new polymers with improved thermal and mechanical properties have emerged, which could be used in the most variable field of applications. In this context, polyesters from 2,5-furandicarboxylic acid are among the most promising. This work presents a comparative study between the new renewable FDCA-based cycloaliphatic homopolyester, poly(1,4-cyclohexylene 2,5-furandicarboxylate) (PCdF) and poly(1,4-cyclohexanedimethylene 2,5-furandicarboxylate) (PCF). PCF was used for comparative reasons since it is the direct renewable substitute of poly(1,4-cyclohexanedimethylene terephthalate), and also they are structurally related.
PCdF and PCF were synthesized from dimethyl-2,5-furandicarboxylate, 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol, respectively, through a typical two-step polycondensation approach. The ensuing homopolyesters were extensively characterized using structural, thermal, thermo-mechanical and crystallographic techniques. PCdF and PCF have shown to possess semi-crystalline character, exhibiting both glass transition and melting temperatures around 174.9, 104.8, >300 and 201.9 ºC, respectively. Moreover, PCdF and PCF are highly thermally stable materials, with degradation temperatures around 380 and 377 °C, respectively. These results are very promising since PCdF presents a thermal behavior very similar to its related petro-based counterpart PCdT (T_d around 290 °C), which could find applications in the field of optical films and molding materials.



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Advances in composites and hybrid materials (B4)

Preparation of polyamide laminate composites with tailored electrical properties

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This work presents a method for preparation of polyamide laminate composites based on polyamide 6 (PA6) matrix dually reinforced by carbon fiber (CF) textile structure and different metal particles, *e.g.*, Fe, Al, Cu or Mg. In the first stage, shell-core polyamide 6 microcapsules (PAMC) were synthesized by activated anionic ring-opening polymerization (AAROP) of ε-caprolactam in solution, in the presence of the metal powders. All metal-containing PAMC obtained have controlled molecular weight, composition and granulometry, the metal load varying in the 10-20% range (according to TGA). In the second stage, the PAMC are compression molded in the presence of CF textile structures to produce the reinforced laminate composites, comprising volume fractions of CF from $V_f = 0.25$ to $V_f = 0.50$. Previous studies on polyamide powders preparation by AAROP in solution proved the simultaneous introduction into the polyamide matrix of organic or inorganic fillers without any functionalization [1, 2] and the preparation of polyamide laminate composites based on PA6 matrices reinforced by polyamide 66 (PA66) textile structures and different types of nanoclays [3]. All laminates showed significantly improved conductivity in AC/DC mode. Light- and scanning electron microscopy, DSC and X-ray diffraction techniques are used for structural characterization. The mechanical performance of all composite materials is characterized in tension, flexion and impact. This fabrication concept permits to obtain polyamide laminate composites with improved mechanical performance and tailored electrical and dielectric properties.

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Potencial use of glulam beams made with teak wood in architecture

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Technological development of glulam wood was driven by the advent of synthetic adhesives in the 1940s. The need to optimize wood use for structural purposes in countries of the northern hemisphere, coupled with the creative appeals of architects and engineers who looked foward for large free spans and differentiated forms, made glulam wood widely accepted in these countries. In Brazil, its use is still incipient, however, pine and eucalyptus species have already been used commercially in the production of glulam beams, albeit on a reduced scale. Teak wood (*Tectona grandis*), original from the Indian subcontinent and Southeast Asia, was introduced into national territory in the 1960s and had a good adaptation to local environmental conditions. Of good natural durability, dimensional stability and workability, it is in the visual aspect that the teak most stands out. Its wood of brown-gold tone and of homogenous veins is appreciated world-wide, being considered a noble wood. In Brazilian forest plantings, it is cut from small diameters and used mainly in the production of eged glued panels (EGP) for furniture manufacture. Due to its aesthetic attributes, teak wood differs from those of pine and eucalyptus, revealing great potential for construction elements pre-fabrication, especially when the intention is to highlight them in architecture. Confronted with this, this article aims to evaluate the feasibility of using teak wood in glulam beams. For this, the influence of three variables on mechanical properties of glulam beams made with the studied species was evaluated: type and quantity of adhesive and pressing time. For adhesion, resorcinol-phenol-formaldehyde (RPF) and emulsion polymer isocyanate (EPI) adhesives were tested, EPI of lower cost. With the exception of EPI adhesive, for the pressing time of 3 hours, increasing the amount of adhesive did not affect the modulus of elasticity and the rupture of the beams. The beams produced with EPI presented higher values of MOE and MOR. Regarding glue line strength, RPF adhesive presented better performance, however, this result did not affect the structural strength of the glulam beams. For the beams bonded with RPF, the increase in the amount of adhesive and the pressing time did not influence the resistance of the glue line. For the beams bonded with EPI, the treatment with less adhesive and less pressing time was statistically inferior to the other treatments.

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Preparation of ZnS-PMMA nanocomposites thin films, study of its optical properties

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In this paper we report linear and non linear properties of thin films based on ZnS, nanocrystals dispersed into centro symmetric and transparent polymer matrix the Polymethyl-Methacrylate (PMMA). Samples were prepared from colloidal solution and deposited in glass substrate by spin coating technique .The resulting samples are characterized by UV−visible spectroscopy, the absorption spectrum exhibit a blue shift equal to 0.80 eV compared to the gap of respective bulk material.

Keywords: exciton, linear , quantum confinement effect

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Characterisation of Nanostructured Copper-Graphene Composites Processed by Mechanical Milling

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Copper and copper-based alloys and composites present the unique combination of high thermal and electric conductivity allied with strength and ductility and with creep, fatigue and corrosion resistance. They are thus a recognizable material choice for applications where the combination of transport, mechanical and tribological properties is required. However strength and hardness issues still subsist, and the development of new copper-based materials for improved part service life, reliability and suitability under extreme conditions is a target for players in the thermomechanical and thermoelectric industries.

This work reports on the production of Cu-matrix composites with increased properties via mechanical milling. The used approach envisages increased mechanical resistance through copper microstructural refinement to the nanoscale; functional properties are developed through the introduction of second phase graphene dispersions. Mechanical milling of mixtures containing copper and graphene platelets (2 wt%) took place in a planetary ball mill for times varying between 1-16 h, at 400 rpm. A ball-to-powder ratio of 20:1 and alumina vial and copper spheres were used, under dry conditions or with addition of isopropyl alcohol. SEM/EDS, size distribution, Raman spectroscopy, X-ray diffraction, and microhardness measurements were used to study the produced powders.

Attained results show that mechanical milling of the studied system produces nanostructured powders, with severe copper grain refinement and second phase graphene mainly distributed in particle boundaries.

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Nano-sized YSZ-metal composites produced by Mechanosynthesis

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Yttria stabilized Zirconia (YSZ) is an intensively studied material. It is known for its structural and biomedical applications, being the high mechanical resistance (when tetragonal phase is stabilized) the principal responsible [1]. Nano-sized dispersed metal in a YSZ ceramic matrix composites, commonly designated as a type of CERMET, are known for their high mechanical resistance associated with magnetic detectability [2,3]. An increase in thermal conductivity can also be found [4]. These CERMETs may find, for instance, application as a high resistance material allowing the detection of a contamination or degradation of the CERMET functional part.

Emulsion Detonation Synthesis (EDS) is an INNOVNANO patented production method used to produce, among other products, YSZ nano-sized homogeneous powders. The ceramic powders were used to obtain CERMET powders through mechanosynthesis of the YSZ powder with metal (<10 wt%) and sintered parts through vacuum sintering at 1400 ºC.

The results showed that the addition of small quantities of metal to YSZ markedly affects processing and properties. The CERMET powders revealed a higher aggregation than in the correspondent ceramic powder and the densification was negatively affected by the metal addition, delaying it to higher temperatures. The presence of metal changed the final phase composition and the higher the amount of metal the lower the stabilized t-ZrO_2 phase in the sintered parts.

The added amount of metal was not enough to attain percolation levels and the electrical and thermal conductivity was not much affected. On contrary, the VSM magnetic response exposed that the produced CERMETs powders and sintered products have a significant magnetic response.

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Thermal performance assessment/evaluation of polyurethane foams with phase change materials

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The use of thermal insulation materials is regarded as one of the most effective means of energy conservation in buildings. Polyurethane foams (PU) are widely used as insulation layers incorporated or associated to opaque building envelope solutions, as well as for other applications such as transportation, decoration and appliances, accounting for almost one-third of the polyurethane market. The PU foams have good insulating properties but their thermal regulation capacity can be enhanced by the incorporation of phase change materials (PCMs). The main goal of the present work is to assess the thermal characteristics of PU foams with PCMs and to quantify the potential as thermal regulator of indoor spaces, reducing the temperature peaks and decreasing the temperature swing through the PCMs capacity to store and release energy.

PU composite foams containing 5.0 wt% of PCMs were produced using general PU synthesis (reaction between an isocyanate and a polyol). The thermal and energy storage properties were evaluated for four different PU composite foams (rigid PU foam, a layered structured composite of rigid and soft foam, both with and without PCMs).To characterize the energy storage properties of the PU foams with PCMs (melting and solidification temperature and enthalpy), a dynamic scanning calorimeter (DSC 4000, PerkinElmer) was used, at a heating and cooling rate of 1ºC/min, in the range of 10ºC to 50ºC under a nitrogen atmosphere. PU foams with PCM have an endothermic peak and an exothermic peak in the process of heating and cooling in the range of 20–30ºC, respectively. The rigid PU foam has the highest value for the latent heat storage capacity comparatively for the composite rigid and soft PU foam. The thermal conductivity of the composites was measured using a transient plane heat source method (HotDisk Analyser, TPS 2500 S) and thermal flux meter method (steady-state method). In the temperature range before and after the peak phase transition (18°C to 26°C) of the PCMs, the thermal conductivity values are near to those expected for the rigid PU foam and composite rigid and soft PU foam. Results revealed that the value of the thermal conductivity increases with the presence of the PCMs in the PU foams in both methods.

Comparing the experimental results obtained for rigid PU foam with and without PCM, it was observed that the presence of PCMs led to a thermal amplitude reduction of about 2-3ºC. A similar behaviour was also attained for the composite rigid and the soft PU foam with and without PCMs, but the reduction attained is smaller (1-2ºC).

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Comparative analysis on the bond of ribbed carbon fiber reinforced polymer bars (CFRP) and ribbed steel bars under moderate temperatures

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This study analyzes the influence of different environmental conditions (freeze/thaw, 5 ºC, 20 ºC, 40 ºC and 80 ºC) on the bond of Ribbed CFRP bars, and the results are compared with those obtained on tests with steel bars. The tests included Pullout, SEM, AFM, TGA and DSC. The experimental results show that there are differences in the behaviour of Ribbed CFRP bar and also that temperature variations have an influence on their bond due to changes in the mechanical properties of the polymer resin. Ribbed CFRP bars have elevated $\tau\mathrm{max}$ values, similar to those obtained from steel bars, except at high temperatures (80ºC). Their failure mode varies according to the relationship between the shear resistance of the ribs and that of the concrete. Their slip at $\tau\mathrm{max}^{*}$ is similar. Instead the initial bond behavior of Ribbed CFRP bars is much less stiff than steel bars. However, after failure, ribbed CFRP bars have less ductile behaviour than steel bars. No differences were observed in $\tau\mathrm{residual}$ between the two types at temperatures of 20ºC or less, although at 40 and 80ºC this value is higher with steel than CFRP bars. This is due to the type of failure.

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Photocatalytic activity of TiO_2/graphene and TiO_2/graphene oxide nanocomposites

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Semiconductor-based heterogeneous photocatalysis has been one of the most promising processes for the treatment of contaminated water. Among the available catalysts, titanium dioxide (TiO_2) presents the best photocatalytic properties, being chemically and biologically inert, stable, non-toxic, cheap and easy to produce. However, its energy bang gap lies in the ultraviolet (UV) range, which is responsible for a reduced spectral activation, since UV radiation corresponds to only 5% of the solar spectrum [1]. For this reason, one of the main purposes of the scientific community has been to improve the photocatalytic performance of TiO_2, namely through an adequate doping of this material, or through the creation of nanocomposites, to enable photocatalysis occurrence by the incidence of visible light. One alternative concerns the application of nanocomposites of TiO_2 with graphene and graphene oxide to photocatalytic processes [2].

In this work, nanocomposites of TiO_2 with different weight concentrations of graphene and graphene oxide (namely 0.5%, 1%, 1.5% and 3%) were synthetized by a one-step hydrothermal method and characterized in terms of morphology, crystalline structure, vibrational modes and optical band gap. The photocatalytic activity of these nanocomposites was then evaluated through the degradation of methylene blue and ciprofloxacin solutions under UV and visible radiation. The results indicated that the studied nanocomposites presented higher degradation rates of the methylene blue than the pure TiO_2, which increased with the content of graphene/graphene oxide. However, these composites proved to be less suitable to degrade the ciprofloxacin solution than the pure TiO_2 nanoparticles.

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Processing using laser/plasma/electric field technologies (C1)

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Portland cement clinker production by concentrated solar radiation

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Concrete produced from Portland cement is one of the most versatile construction materials used in the world. The European Standard EN 197-1 defines Portland cement clinker (PCC) as a hydraulic material consisting of at least two-thirds by mass of calcium silicates, the remainder being Al- and Fe-containing clinker phases, among others. PCC is typically made by heating, in a rotary kiln, a homogenous mixture of raw materials to a calcining temperature above 600 °C and then a fusion temperature, normally around 1450 °C, to sinter them into clinker. Typically the materials in PCC are alite (C3S; Ca_3SiO_5), belite (C2S; Ca_2SiO_4), tri-calcium aluminate (C3A; $Ca_3Al_2O_6$), and tetra-calcium alumino ferrite (C4AF; $Ca_4Al_2Fe_2O_{10}$). Once the clinker is formed, it must be cooled rapidly to ensure maximum yield of C3S, an important component for the hardening properties of cement. PCC production is the most energy-intensive stage in cement production, accounting for more than 90% of total industry energy use. The typical fuel consumption of a five-stage preheating dry kiln can reach up 3.2 - 3.5 GJ/tonne clinker. So, alternative heating sources ought to be sought. Among them, concentrating solar thermal power facilities are capital intensive, but have virtually zero fuel costs. In practice, solar furnaces are advanced facilities which produce concentrated radiation fluxes up to 7000 kW/m^2 (“7000 suns”), and surface temperatures over 3000 K. However, not only is there an investment cost hurdle, but also there are technical challenges to overcome, in particular solutions for temperature control of large scale production reactors are still lacking. In processing grey clinker, it is known that the material becomes darker with increasing sintering temperature. Thence, the use of so-called ‘‘solar blind” pyrometers with a band-pass filter centred at around 1400 nm ought to work pretty well at temperatures above 1100 K thereby allowing reliable processing through better temperature control. In addition, closing the slat shutter immediately after the heating process should allow rapid quenching of the resulting product so that a high yield of C3S can be achieved. In this context, some exploratory tests were performed using the new PSA high concentration solar furnace SF40 in order to demonstrate the feasibility of producing grey clinker upon direct exposure of a mixture of clay and limestone under concentrated solar radiation. For this purpose, a short thermal cycle (<40 min) was devised including 5 min dwell times at temperatures in the range 900-950ºC and 1250-1300ºC, followed by 10-15 min at 1500-1550ºC. The chemical and mineralogical data of the solar clinker produced are encouraging since values of 51.0±6.9% C3S, 22.7±5.4% C2S, 8.6±0.4% C3A and 10.8±0.7% C4AF are similar to those observed for conventional type I Portland cement (according to EN 197-1). A decrease in lime residue from 1-2 to 0.2 wt% has resulted when the dwell time was increased from 10 to 15 min at 1500-1550ºC.

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Microstructure of zirconia/titanium composites prepared by Spark Plasma Sintering

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Advanced zirconia materials are promising engineering materials due to their excellent properties such as high wear resistance, chemical inertness or high bending strength. However, the application of these ceramic materials is still limited due to the sensitivities to crack propagation. It has been widely tested that incorporation of metal phase into ceramic matrix can improve the fracture toughness of the composite.

This work focuses on the fabrication of zirconia-titanium composites. A material of yttria-stabilized (3Y-TZP) matrix with addition of Ti metal particles were obtained by spark plasma sintering method. The different titanium content (0.0 vol% - 90 vol%) have been selected. The paper presents the results concerning the processing and characterization of ZrO_2-Ti composites. The phase composition, microstructure, selected physical and mechanical properties of obtained ceramic-metal composites have been studied. The effect of the addition of titanium on the grain size of ceramic matrix were determined.

The addition of titanium hindered densification of material. The composites were characterized by lower hardness than the ceramic samples with an increase in fracture toughness.

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Surface characteristics of austenitic stainless and tool steels parts manufactured by selective laser melting (SLM)

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Selective Laser Melting (SLM) is an effective process for creating intricate geometries in small parts. As the process evolves, surface roughness of non-conventional SLM materials still presents a challenge and is one of the major weaknesses of this additive manufacturing method for some applications. On this study, it is compared the productions of different geometries on one of the most SLM-friendly materials, 316L (AISI/SAE) austenitic stainless steel, and H13 (AISI) tool steel, mostly used in mould productions. The different powders were characterized in this study concerning shape, size, size distribution and structure. The parameters were varied in order to access the influence of the principal parameters on the surface roughness of 316L spheres, one of the most difficult geometries for layer-by-layer processes. It was also produced three different geometries in H13 tool steel: semi-sphere, cube and pyramid using different parameters. The results of the different processing parameters were compared and integrated, always focusing on the optimal point of energy density for the best surface roughness possible. For each geometry there are an optimal point within the same production, obliging to adjust the parameters to the different geometries having in mind the reduction in area between the STL file and the resulting part. Moreover, the difference in surface roughness depends on the geometry, showing that to produce some geometries with good surface roughness is difficult, requiring finishing procedure.

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Cerwave – Microwave/gas oven project to fire industrial porcelain

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Nowadays, the portuguese energy dependence on fossil resources exceeds 85%. The ceramic industry is a highly consuming of thermal energy, required in the drying and firing process. The growing competitiveness, needs and opportunities, boost us in the search of alternative and more energy efficient technologies. In this context, a new method that uses microwave radiation for the porcelain firing is presented. The specificities of highest volumetric heating, centred in the material as direct result of the electromagnetic radiation absorption, allow to predict shorter processing times, speeding up the processes, with possible reduction of the sintering temperature.

According to tests carried out in a tunnel hybrid oven, which combines the microwave radiation with the conventional gas technology, we achieve an energy consummation of 4%. Figure presents the hybrid microwave/gas oven.

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Multiferroic Ceramics of the $Bi_{1-x}La_xFe_{0.50}Sc_{0.50}O_3$ Metastable Solid Solutions System Prepared Using High-Power Activation

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Single-phase perovskite ceramics of the $Bi_{1-x}La_xFe_{0.50}Sc_{0.50}O_3$ system can be prepared using the conventional ceramic route, only when the lanthanum substitution rate (x) is at least 80 at.%, while application of the high-pressure synthesis is needed if $x<0.80$. The $Bi_{1-x}La_xFe_{0.50}Sc_{0.50}O_3$ ceramics ($0\leq x\leq 0.80$) were prepared at 6 GPa and 1370-1470 K from the pre-synthesized (10 min at 1140 K at ambient pressure) stoichiometric oxide mixtures. Three structural phases were found in the $Bi_{1-x}La_xFe_{0.50}Sc_{0.50}O_3$ system. The as-prepared phase at $x\leq 0.05$ is an antipolar *Pnma* with the $\sqrt{2}a_p\times 4a_p\times 2\sqrt{2}a_p$ superstructure. An incommensurately modulated structural phase with the *Imma*(00γ)s00 superspace group is observed for $0.10\leq x\leq 0.33$, while a non-polar *Pnma* phase ($\sqrt{2}a_p\times 2a_p\times\sqrt{2}a_p$) forms at $x\geq 0.34$. Below T_N ~220 K, all the obtained phases exhibit the same long-range *G*-type antiferromagnetic order with a weak-ferromagnetic component. The very narrow compositional range of $0.33\leq x\leq 0.34$ is of a great interest since it corresponds to solid solutions with T_C close to T_N and, therefore, with the maximal lattice-magnetic coupling effect expected.

The $Bi_{1-x}La_xFe_{0.50}Sc_{0.50}O_3$ ceramics synthesized under high-pressure from the oxide mixtures were rather inhomogeneous and porous. Although quality of those ceramics was satisfactory for structural and magnetic studies, dielectric measurements were hardly possible because of high electrical conductivity. In this work, the advanced preparation methods were applied. The powders corresponding to the compositions with $x=0.33$ and 0.34 were prepared using a sol-gel method followed by calcination at 870 K. The calcined product was found to be a single phase perovskite although poorly crystallized. The powders were then sonicated in ethanol media at 4 kW for 10 min. It was found that such a treatment results in further crystallization. Then the powders were compacted and subjected to a quasi-hydrostatic pressure of 8 GPa for 5 min at room temperature. Single-phase dense ceramics were obtained as a result of sintering of the compacts at 800 K for 48 h in air. We report on structure, microstructure characterization and measurements of dielectric response of these ceramics in comparison with those synthesized under high pressure.

This work was supported by project TUMOCS. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 645660.

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Additive manufacturing (C2)

Free form fabrication of porcelain products by robocasting

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Robocasting, an innovative technique, can be used for free form fabrication of ceramic components. Ceramic slurries are deposited, through a nozzle system, layer-by-layer using an extruder deposition system robotically controlled. Ceramic industry is becoming more interested in this technology due to it's capabilities in processing liquids, suspension or pastes to develop new product shapes and functionalities.

The aim of the present work is to develop industrial ceramic pastes with appropriate rheological properties to be applied in a robocasting system (WASP delta 2040 turbo).
With this purpose, commercial roller paste (paste 1) was modified with alginate (paste 2), to observe the influence of the organic compound in the paste processability.

Raw materials were characterized by Coulter Counter method, Brunauer–Emmett–Teller isotherm (BET), Thermogravimetry (TG) and Differential Thermal Analysis (DTA), Dilatometry, Scanning Electron Microscopy (SEM). Pastes' rheology was accessed through a cone-plate rheometer.

For paste 1 and paste 2, samples with 20×20×40 mm and 20×10×60 mm were printed to be used in compression tests and flexural tests, respectively. After sintering at 1350C during four hours, the samples were characterized in terms of porosity by Arquimedes method and linear retraction on three directions (x, y, z). The mechanical properties were accessed from dried and sintered samples. The fractured surface was observed by SEM.
To test the processing capabilities of the pastes, two models with 3D complex geometry were printed with either paste 1 and paste 2.

The incoming results show that robocasting technique is a promise new technique for the ceramic industry. Regarding the level of precision and surface quality of the printed models, the advance of this technology will be influenced by the study and optimization of the process parameters.

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Cork-Polymer Composites based on Polylatic Acid for Fused Filament Fabrication

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The need of new materials for 3D-Printing (3DP) world is arising. The combination of biodegradable polymer matrices with natural materials can be a solution for the development of new materials for 3DP. Cork is a natural, versatile and sustainable material, being an emblematic material in Portugal. It is the outer bark of the cork oak tree *Quercus suber L.* and its main chemical composition is based on suberin (33-50%), lignin (20-25%); polysaccharides (12-20%) and extractives (14-18%). Structurally, cork presents tiny hollow cells of hexagonal shape in closed-cell foam [1].

Fused filament fabrication (FFF) is one of the 3DP techniques and it is based on additive principle, an extrusion-based process, in which a plastic filament is heated and selectively extruded via a nozzle layer by layer.

The present study is focused on the development of cork-polymer composites (CPC) based on polylatic acid (PLA) for FFF. Cork powder from a Portuguese cork producer and an Ingeo^{TM} Biopolymer PLA 4032D from NatureWorks were used. CPC were prepared in a Brabender type internal mixer.

PLA usually exhibits cold crystallization behaviour during melting and post-melting crystallization behaviour during cooling. This work proposes the study of CPC non-isothermal cold crystallization kinetics to better describe the cold crystallization behaviour during FFF. The mechanical properties of CPC can be partially dependent on how cork influences the crystallization. The influence of cork on the nucleation and crystal growth behaviour of PLA were studied by Liu model [2], a combination of Avrami [3,4] and Ozawa [5] models. Crystallization activation energy (ΔE_c) was determined through Kissinger model [6].

Results showed that both cold crystallization temperature (T_{cc}) and melting temperature (T_m) of PLA matrix decreased with the addition of cork. It was shown that cork powder surface acted as a nucleating agent during non-isothermal crystallization.

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Additive Manufacturing of porcelain parts by robocasting

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Additive manufacturing (AM) is a technique well stablished for metals and polymers. In this particular case, robocasting with ceramic materials, is targeted to biomedical applications such bioglasses and pourous structures as scaffolds of calcium-phosphates. Robocasting is one of the AM techniques in which a nozzle is used to extrude and deposit a high concentrated suspension (ink) in filaments, layer by layer. This method has the advantage of making it possible to obtain a piece in less than 24 hours, since the deposition until the sintering process of the piece. Also, it provides a piece with a good green density resistance due to a high concentration of solids.

This work includes different steps such as: (i) preparing robocasting inks, using the raw material of porcelain for the production of different suspensions with high solid content and the minimum amount of additives, (ii) thermal, morphological and and rheological characterization of the particle suspensions; (iii) printing with optimized porcelain inks and characterization of printed bodies.

In (i) it was maximized the concentration of solids to 62.5 wt.%, and studied different additives like Dolapix (as dispersant) and Polyethylenimine- PEI (as floculant).

In (ii) it was analysed the influence of those additives in sintering process. In addition, the maximum diameter of the particles in suspension was established in 10µm, and the media rounding 4µm. The rheological properties were studied using a rotational rheometer Kinexus Lab+ (Malvern) majoring the viscosity, elastic modulus (G') and the yield stress point. Those tests are the main focus of this work to guarantee that the ink as a viscous component and an elastic one. The ink should be capable of remain the shape, during all the deposition process, supporting the weight of the next layers. Furthermore, the amount of 0.15 wt.% of additive PEI is viable at a 100 s^{-1} shear rate with a 1.5 Pa yield stress point.

According to (iii) the printed bodies had a regular and homogeneous geometry and the layers joined successfully. Although, this porcelain pieces have some porosity associated and a water absorption of 0.07%. The densification obtained was 91%

The results obtained demonstrated that it is possible to produce ceramic parts from suspensions with a high amount of solids and appropriate rheological properties, by robocasting.

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Fully-Printed Zinc Oxide Transistors on Paper

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The implementation of solution-processed or printed inorganic semiconductors, such as zinc oxide (ZnO) is becoming a real alternative to organic semiconductors in printed electronics regarding chemical stability, switching speeds and mobility. We report the development of a fully-printed inorganic transistors on glass and paper substrates, whose channel is based on ZnO nanoparticles blended in ethyl cellulose (EC). These devices exhibit low operation voltages (-2 to 4 V) where those on glass have a subthreshold swing (SS) of 0.06 $\mathrm{Vdec^{-1}}$, a saturation mobility of 5.73 $\mathrm{cm^2\,V^{-1}s^{-1}}$ and an on/off ratio of $8.74\mathrm{x}10^3$ after annealing at 350 °C. On the other hand, when printing them on paper, the processing temperature is limited to 150ºC and the devices present a SS of 0.11 $\mathrm{Vdec^{-1}}$, a saturation mobility of 0.08 $\mathrm{cm^2\,V^{-1}s^{-1}}$ and an on/off ratio of $6.70\mathrm{x}10^3$.

Investigation in this field could potentiate effective roll-to-roll fabrication of printed logic circuits, showing huge implications for industrial printing standards. In the near future, we foresee this technology to be omnipresent in a wide range of applications, reaching from smart packaging to wearable electronics owing to the present proof-of-concept of a fully-printed inorganic transistors.

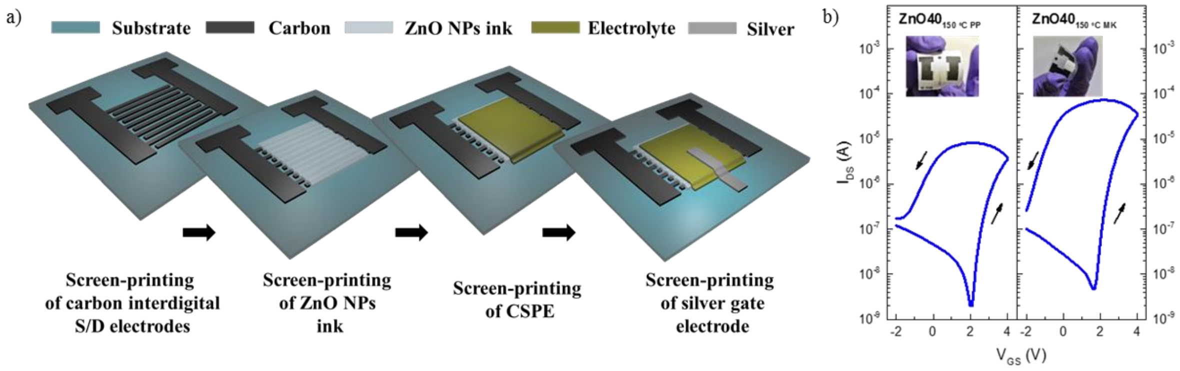

Figure 1. a) Schematic representation of the developed fabrication steps for the fully-printed ZnO transistors. b) Representative transfer characteristics of the ZnO40 transistor on printing paper and the ZnO40 transistor on MFC Kraft, respectively.

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Binder selection for 3D printing of porcelain parts

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Additive manufacturing (AM) is a disruptive conformation process which allows fabrication of parts with complex shapes and functionality. 3D Printing (3DP), also known as Binder Jetting Printing (BJP) is one of the additive manufacturing techniques in which the material is used in powder form. In the last years, this technique has been used as prototyping tool. However, due to its potential to open new markets and products, there is an increase interest from industrial companies to use and exploit AM as a production route. This is the case of Porcelanas da Costa Verde and its interest in producing porcelain parts trough 3DP. Although AM is relatively well developed for polymers and metals, this is not the reality of ceramics. AM of ceramics has enormous challenges, from the preparation of the batch, to the layer deposition and finally to the consolidation of the layers. In the case of 3DP of porcelain powders, one of the first concerns is the choice of appropriate binders as additive for the porcelain powders in order to achieve high mechanical strength in the green printed parts.

In this work several binders are studied as additives for Costa Verde porcelain powders. The influence of the binders in the porcelain powders “printability” is studied, discussed and compared among them. The ratio of porcelain/binder is also a key parameter and is under study in this work. Printed parts are characterized in the different steps of the production cycle, from the green parts until densification. Density, porosity, microstructure and dimensional stability are reported for all the printed parts. The relations between nature and content of the binders, printability and final properties are established. The comparison with parts produced trough conventional method is presented.

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Coatings and interfaces (C3)

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Preliminary Deposition and Study of Multilayer (Ti,Al)N/(Si,Al)N Fillms

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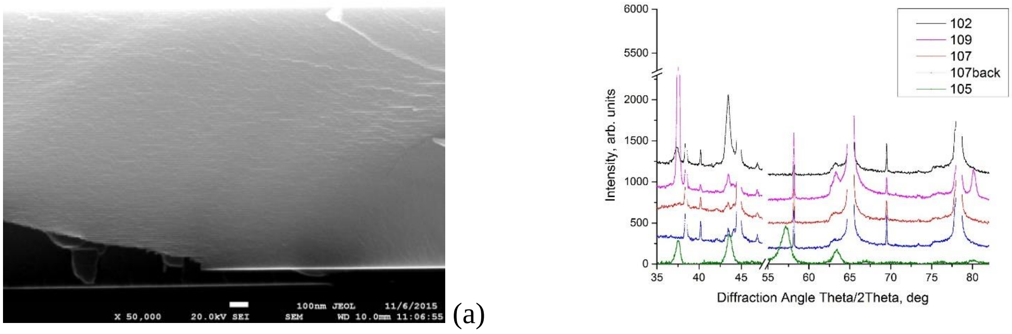
The performed study is about deposition and characterisation of multilayer TiAlN/SiAlN thin films deposited by reactive magnetron sputtering. The deposition and calibration were done first with single layer films of TiAlN and SiAlN. Then multilayer (Ti,Al)N/(Si,Al)N films were obtained with total thickness around 1÷1.5 microns and various bilayer thickness in range of 10÷48 nanometers.



(a) (b)

Figure 1. SEM-image of multilayer TiAlN/SiAlN film, cross-section view (a); X-ray diffraction patterns of studied multilayer films.

The elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS) and wavelength-dispersive X-Ray spectroscopy (WDS). Surface morphology and cross-section were analyzed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Bilayer thickness and surface roughness were evaluated by X-ray reflectivity analysis (XRR). The phase composition and microstructure were studied by X-ray diffraction measurement (XRD. Mechanical properties were studied by hardness and elastic modulus measurements by nanoindentation.

Relations between elemental composition, especially Nitrogen level, and mechanical properties were found. The bilayer thickness impact to the microstructure, phase composition and values of hardness were studied.

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Surface Analysis of Materials by Elastic Scattering of MeV Ions

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A wide range of surface analysis techniques has been developed, involving e.g. ion, electron and photon beams interacting with a solid target. The techniques are, generally, complementary and provide target information for depths near the surface. Nuclear techniques, which are non-destructive, provide for analysis over a few microns close to the surface giving absolute values of concentrations of isotopes and elements. Their main applications have been given in areas such as scientific, technologic, industry, arts, archaeology and medicine, using MeV ion beams [1-7]. Tracing of isotopes with high sensitivities is possible by nuclear reactions. We use elastic scattering of light low energy ions and the energy analysis method. At a suitably chosen energy of the incident ion beam, an energy spectrum is acquired of ions from elastic scattering events, coming from several depths in the target. Such spectra are computer simulated and compared to experimental data, giving target composition and concentration profile information [4-7]. Elastic scattering is a particular and important case of nuclear reactions. A computer program has been developed in this context, mainly for flat targets [4-6]. The non-flat target situation arises as an extension.

Elastic scattering of α particles was used for analysis. The simulations used published nuclear data, namely for stopping power. Rutherford differential cross section was used. Very good computed fits were obtained to spectral data obtained for two main targets. T1 was a flat target consisting of a thin film of Ag deposited onto a thick Al flat substrate (Al/Ag). An Ag film of very good uniformity, with an estimated thickness of 0.1714 μm, was expected. Analysis was made through a $(^4\mathrm{He})^+$ ion beam at E_α=2.9 MeV and Θ_L=165°, giving an Ag film with excellent uniformity and thickness X_1=0.1610 μm, close to the expectation. T2 was a thick flat target of zinc sulphide (ZnS). Uniform distributions of Zn and S were expected in the target substrate. It was analysed through a $(^4\mathrm{He})^+$ ion beam at E_α=3.1 MeV and Θ_L=165°. Uniform concentration profiles were used with X_1 parameters of 2.5 and 1.5 μm for Zn and S, respectively. Elastic scattering, as a nuclear technique, has shown to be a powerful non-destructive surface analysis analytical tool.

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Nuclear Reaction Analysis of Materials using MeV Ion Beams

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A wide range of surface analysis techniques has been developed, involving e.g. ion, electron and photon beams interacting with a solid target. The techniques are, generally, complementary and provide target information for depths near the surface. Nuclear techniques, which are non-destructive, provide for analysis over a few microns close to the surface giving absolute values of concentrations of isotopes and elements. Their main applications have been given in areas such as scientific, technologic, industry, arts, archaeology and medicine, using MeV ion beams [1-7]. Tracing of isotopes with high sensitivities is possible by nuclear reactions. We use elastic scattering of light low energy ions and the energy analysis method. At a suitably chosen energy of the incident ion beam, an energy spectrum is acquired of ions from elastic scattering events, coming from several depths in the target. Such spectra are computer simulated and compared to experimental data, giving target composition and concentration profile information [4-7]. Elastic scattering is a particular and important case of nuclear reactions. A computer program has been developed in this context, mainly for flat targets [4-6]. The non-flat target situation arises as an extension.

Ion-ion nuclear reactions were used for analysis. The simulations used published nuclear data, namely for differential cross section and stopping power. Very good computed fits were reached to spectral data obtained for two main targets. T1 was a thick flat target of extremely high purity pyrolitic graphite. It was analysed through the $^{12}C(d,p_0)^{13}C$ reaction at $E_d=1.40$ MeV and $\Theta_L=165^o$, permitting to find a ^{12}C step concentration profile along a depth of $X_1= 10$ µm. T2, obtained by high temperature oxidation of austenitic steel in C $^{18}O_2$ gas, had a reasonably flat oxide. A uniform concentration profile of ^{18}O was expected along 4.2 µm. It was analysed through the $^{18}O(p,\alpha_0)^{15}N$ reaction at $E_p=1.78$ MeV and $\Theta_L=165^o$, permitting to find a uniform concentration profile of ^{18}O with $X_1=4.5$ µm. Nuclear reaction analysis, as a nuclear technique, has shown to be a very powerful non-destructive surface analysis technique. The results which were obtained would be difficult to reach by other techniques.

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Formation of black silicon by application of different parameters of Ni-assisted chemical etching

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Black silicon (bSi) is a semiconductor material, a surface modification of silicon with very low reflectivity and correspondingly high absorption of visible (and infrared) light. The unusual optical characteristics, combined with the semiconducting properties of silicon make this material interesting for sensor applications. There has been significant interest in using bSi for silicon solar cells due to the excellent bSi AR and the potential for cost savings during industrial scale manufacturing.
The bSi can be produced by reactive ion etching (RIE) in fluorine, bromine and chlorine plasmas. Also, it can be formed by a maskless RIE employing CF_4 due to auto-masking of the surface at random spots.
In recent years, there has been much interest in the chemical formation of the silicon nanostructures by methods without electrical bias. Treatment of powder and group etching of several wafers for producing porous and pillar structures can be carry out stain etching, metal-assisted chemical etching - MACE with different metals (Ag, Au, Pt et al.), galvanic etching. Many studies have been devoted to etching of silicon covered with Pt, Au, Pd and Ag clusters and thin films. Non-precious metals include Ni, Cu and Fe is rarely used for MACE. The treatment of Si with thin film of Ni in HF and H_2O_2 promotes to form black silicon layers. Then, the various influences of the film thickness, etchant, temperature, illumination, treatment duration on bSi morphology are presented. The etching behaviors of silicon under various conditions are presented.
Formation of *por*-Si with Ni in HF-H_2O_2-H_2O is Ni-assisted chemical and photo-electrochemical etching of Si. Therefore, silicon etching proceeds in three steps:
Step 1: Ni-assisted chemical etching;
Step 2: *por*-Si formation without Ni;
Step 3: *por*-Si dissolution without Ni. The second and third step can occur simultaneously.
The *por*-Si morphology effects due to the illumination. The higher the reaction zone illumination, the greater the height of the Si agglomerates. *Por*-Si thickness is directly proportional to the Ni films thickness. The temperature and duration of treatment promotes growth rate of *por*-Si dissolution without Ni.

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Atomic layer deposition of high dielectric Ta_2O_5 films on boron doped diamond

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High-k dielectrics with values greater than that of Al_2O_3 have been targeted for use as the gate material in field effect transistors (FETs) as they suppress gate leakage current and are expected to control higher charge carrier densities for the same applied electric field compared to their lower-k dielectric counterparts. Coupled with boron doped diamond (BDD) semiconductors, these high-k dielectric gates are also well positioned for use in high power high temperature (HPHT) devices attributed to the efficient heat extraction properties of diamond.

The vital gate function of controlling current flow in the semiconductor is mainly influenced by the properties of the gate material (k value, insulation, presence of impurities) and interfacial properties between gate and semiconductor (coupling, presence of defects and interface traps). The gate deposition technique therefore becomes a crucial factor for ensuring desired composition and conformity to the semiconductor surface. Atomic layer deposition (ALD) is already a proven technique for the deposition of continuous, conformal thin films via sequential and self-limiting atomic reactions. It is beneficial to this application as gate thickness can be easily controlled and film impurities can be minimized by optimization of saturation conditions. ALD has been used extensively in the fabrication of Al_2O_3 gates for different wide bandgap semiconductor materials.

In this work tantalum pentoxide (Ta_2O_5), with k value greater than 20, is deposited via ALD onto BDD. In recent years ALD of Ta_2O_5 has been investigated using a variety of Ta and O precursors but its optimization for BDD substrates is undersupplied in literature, suggesting also that characterization of the Ta_2O_5-BDD interface is necessary, prior to any application. Steady growth rates have been achieved between 200 and 325 ^oC, as demonstrated by the ALD window with the steady growth rate of approximately 0.9 Å/cycle. It is anticipated that oxygen plasma on the BDD surface is necessary to activate it for ALD and possibly minimize the formation of traps and defects at the interface. SEM is used to obtain images of the film and interface made with BDD, XRR is performed to determine the film thickness and growth rate, and FTIR is used to demonstrate film composition. C-V measurements characterize the electronic properties of the Ta_2O_5-BDD stack and interface, so that the expected low leakage current could be determined.

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Deposition and characterization of CrN_x thin films obtained using the PVD technique

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In the last years there has been a huge demand for polymeric materials in replacement of the more traditional ones (i.e. metals), particularly in the automobile and electronics industry. In addition to their low density, superior design flexibility and low production costs, such polymeric materials can also be obtained with shining and highly reflective surfaces. Ultimately, these metallic looking surfaces will have improved chemical and wear resistance as well the ability to conduct electricity. To achieve this metallization on a particular surface, several plating techniques can be applied. One of such techniques is PVD (Physical Vapor Deposition) which can be used on polymeric surfaces and has low materials consumption and reduced environmental impact.

In this work, we report the results for the PVD (Physical Vapour Deposition) deposition of CrNx films on Si and ABS (Acrylonitrile butadiene styrene) substrates. Two sets of coatings on monocrystalline Si wafers were obtained: one in which the N_2 flow was varied and the other with increasing deposition time and constant N_2 flow. For the ABS substrates (oven type buttons) a plasma treatment with Ar, O_2 and N_2 gases was applied prior to the CrNx deposition. The CrN_x thin films on the Si substrates were morphologically, chemically and structurally characterized, whereas colorimetry analysis was used on the coatings deposited on the polymer substrates. Overal, the results have shown that the morphology, the chemical composition and the microcrystalline structure of the CrN_x coatings are influenced by the N_2 flow. The metallic looking films show CrN crystalline phases for N_2 flows above 2sccm. At the same time the stoichiometric relation CrN is achieved for 3sccm N_2 flow.

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$NaNbO_3$: the importance of anisotropy in multifunctionality

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$NaNbO_3$ is a multifunctional lead-free piezoelectric material with perovskite structure. In the present work, we report the characteristics of $NaNbO_3$ particles obtained by microwave-assisted hydrothermal method. The particles were obtained from the reaction between Nb_2O_5 and NaOH varying the time and synthesis temperature. The composition and morphology of products are related to synthesis conditions, being that fiber-like and cubic-like $NaNbO_3$ particles were obtained. The crystallization of $NaNbO_3$ particles produced $Na_2Nb_2O_6.nH_2O$ intermediate phase which is used as template to obtain $NaNbO_3$ in fiber-like particles. The particles were applied in flexible composites constituted by $NaNbO_3$ and PVDF polymer. The composites showed piezoelectric coefficient value between 0.9 and 8.0 pC/N, being that the higher value was to composite constituted by fiber-like particles. This can be explained by the fact that the fiber morphology allows the polarization to reach a long distance over the length of the fiber. About the photoluminescence emission, both fiber and cubic-like $NaNbO_3$ particles have emission in blue region (450 nm) and the metastable phase ($Na_2Nb_2O_6.nH_2O$) emits in 525 nm (green emission). The region of emission is related to different structural defects of materials. As photocatalyst, the efficiency of $NaNbO_3$ in fiber like particles is around 90% against 55% when $NaNbO_3$ in cubic-like particles are applied in decomposition of the Rhodamine B dye. Based on results, it is possible to observe that the anisotropic of particles is an important factor to improve the multifunctionality of $NaNbO_3$ particles.

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Post-deposition Hydrogen treatment effect on surface roughness and hydrophobicity of amorphous silicon films

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Amorphous silicon films were deposited by radiofrequency (rf) magnetron sputtering. Then, the films were treated by pure hydrogen gas at different pressures (1, 2 and 3 Pa) for 20 min, to investigate its effect on surface hydrophobicity (or un-wettability) and roughness. Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy was used to evaluate presence of Si-H bonds at the surface. Results obtained by the atomic force microscopy (AFM) showed a sharp decrease (the non-treated film had a root mean square value of 10.94 nm, which then dropped significantly to 6.69 nm for the 3 Pa hydrogenated film) in surface roughness as a result of hydrogenation. Optical transmission results revealed that optical properties were not affected. Contact angle measurements showed an enhanced hydrophobicity by 15 degrees for the 1 Pa hydrogenated film, and then it decreased for the 2 Pa and 3 Pa hydrogenated films. This result indicates that the decrease in roughness compromised the hydrophobization process.

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Effect of hydrogenation of amorphous silicon surfaces on protein adsorption

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We studied in this work, the adsorption of proteins on thin layers of amorphous silicon, depending on the surface conditions. We have a set of samples of sputtered silicon thin films, with different hydrogen concentration at the surface. Infrared spectroscopic analysis with the ATR method, ellipsometry and scanning electron microscopy revealed that the adsorption on the surfaces is enhanced on samples with highest hydrogen surface concentration. This result leads to the conclusion that the adsorption is caused by hydrogen bonds at the film / protein interface, which seems to be the dominant effect compared to surface roughness and wettability, which were found to decrease as hydrogen surface concentration increases.

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Adhesion between amorphous thermoplastics (Polycarbonate) and PVC membranes: a case study

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This work aimed at studying the adhesion between two polymeric materials, presenting different characteristics with respect to their adhesion interfaces: the i) polycarbonate, an amorphous thermoplastic and ii) PVC in the form of architectural membranes. At the beginning of this study, two different adhesives were selected, in order to study, which would promote better adhesion between the materials. The selected adhesives were based on silicone and on methacrylate, both of them with different chemical constitution to promote greater interconnection with the substrates. Polymeric adhesives have many benefits over conventional bonding methods. Namely, the ability to distribute the load evenly throughout its area, reducing the tension on a specific point, and the ability to join surfaces with low Van der Waals forces.

Polymeric materials such as PVC, at the molecular and atomic level, have bonds in the form of Van der Waals forces, which are very weak. In order to promote an increase in the molecular and atomic level of the surface, a surface treatment was selected to promote a higher molecular affinity between the substrate and the adhesive, thus leading to a stronger bond. A surface activator was used, an alcoholic solution, which has a substance for activating the surface of the substrate.

With the objective of studying the adhesion between the materials, an experimental set up was carried out, which consisted firstly in the evaluation of the contact angles. This test is based on the wettability theory. In order to promote good adhesion, the adhesive should have a high contact with the material, which means that the surface of the adhered material should be completely wetted by the adhesive. Thus, two samples were tested, with and without surface treatment. The untreated sample presented a hydrophobic behaviour, as shown by the high contact angle obtained. On the other hand, the treated sample presented a lower contact angle, promoting an increased wettability and thus better adhesion. The main objective of this test was to evaluate the effectiveness of the applied surface treatment. Finally, peel adhesion tests were carried out to verify the adhesion of the materials and to verify the best adhesive to use to obtain a better bond between the two materials. This test was intended to determine the adhesive strength of the bonding member and the adhesive strength between the two materials.

It was first observed that surface treatment resulted in good adhesion between the substrates and the adhesive. Then, the results show that a good adhesion between polycarbonate and PVC was achieved by using either silane-based or methacrylate-based adhesives, despite the last showed a significant better performance.

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Alloying effects at bicomponent Au-Cu and In-Sn particle arrays formation by vacuum-thermal evaporation

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Recently, the metal nanoparticles arrays (NPs) become an interesting material for technological processes such as (CNT's and other nanowires synthesis) and for different devices (e.g. sensors).

One of the attractive methods for forming arrays of nanoparticles with predetermined particle size is vacuum thermal evaporation using small amounts of evaporated material.

In this paper we tried to improve this technique for the formation of bicomponent metallic nanoparticle alloys, namely Au-Co and In-Sn, and investigate the structure and composition of obtained arrays by TEM.

Bicomponent nanoparticle arrays of Au-Cu and In-Sn were formed by sequential evaporation of preweighed portions of respective metals on amorphous 20 nm thick carbon layer. These samples were investigated using a transmission electron microscope FEI Tecnai G2 20 S-Twin, equipped with an energy dispersive X-ray attachment for microanalysis EDAX.

It is found that during sequential deposition of gold on copper (and copper on gold) particles consisting of Au-Cu alloy are formed. It should be noted that the particles of pure Au and Cu components were not found in the obtained bicomponent arrays. In the case of sequential deposition of In on Sn formation of nanoparticles that consists from pure In and Sn, instead of alloyed In-Sn in the obtained bicomponent arrays were found.

These phenomena can be explained in terms of phase diagrams. The "gold-copper" binary system that forms a continuous series of solid solutions, which indicates the Gibbs free energy of mixing, is negative, so such binary system shows tendency for mixing. In contrast, a binary system "indium-antimony" has a eutectic phase diagram that indicates a positive energy of mixing and tendency to partial delamination.

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Changing the polystyrene surface topography by phase separation

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Targeted treatment of the surface of materials with respect to maximum wettability or water repellency has been examined from many aspects for both organic and inorganic materials. The development of these patterns is inspired by nature, particularly by hierarchically structured materials such as lotus leaf.

In this study, we present a novel approach to modifications of polystyrene substrates by phase separation. The polystyrene surface topography was changed by the time sequence of dispensing a mixture of good and poor solvents, mutual proportions of these solvents and temperature of both, the substrate and the solvent. This leads to variation of the surface structure and thus to the affection of wettability, fate of cultivated cells or replication abilities of these texture into biomaterial foils.

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Scaling a HFCVD reactor for a semi-industrial operation mode

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CVD diamond-coated carbide tools (drill bits, end mills, indexable inserts) have been widely used in the machining of pre-sintered hardmetal and abrasive composites such as MMC and CRF. These tools combine the strength of the hard metal with the hardness of the diamond coating, prolong the life of the tool, allow machining without refrigeration and increase the dimensional precision. Most importantly, the machining speeds can also be increased without compromising the workpiece or the tool. The CVD diamond coatings are usually made by commercial hot filament (HFCVD) reactors made by very few specialized foreign companies. The know-how for the construction of such reactors for coating dozens of tools is in the hands of a few foreign companies.

In this work we report the results of the work involved in the scaling-up of a large homemade HFCVD reactor available at the University of Aveiro. Initially the reactor had the capacity to coat a maximum of 5 tools simultaneously, without guarantee of reproducibility of the coatings from deposition to deposition. After scaling-up, the reactor was able to coat up to 33 tools (drill bits and end mills) simultaneously ensuring maximum safety and reproducibility of the coatings. The tools can have diameters from 2 mm to 12 mm and heights to coat up to 100 mm. The modifications in the reactor included altering the deposition parameters such as total pressure (P), filament (T_f) and substrate temperature (T_S), that depend on the thermal load (number and size of tools) being coated, or the gas composition (CH_4, H_2) that had to be adapted to the new P, T_f and T_S values. As important as these are the more technical aspects related to the: - construction of the tool holders (material, materials of the base, geometry, placement of the tools); - filament holders (multiple lines of tools, space between filaments in the vertical and horizontal directions, total length); - inlet of gas (location of entry points relatively to tools and filaments, geometry and number of gas inlets in the reactor); - measurement of filament and tools (location of the measurement, thermocouple/pyrometer). All these are variables that have to be taken into account in the construction and development of HFCVD reactors for diamond deposition as they affect the deposition parameters, growth rate and type of diamond obtained. The development was closely followed in every step with a characterization of the coated sample tools by μ-Raman spectroscopy and scanning electron microscopy.

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Influence of processing conditions on the grain structure of sputtered copper thin films

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The need for ever-increasing energy efficiency and resource optimization has increased the expectation concerning the use of the latest technological developments to achieve those goals in several industries. Sputtering is an extensively studied deposition process, in which through the optimization of the deposition parameters it allows for obtaining tailor made materials with the appropriate set of properties and characteristics, such as grain size and preferential crystallographic orientations [1, 2].

The deposition process influences the materials propensity to develop twins within its matrix in low stacking fault energy materials, such as copper, as well as the density of dislocations inside the grains, for all metallic materials. Twins have been shown to have a contribution to mechanical resistance similar to grain boundaries, and thus position themselves as interesting hardening mechanisms for structural reinforcement of nanomaterials [2 -4].

In this context, the objective of this work is to compare the results of different sputtering conditions on the grain structure of thin copper films, including the resulting grain orientation and twin density. The microstructure characterization, grain size and twin density evaluations were performed by transmission electron microscopy (TEM). The crystallographic orientation was evaluated by X-ray diffraction (XRD) and by electron backscatter diffraction (EBSD).

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Controlling the Au/Iron Oxide interface to optimise plasmonic resonance for Magneto-Optic Diagnostics

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Anisotropic magnetic nanoparticles coated in plasmonically active metals (e.g., gold) have a number of applications such as surface enhanced Raman spectroscopy (SERS). Their combination of plasmonic and magnetic properties makes them uniquely suited to homogenous magneto-optic nanoprobe analysis. Unlike their counterparts in SERS, these particles require smooth surfaces for reliable analysis. However, the crystallinity of such nanoparticles may result in rough coatings when gold is nucleated upon their surface. In the present study, Iron Oxide particles were precipitated from ferric chloride with aspect ratios controlled by phosphate concentration. To maximise smoothness, sandwich like anisotropic nanoparticles were prepared consisting of a hematite core, silicon intermediate and an outer gold coat. The structure and surfaces of these particles were analysed by TEM, UV and XPS

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Recycling (C4)

Obtaining and characterization of granitic waste processed by hydrocyclone

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The reuse of pollutant solid wastes produced in distinct industrial activities as a source of alternative raw material it is of great interest. The waste generated in granite processing has caused great social and environmental concern due to the release of its solid effluents into landfills and other places. The recycling and reuse of waste from different industrial processes as new raw materials has been the object of various researches. The use of hydrocyclone in the treatment of residues can represent a very efficient tool for separation and purification of the granite residue. This work aims to characterize and analyse the technological properties of the granite sawdust residues submitted to the hydrocyclone process in comparison with the same residue without going through the hydrocyclone process. The results indicate that the material resulting from this process presented different characteristics from the material without the process, mainly in terms of granulometric distribution and technological properties. Was observed an efficient purification system to removal of coarse fractions, and the material resulted from this process exhibited different characteristics from the material without hydrocycloning. The specimens produced from the processed material (hydrocycloned) in comparison to the ones without hydrocycloning, showed a greater physical properties change related to the final temperature of burning, concluding that the process provides a better choice of usage temperature.

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Physic-mechanical behavior of stabilized soil block with lime based-fibers (waste tyre rubber and glass fibers)

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The use of scrap tyre rubber fiber is one of the methods of waste management. This paper highlights the salient observations from an experimental survey on the effect of the use of fibers of scrap tyre rubber and glass on the mechanical properties and behavior of stabilized compressed soil's blocks (SCSB). In this study a ratio of 12% of lime beside 0.05%, 0.1%, 0.15%, 0.20%, 0.25% and 0.30% of fibre to the weight of dry soil. The results indicate that the compressive as well as shear strength and ductility increase with the proportion of fiber.

Keywords: Compressed Earth Blocks, Scrap tyre rubber fiber, Glass fiber, behavior, Compressive strength.

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Reuse of Gypsum Residue in the Manufacturing of 3D Decorative Wall Covering Panels

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This article focuses on the application of recycled gypsum in the manufacturing of 3D decorative wall covering plates and their possible economic and environmental impacts. The gypsum recycling process used in this research consisted in two simple steps: waste collection in constructions and demolitions, and hand trituration. 3D decorative wall covering panels are commonly a composite of cement, sand and gypsum, and they must meet the following requirements: aesthetics, watertightness, thermal and acoustic comfort. Five alternative compositions were made with partial and complete replacement of commercial gypsum by recycling, and a standard composition, with only commercial gypsum for comparison purposes. Two samples were produced for each composition to perform technical-functional performance tests, economic feasibility analysis and subsequent prototype molding. The visual analysis of the plates produced for the tests proved to be favorable in the aesthetic aspect. Following the recommendations of the Associação Brasileira de Normas Técnicas - ABNT (Brazilian Association of Technical Standards), water absorption and density tests were performed for each sample. The results were satisfactory, presenting to the market three compositions with the use of recycled gypsum, without loss of performance, and up to 38% more economical than conventional. Among the five compositions, three presented a lower percentage of water absorption than the standard. In the environmental issue, it is possible to reduce up to 1 ton of CO2 emissions per cubic meter produced from the proposed compositions. Finally, the produced 3D gypsum panels meet the sustainability tripod: environmental, economic and social viability.

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End-of-Life Vehicle Residues as Raw Materials for Brake Pads

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For a sustainable world it is need to reuse waste as raw material for made parts, up to now produced using natural raw-materials. Reusing and recycling materials allows to reduce environmental impacts of extraction and transport of new raw materials, as well as decreasing the amount of waste sent to landfill. But another reason emerges to now of needing to decrease the use of raw materials from natural resources due their precariousness. End of life vehicles are a source of a different types of materials, which consequently generates a large volume of waste, particularly of ferrous and nonferrous metal alloys, making them a great opportunity for new raw material. This study had as target to reuse waste generated by fragmentation and milling of end of life vehicles, using them as the raw material for friction parts, like brake pads. After characterization of the mixtures and analyses of their reproducibility, brake pads were processed. The residue mixture was applied directly as a brake pad formulation, only organic polymer was added as a binder. This procedure let to create brake pads by a simple process keeping the costs of production as low as possible. All pads were characterized relatively to hardness, density, and friction and wear behaviour function of time/temperature. The main tests were also performed under the same conditions using as standard two commercial brake pads. Concerning friction coefficient, at low temperatures, brake pads produced from waste have friction coefficient values equal or higher than commercial brake pads. However, with the increase of the temperature they may present tendency to undergo fade. The wear measured during the tests was the lowest for commercial brake pads. The results are encouraging and show that using end life vehicles residues as a starting point for a formulation of brake pads based on recycled materials may be viable. Nevertheless, there is possible to increase the stability of friction at the highest temperatures as well as to increase the wear resistance by adding other key material resulting from other kind of waste.

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Preliminary investigations of geopolymeric mixtures based on phosphate washing waste

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Waste recycling is an important feature in the context of sustainable development and also important to the circular economy. The extraction of the phosphate ore produces a lot of waste which is deposited in large ponds and cause environmental problems. This waste, named phosphate sludge, was filtered to remove the water, and dried at 105°C for 24 h. The dried phosphate sludge was crushed and then sieved in a 100 µm sieve. The resulting phosphate sludge has the majority of the particles with a size below 70 µm. This waste was investigated with X-ray fluorescence (XRF), X-ray powder diffraction (DRX), Fourier transform infrared (FTIR) with attenuated total reflectance (ATR), simultaneous differential thermal and thermogravimetric analyses (DTA-TG) and particle size analysis. The waste was calcined at 700°C and 900°C and investigated with XRF, DRX and FTIR, and compared with the uncalcined. The XFR results show that the silicon dioxide (SiO_2) is the major compound in the calcined and uncalcined phosphate sludge. The mixture of these three powders with sodium hydroxide (NaOH), sodium silicate and with/without 15% of metakaolin to produce geopolymeric materials showed different results. The powder calcined at 700°C is the only one that gave the consolidated materials. The compressive strength decreases with the increase of NaOH concentrations.

Sustainable development of a plaster-based composite ($CaSO_4 \cdot 0,5H_2O$) reinforced PET bottles fibers (polyethylene terephthalate) recycled

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Plaster is a simple binder resulting from calcination of gypsite and basically consists of hydrated sulfates and calcium anhydrous. It is used on the construction industry for manufacture of blocks and boards coatings, etc. Polyethylene terephthalate is an engineering thermoplastic that presents great mechanical and chemical properties. It is used in fibrous composites, soda bottles, among others. This work objective was develop a composite plaster and PET bottles recycled fibers. Water/plaster 0.70; fiber percentage was 0.4% on the mass of the power. The fibers were heat treated for 130 °C for 40 minutes and cooled rapidly. The roughness was evaluated roughness by atomic force microscopy; Mechanical properties were evaluated by tensile and compression tests; the reinforcing degradation was evaluated by infrared spectroscopy at 7, 14 and 28 days. Was produced (248x42x1.5 cm) a plate showing the applicability of this composite. In the fibers were positioned continuously and randomly intertwined in two perpendicular directions. At 14 days the fibers provided double the axial strength of the plaster and increase (32.07%) at 28. Flexion: at 14 day the fibers showed an increase in adhesion, to 28 ruptured of two fibers but not fiber degradation. This shows the contribution of recycling to the sustainability and contributing to industrial and technological scientific development.

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Valorisation of dregs by its incorporation in geopolymer mixtures

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Geopolymers are aluminosilicate materials that emerge as a promising and environmental friendlier alternative to Portland cement [1]. In fact, it is estimated that the production of 1 ton of geopolymer cement emits around six times less CO_2 that the production of equal amount of Portland cement [2]. These binder materials are synthesized by alkali activation of silica and alumina rich materials at relatively low temperatures. Sodium hydroxide and sodium silicate are typically employed as alkaline activators in geopolymers production [3, 4]. However using wastes to partially or totally replace these commercial activators would be advantageous from the environmental and economical view point.
Dregs are solid residues produced from the paper and pulp production process. They are by-products generated from smelt dissolution with the white liquor [5]. These wastes contain, among others, sodium and calcium carbonates, sodium sulphide and an organic fraction. Up to known the only management strategy is their deposition in landfills, which represents a huge environmental and economic burden. Therefore the use of this waste as alternative alkaline activators in geopolymers production, as proposed here, would mitigate the wastes landfilling while simultaneously decrease the carbon footprint associated with geopolymers production.
In this study the feasibility of using dregs, instead of sodium hydroxide, as alkaline activators in the geopolymers production was investigated. The effect of the dregs content and the NaOH concentration on the hardened-state properties (compressive strength and porosity) was evaluated. Moreover lightweight geopolymers for novel applications were also prepared using aluminium powder as a blowing agent.

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Shrinkage Performance of Waste Based Geopolymers Reinforced with Short Hybrid Polymer Fibres

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Shrinkage performance is a very important property for concrete composites just because a high shrinkage performance is associated to cracking tendency that leads to durability problems that reduce the service life of concrete infrastructure. Several authors reported that geopolymers show higher drying shrinkage than Portland cement based composites because they use a lower amount of structural water and thus have a much higher pore content. Therefore, the use of fibres is especially important in geopolymer composites to counteract its shrinkage tendency. This paper provides results on restrained and unrestrained shrinkage performance of fly ash geopolymers reinforced with short polymer hybrid fibres (SPHF). The results show that the SPHF reduce restrained shrinkage. A low content of SPHF AS 0.08% was able to reduce the average cracking width by four times when compared to non-reinforced geopolymers. Increasing the SPHF content from 0.08% to 0.8% reduce the appearance of the first crack by one day and reduced the average crack width by two times.

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Valorization of dredging sediment of Safi port in port works (Safi, Morocco)

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In Morocco, the accumulation of sediment at the bottom of the ports is a natural phenomenon that reduces the capacity of the vessels. To facilitate the access of boats to ports, it is essential to carry out regular maintenance dredging. On average, 3 million m^3 of sediment are dredged annually in Moroccan ports and discharged into the marine environment. Moreover, the demographic and economic development of Morocco resulted in increased resource requirements and their scarcity, including building materials resources.
In this context, our research focus first on identifying the characteristics of the dredged sediment from the port of Safi. Then, on the development of a scientific methodology to valorize this sediment and implement an alternative and sustainable material acceptable in eventual port works.

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Application of automotive paint sludge in the production of white ceramic

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Paint wastes of an automotive industry were evaluated in terms of their chemical and mineralogical characteristics in order to analyse its potential use as a reinforcing agent in white ceramic. Both kaolin and sludge paint were analysed using the techniques of XRF, XRD. In order to understand the behaviour of the sludge during firing, TGA and DTA analysis were done. Samples containing kaolin and 0, 1, 2, 4 and 8 (wt.%) sludge paint were prepared. The ceramics were compacted at 10MPa and sintered at 1000 °C, 1200 °C, 1250 °C and 1300 °C. Water absorption, linear shrinkage and flexural strength were the mechanical properties evaluated in the samples. The experimental results showed that the samples with lagers amounts of sludge performed better or similar to the samples that only contained kaolin. The insertion of 8 (wt.%) of sludge in the specimen increased flexural strength in 63%.

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Synthetic stone processing from waste glass

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Nowadays, one of the most interesting fields of construction community is focused on development of new sustainable materials based on recycling [1]. In this sense, the processing of waste glasses can be considered as an ecological alternative to natural stones employed in construction [2]. In this research, waste glass have been recycled, using polymeric resin as binder, for processing artificial stone. The precursor waste glass was obtained from Cathode Ray Tubes and glass containers, which were reduced to powder of different grain sizes (from 500 µm to less than 63 µm) and confirmed to be completely amorphous by X-ray powder diffraction technique. After sintering the probes and subsequent surface treatment and cutting, with the aim of study the quality of these artificial stones, processed samples were physically characterized, obtaining important parameters as density, electrical resistivity, thermal stress and water absorption. Besides, mechanical studies were carried out in order to determinate hardness, flexural and compressive strength. Finally, the obtained results were compared with the properties of conventional stones, elucidating, in some cases, very good properties. This promising waste glass could be an excellent candidate for the manufacture of artificial stones as an ecological and economic real alternative to natural stones.

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Symposium D - Characterization and Modelling

Physical, chemical and structural characterization (D1)

FTIR-ATR spectroscopy applied to coated paper ageing characterization

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Oxidative degradation induced by atmospheric oxygen and light, as well as, thermal degradation, are two of the most important causes of papers' natural yellowing phenomena.

The mail goal of this work is the evaluation of Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance technique (FTIR-ATR) on the characterization of coated paper ageing modifications.

The study included six different multilayer boards usually applied in packaging industrial sector. These papers were coated with calcium carbonate and kaolin as mineral pigments and styrene-butadiene latex as binder agent, among other additives. The accelerated ageing process was performed according the international standard ISO 5630 part 4: Dry heat treatment at 120 or 150ºC (1986) and part 7: Exposure to light (2014). Pure pigments and binder were also analyzed by FTIR spectroscopy in order to identify its characteristic absorption bands.

FTIR obtained results were compared with conventional optical properties of papers, namely ISO Brightness (Diffuse Blue Reflectance Factor - 457 nm), Yellowness and Colour coordinates (CIELab colour space). It was verified that the temperature effect promoted more detrimental changes in ISO brightness and yellowness than UV exposure. Between the two temperature/time experiment conditions, 150ºC/24 hours proved to be the most aggressive concerning optical properties. FTIR results also revealed temperature as the highest degrading factor to pigments and latex.

The analytical technique used presented high sensitivity for the coated papers characterization and great compatibility with the traditional method of optical properties assessment, demonstrating the complementary roles of both techniques.

With reference to the typical chemical bonds of the used pigments, it was possible to conclude that the Si-O (stretching) of kaolin and the carbonate ion bonds (asymmetric stretching) were degraded in a greater extent with the applied ageing processes.

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Development of sensors and calibration methods for online measurement of viscosity, volume and solid content of non-newtonian fluids

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The rheological characterization of non-Newtonian fluids is of extreme relevance for many industries, particularly for the oil and gas industries. However, the current absence of measurement standards for these fluids leads to an inability in the metrological evaluation of the instruments for measuring viscosity, density and solids content. In these sense metrologists, manufacturers of measuring instruments and the industry itself met to give rise to the project EMRP ENG59 NNL - Sensor development and calibration method for inline detection of viscosity and solids content of non-Newtonian fluids, approved under the EMRP 2013 - Energy. The specific objectives of this project relate to the development of non-Newtonian reference materials, with the development and optimization of the performance of viscosity, density and solids measurement instruments to be used in measurements made in real time As well as the development of appropriate calibration methodologies. This project also aims to evaluate the impact of the physical properties of non-Newtonian fluids on rheological measurements.

The work presented is part of the ENG59-NNL project of the European Metrological Research Project (EMRP) and received funding from the countries participating in the EMRP under EURAMET and the European Union.

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Characterization of mortars from built heritage using XRD, XRF and ATD-TG. The case study of the medieval fortification of Safim, Morocco

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Studies in conservation on built heritage are of increasing importance since there is a driving force towards preserving our heritage as the source of a common identity for future generations and due to societal impacts to populations as an important source of income and economic growth of cities owing to the ever-increasing influx of cultural tourism. A recurring question in conservation and restoration practices is the knowledge of construction techniques and compatibility of materials to be used in interventions, leading to the search of knowledge on the monuments to be intervened through modern characterization techniques, where a special care is given to non-destructive or non-invasive approaches, leading to a careful sampling and analysis planning.

The study to be presented refers to the case study of the fortification of Safim in Morocco, where a set of samples from Portuguese and Islamic origins have been characterized in order to determine mineralogical and chemical compositions along with thermal behaviour and morphology. For that purpose, X-ray diffraction, X-ray fluorescence, optical microscopy, and simultaneous differential thermal analysis and thermogravimetry were used to discern trends in different constructions periods. A comparison will be attempted with results from different monuments in northern Africa such as the Roman aqueduct of Carthage in Tunisia that also underwent several periods of reconstruction [1]. Also profiting from the recently approved European Union Horizon 2020 HERACLES project [2], an approach will be devised to enhance comprehension on materials with cultural value and different conservation approaches in other monuments, namely the medieval town of Gubbio in Italy or the fortress of Koules and the Knossos Palace in Crete, Greece.

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Synchrotron Radiation X-ray Absorption Spectroscopy in 19th century Portuguese glazed tiles from Pena National Palace, Sintra, Portugal

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Synchrotron radiation based techniques have unique potentialities since non-destructive emission and absorption data may be collected simultaneously at the irradiated point, while micro focusing allows remarkable spatial resolution. Elemental analysis by X-ray fluorescence plus topochemical mappings and local environment and valence assessment through X-ray absorption data are powerful tools for understanding chemistry and phase constitution.

Glazed tiles have been used for centuries in decorative tile panels and wall claddings and are an important Portuguese art form. To recover such cultural pieces, a concise knowledge is required about the basic materials and colourants originally used, so that only conformable new products are employed in tile restoration. 19th century Portuguese tiles from the UNESCO World Heritage Pena National Palace (Sintra, Portugal), were chemically and structurally characterized using XRD, µ-PIXE, µ-Raman, Optical Microscopy and VP-SEM [1]. XANES (X-ray Absorption Near Edge Spectroscopy) was used in order to ascertain the chemical state of Sb in the vitreous matrix to clarify its role in pigment incorporation and the possible relationship between the chemical evolution and the ageing mechanisms of the glaze.

The comparison with XANES spectra from model compounds along with theoretical modelling using the FEFF code [2] will be presented has they suggest the structural role of additives as glass network formers or modifiers or integration in crystalline colouring phases A correlation will be attempted with other XANES successful application to other type of tile glazes [3, 4].

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Mineral Characterization of Bauxite Tailings from the Juruti-Pará-Brazil Mine by X-ray Diffraction and X-ray Fluorescence

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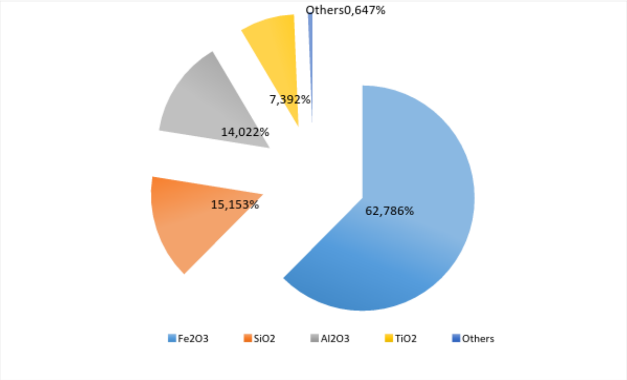
Bauxite is the main source of alumina having differences in types of betonies deposits characterizing its specific uses. About 25% of the product extracted from the Juruti-PA mine is discarded by low ore content being denominated tailings, and not going through any analysis before being sent to the basin where it is deposited. An analysis of the mineralogical composition in order to verify the possibility of obtaining new materials. Six samples were collected and submitted to X-ray diffraction (XRD) and X-ray fluorescence (XRF). Preliminarily XRD was preliminarily tested with a standard with the main phases crystallographic: Hematite (□□$_2$□$_3$), Kaolin (□□$_2$□□$_2$□$_5$), Gibbsite (□□(□□)$_3$), Anatase (□□□$_2$) and Quartz (□□□$_2$). The FRX measurements confirmed quantitatively with the main oxides: □□$_2$□$_3$(62,78%); □□□$_2$(15,15%); □□$_2$□$_3$(14,02%); □□□$_2$(7,39%). The results show that discarded tailings without any analysis has the potential to be reused in the synthesis of new materials.



Graphic 1- Composition of bauxite tailings (%)

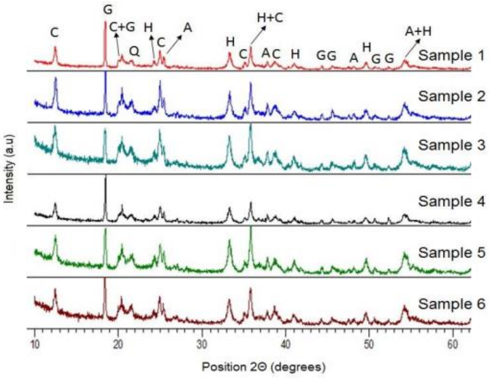


Figure 1: Diffractograms with identification of the spikes of the 6 samples collected in different regions of the pulp in the Juruti mine.

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Piezoelectric and electrical properties of ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$ films with different thickness

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In this work, we have systematically studied the thickness effect on electrical, ferro- and piezoelectric properties of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST 80/20) films in order to understand its functional properties for future flash memory applications. The choice of the composition of ferroelectric $Ba_xSr_{1-x}TiO_3$ material is conditioned by the fact that this composition has a pronounced hysteresis of polarization by an applied voltage.

Ferroelectric BST 80/20 films with a thickness of 150-550 nm were prepared by the high-frequency reactive sputtering of a ceramic target in an oxygen atmosphere. The *p*-type and *n*-type silicon with the crystallographic orientation (100) were used as a substrate with a resistivity of about 20 Ω cm. The substrate thickness was 200 ± 2 µm. The film growth rate was 15.0 nm/min. For measurements of electrical properties, dot-shaped Au top electrodes with an area of $\sim 2.7\times10^{-4}$ cm^2 were deposited on the surface of BST films using a shadow mask by the vacuum evaporation. The surface morphology and the piezoelectric response of BST 80/20 films were measured by the scanning probe microscopy Asylum MFP-3D in the Piezoresponse Force Microscopy mode (PFM).

PFM illustrated that the deposition time or thickness had an influence on the surface morphology and lateral grain sizes of BST 80/20 films. The MFS structure (Au/BST/Si) showed hysteretic characteristics in the C-V plot with a typical window memory, and this parameter depended from the film thickness. Increasing the thickness would result in an increase in the dielectric constant, which mainly stems from dielectric grain size effect and the interfacial-layers effect. The piezoelectric coefficient (d_{33}) and the remnant piezoelectric response (ΔPR) of BST 80/20 films are found to be increased with the increasing thickness of the film. Our studies on ferroelectric BST 80/20 thin films therefore indicate that although ferroelectricity is maintained down to hundred nanometer level thickness, switchable polarization (value of ΔPR) is severely affected, while the type of the conductivity of the silicon substrate does not contribute significantly to the piezoelectric and electrical properties of BST films [1].

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Influence of ambient temperature on the performance of PCPDTBT:PC71BM BHJ solar cells

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In this research article, the influence of environment temperature on the performance of the organic bulk-heterojuction organic solar cells has been investigated. we describe the effect of ambient temperature on the efficiency of Poly-[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta-[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and [6,6]-PhenylC71-butyric-acid-methyl-ester ($PC_{71}BM$) based bulk hetero-junction (BHJ) organic solar cells. The current-voltage characteristics of the ITO / PEDOT:PSS / PCPDTBT:PC71BM /Al solar cells are recorded in the temperature range of 25 - 60 °C under 100 mW/cm2 solar irradiation. The short-circuit-current (Jsc) of the solar cells increased from 4.28 mAcm-2 to 9.23 mAcm-2 when the temperature elevated from 25 °C to 55 ºC. However, the open-circuit-voltage (V_{oc}) and fill-factor (FF) of the cells almost remained unchanged over the whole investigated temperature range. The values of Voc and FF are found to be 0.58±01 V and 0.60±0.12, respectively. The results, clearly indicate that the maximum efficiency of the ITO/PEDOT:PSS/PCPDTBT:PC71BM/Al solar cells can be achieved in the range of 52 °C to 58 °C.

Keywords: Ambient temperature, PCPDTBT:$PC_{71}BM$ BHJ solar cell, Conversion efficiency

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Synergistic Erosion-Corrosion Behavior of API X120 Steel in the Sweet Environment

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The corrosive nature of fluid (oil and gas) and the presence of solid erodent particles in it causes the pipelines to experience severe erosion and corrosion during the transportation process . In this study, erosion-corrosion behaviour of API X120 steel was investigated using aluminium oxide particles (60µm) as erodent and 3.5% (wt. %) NaCl aqueous solution saturated with carbon dioxide as a corrosive medium. Effect of particles speed at an impact angle of 90° and the synergistic effect of erosion-corrosion were investigated using weight loss, potentiodynamic polarization technique, and surface analysis. The erosion results confirm a deeper penetration of the erodent particle into the target steel surface with increasing particles speed. During the corroison-erosin process, the formed iron carbonate layer (during corrosion process) is removed by the erosive erodent particles (erosion process) which results in high corrosion rate and high surface roughness. Furthermore, during the erosion-corrosion process, a significant effect of corrosion on erosion at lower particle's speed is noticed while at higher particle speed erosion has a dominant influence on the corrosion as identified in the Synergy/Total erosion-corrosion ratio (S/T ratio). Finally, our results indicate a simultaneous activation of erosive and corrosive phenomena during erosion-corrosion of API X120 steel.

Mechanical characterization (including at nanoscale) (D2)

Analysis of the statistical significance of factors in the tensile strength optimization of thermoplastic cassava starch nanocomposites with modified clay

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In this study, the factors that significantly influenced the optimization of the mechanical properties of cassava starch nanocomposites were investigated by complete factorial planning 2^3. The factors to be investigated were cassava starch (A), glycerol (B) and modified clay (C) contents. Bentonite clay was used as a filling material of the biofilm, and had its surface modified by an ion exchange in the presence of a quaternary ammonium salt. Glycerol was the plasticizer used to thermoplasticize cassava starch. The factorial analysis suggested a regression model capable of predicting the optimal mechanical property of the cassava starch biofilm from the maximization of the tensile strength. The reliability of the regression model was tested by the correlation established with the experimental data through the following statistical analyzes: student t test, analysis of variance (ANOVA), Pareto graph, normal probability graph and dispersion graph. Student t test determined the significance of the correlation coefficients of the effects. The analysis of variance performed the regression test to ensure an appropriate model. The Pareto graph showed which of the individual factors analyzed, as well as their interactions, contributed significantly to the response. To identify whether the effects found are "real" or "random", a normal probability graph was used. The scatter graph showed how closely the set of observed values followed the theoretical distribution. All factors and their interactions were considered significant to the response variable, except for the interaction between the three factors (ABC) at 95% confidence. The sequence of the degree of statistical significance on the tensile strength in relation to the effects investigated is therefore C> B> A> BC> AC> AB. The modified clay was the factor of bigger statistical significance on the tensile strength observed, being the one that most contributed for the improvement of the mechanical property of the starch biofilm. The factorial experiments showed that the interaction of glycerol with both modified clay and cassava starch was significant for the reduction of biofilm ductility. Modified clay and cassava starch contributed to the maximization of biofilm ductility, while glycerol to the minimization.

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Mechanical characterization of the bead welding of high-density polyethylene (HDPE)

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High-density polyethylene (HDPE) is widely used for many years for pipes of industrial facilities. The range of applications was extended to construction industry: transmission of gas, water, sewage disposal...

Among the consolidation process of pipes made from high-density polyethylene (HDPE), fusion welding or butt weld fusion is considered to be a widely used technique in the thermoplastics industry whereby the mechanical behavior of the weld may approach that of the initial materials.

This study was devoted to the experimental study of the mechanical behavior of a HDPE structure welded by butt fusion welding technique solicited in traction. We are based on experimental tests that were performed to characterize the material studied, introduce the ductility of the welded section and see the effectiveness of the displacement speed and the welding parameters, namely the melting temperature relative to the dimension of the internal diameter of the pipe.

Keywords: high-density polyethylene (HDPE), tensile testing, behavior, characterization, deformation.

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Thermo-mechanical characterization of shape-memory polymeric nanocomposites

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The shape-memory materials are nowadays an important subject in the scientific community due to their huge technological potential. These materials have the capability of being triggered by an external stimulus and, consequently, change their shape. Considering the recent development of the biomedical industry, this work aims to develop the applicability of shape-memory materials into biomedical devices, enabling a more efficient operability. Therefore, the shape-memory polyurethane was chosen to this end due to its high biocompatibility and proximity between its thermal transition temperature and the human body temperature. However, the thermoplastic polyurethane (TPU), and the shape-memory polymers in general, possess major drawbacks related to the inferiority of its mechanical performance as compared with shape-memory alloys (SMAs) and its large shape recovery time. In order to pursue the mechanical reinforcement and improvement of the polyurethane properties, it was conducted an experimental study in which polyurethane nanocomposites containing carbon based nanoparticles were produced. It was used carbon nanotubes (CNTs), treated and non-treated, and graphene. The nanocomposites were produced through mechanical melt mixing and injection moulding and they were incorporated with 0.5, 1.0 and 1.5 vol.% of non-treated CNTs, treated CNTs and graphene. It was performed the morphological, thermal and mechanical characterization of the nanocomposites. Thermo-mechanical properties such as glass transition temperature (T_g), melting temperature (T_m), specific heat capacity (c_p), thermal diffusivity (α), elastic modulus (E), tensile strength at break (σ_b) and elongation at break (ε_b) were evaluated. The influence of the different types of nanoparticles and different concentrations on the thermos-mechanical properties of the produced nanocomposites were analyzed. Through this, the best relation regarding the materials and parameters used in this work was determined. It was also possible to draw some conclusions regarding the shape-memory performance of the nanocomposites.

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Influence of the temperature on the dynamic behavior of composite structures offshore pipe: experimental analysis

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The dynamic properties and damage evaluation in impacted laminated composites used in offshoring applications are discussed. This study presents a continuation of research conducted on composite pipes dedicated to the pumping of oil and gas. After impact on tubular structures using a hemispherical projectile of hardened steel with 50 mm in diameter using a Taylor gun, various non-destructive inspection (NDI) techniques including infrared thermography and microscopic inspections are used to evaluate the effect of temperature on dynamic properties and the damage progressive. The tubular structures are tested for two values of low temperatures -30°C and -60°C.

A significant reduction in the impact resistance was observed for all impacted specimens under low temperatures. Matrix cracking, fiber splitting, fiber breakage and the delamination are the most dominant failure modes in the pipe.

Keywords: Impact behavior, Taylor gun, thermal effect, composite pipes.

Micromechanical Analysis of Interaction between Matrix Crack and Debonding area in an AlfaFiber / Epoxy Resin Biocomposite

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In this work we present a review of the state of the art on composites reinforced with plant fibers. Second, we perform experimental tests to determine the mechanical properties of fibers, matrix and interphase. Third, we perform a series of finite element simulations to predict the initiation of damage and to estimate the propagation of matrix cracks in alfa/epoxy composite.

Different tensile tests are performed to determine the longitudinal Young modulus of alfa fibers and epoxy resin. To obtain the transverse stiffness of the fibers and the rigidity of the interphase, nanoindentation tests were performed.

The experimental results of the characterization are introduced in a micromechanical model to estimate the evolution of the matrix crack and its interaction with an interfacial debonding using the concept of the energy release rate. Wettability problems in the preparation of fiber-based composites and their effects on interfacial debonding are also taken into account.

Key words: Composites, alfa fibers, interphase, micromechanical model, resin.

Experimental and numerical analysis of the fracture toughness of adhesively-bonded joints

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The use of adhesive joints in industrial applications has been increasing, replacing traditional methods such as welding, brazing and bolted and riveted joints. This is due to the advantages they offer, such as the fact that they are lighter, behave well under cyclic loads or fatigue, enable the connection of different materials and have lower stress concentrations. To increase the confidence in the design of adhesive structures, it is important to be able to accurately predict their mechanical strength and corresponding fracture properties (critical strain energy release rate in tension, G_{IC}, and shear, G_{IIC}). These properties are directly related to Fracture Mechanics and are estimated through an energetic analysis. To this end, there are three types of models: models that require the measurement of crack length during propagation of the damage, models that use an equivalent crack length and methods based on the J integral. As in most cases loads induce mixed mode (combination of tension with shear), it is of great importance the perception of fracture in these conditions, especially in the energy release rates for different criteria or fracture envelopes. This comparison allows, for example, to find out which is the best energetic criterion of failure to use in numerical models based on cohesive zone models.

This work presents an experimental and numerical study using the Single-Leg Bending (SLB) test on specimens bonded with three types of adhesive, in order to study and compare their fracture properties. For this purpose, some data reduction methods were applied to estimate the strain energy release rate in tension, G_I, and shear, G_{II}, within the scope of the models that require the measurement of crack length and models using an equivalent crack length. At a later stage, the analysis and comparison of results obtained during the experimental phase of G_I and G_{II} of each adhesive were addressed. The discussion of results was also done by the analysis of the values obtained in several fracture envelopes, to ascertain which criteria are more appropriate for each adhesive. Overall, a very good agreement it was obtained between methods for the determination of G_I and G_{II}. In the numerical simulations it was possible to reproduce the observed behavior of the experimental tests, with a positive validation of the chosen propagation criteria have been validated propagation criteria obtained from the experimental results.

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Advanced characterization using microscopy techniques (D3)

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Detection of nano-heterogeneities in $CaCu_3Ti_4O_{12}$ ceramics using scanning probe microscopy

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Colossal dielectric constant (CDC) materials ($\varepsilon' > 10^3$) currently are the focus of great interest from electronic industry once their using at passive components can represent an improvement of the efficiency of electronic devices and also the miniaturization of capacitive electronic components. Calcium copper titanate ($CaCu_3Ti_4O_{12}$), a non ferroelectric material, whose exceptional dielectric properties were for the first time reported in 2000, attracted the attention of scientific community because of its CDC ($\varepsilon' > 10^5$), observed for ceramic and single crystal forms.

Although all the efforts of the scientific community it is still missing a conclusive explanation about the polarization mechanisms that justify the exhibition of CDC. Discarded the existence of any ferroelectric transition, the experimental data, collected during last decade, point to an extrinsic barrier mechanism(s) as the origin of the main dielectric polarization.

Recently, in a theoretical work, Bueno *et al.*, have shown a polaronic stacking fault defect model as the origin of the huge dielectric properties in $CaCu_3Ti_4O_{12}$ (CCTO) materials. They demonstrated that CCTO crystal structure can handle with stacking fault defects, at the nanoscale level, which is pointed as the origin of the high dielectric constant phenomena.

In this work we present an experimental confirmation that CCTO ceramics present an inhomogeneous electrical conductivity at a nanometric scale that can support polaronic stacking fault defect model as the origin of the CDC feature. Generally, employing a Scanning Probe Microscopy (SPM) technique in contact Spreading Resistance (SR), we confirmed an insulating behavior of the grain boundaries and, most important, a dual behavior of the grain microstructure, containing both conductive and insulating nanometric domains with a layered geometry, as shown at figure 1.

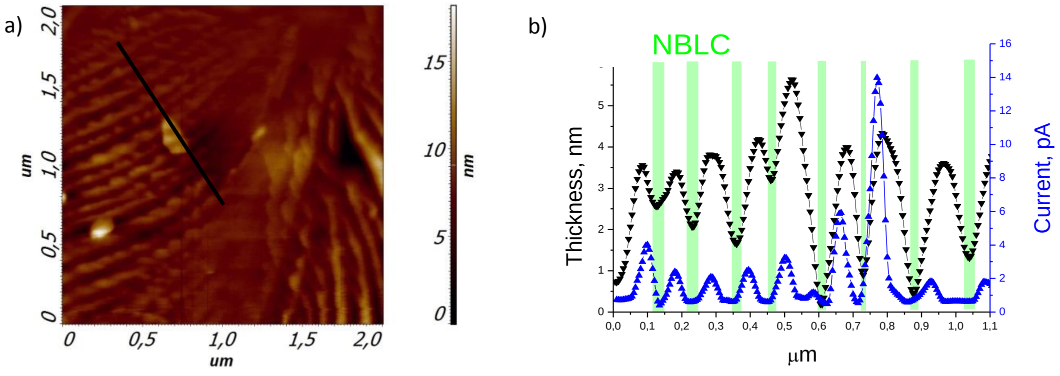

Figure 1 – a) Topography and b) nanobarrier structure height and current profiles inside a CCTO grain.

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Nanostructural Characterization 3D of Phases and Interfaces of Portland Cement Mortar

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The need for research and characterization of materials aimed at the construction has been growing due to the need for proper selection of materials, based on the performance of the system under study. In this sense this paper proposes to go further in the characterization and micro nanostructural surfaces and interfaces of Portland cement mortars used for flooring in civil works in a new way and the use of atomic force microscopy (AFM) as a tool of characterization of Portland cement mortar. In recent decades, many new aspects of calcium silicate hydrate (CSH) were revealed with the advances in analytical techniques and application of new methods such as nuclear magnetic resonance (NMR) and atomic force microscopy (AFM), the latter is the subject of this research. The nanostructure of CSH has been the subject of much research, but it is still not clearly understood, some suggested models point ranging from colloidal "layers - sheets". The atomic force microscopy (AFM) was used in this work in an unprecedented way for cementitious materials, in the case of this study, Portland cement mortars. There are no bibliographic reports of successful attempts to characterize these materials using such important technique to anostructures. The preparation of the samples showed a positive surprise because as we had no previous parameters, we chose the simplest possible preparation that consisted of embedding a fragment of fractured mortar in Bakelite and do the surface polishing. The topographic characterization is important because it shows the classical morphology of portlandite and calcite in the samples at the nanometer scale. These topographical micrographs and three-dimensional topographic profiles give us an exact picture of the morphology of cementitious materials in the interface ceramic block/mortar, interface roughcast mortar/mortar coating and top view of the mortar, being a powerful and effective characterization technique for micro and nanostructural.

Keywords: Nanostructural characterization, mortar, atomic force microscopy, interfaces and surfaces, cementitious materials.

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Nano and Microstructural Characterization of Phases and Interfaces of Portlant Cement Mortar Using High Resolution Microscopy

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This paper proposes to go a little further on the microstructural characterization of surfaces and interfaces of Portland cement mortars used for flooring in construction works. Using scanning electron microscope high-resolution (SEM - FEG), will be used to clarify the micro and nanometric details of cementitious material in Portland cement mortars that have in their composition, and proved extremely important in the characterization of cementitious materials in the case of this study, Portland cement mortars. The technique of sample preparation is relatively simple compared to other devices and allows the analysis of samples in a natural state which ensures ideal conditions for the characterization of the material, moreover, the quality of the photomicrographs is substantially better than the conventional microscopes combined with the chemical microanalysis by energy-dispersive (X-ray) spectrometer (EDS), which allows a substantial advance in the search and characterization of cementitious materials. In photomicrographs using high resolution scanning electron microscope (SEM - FEG), increases of about 80 thousand times with great quality were possible, in this paper, we can see above, photomicrographs with an increase of up to 50 thousand times, which enables the visualization of nanopores in mortar matrix. Photomicrographs made in SEM – FEG dual FIB 3D and SEM - FEG Quanta confirm the predominance of euhedral crystals of ettringite in the block - ceramic mortar, characterized by their morphology of hexagonal crystals acicular interface region, and we can also check the lamellar morphology characteristic of portlandite. Photomicrographs made with the SEM-FEG Dual-FIB and SEM-FEG Quanta have confirmed the predominance of euhedral crystals of ettringite in the block-ceramic mortar interface region, characterized by their morphology of hexagonal acicular crystals. Also, the typical morphologies of portlandite, calcite and CSH have been observed with great detail.

Keywords: Nano and microstructural characterization, mortar, scanning electron microscopy, interfaces and surfaces, cementitious materials.

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Microstructural characterization of BFRP bars used as replacement for conventional corrugated steel bars

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Corrugated steel bars are used for reinforced concrete constructions to give the tensile and flexion capabilities that concrete does not possess.

Steel provides advantages such as malleability, weldability, tensile and flexural strength. Although, it also presents disadvantages such as oxidation, which can lead to decrease in the resistant capacity of the structures as a result of the cracking of the concrete, the reduction of the resistant section of the reinforcement and, mainly, the loss of steel-concrete adhesion.

Currently being used as an alternative of these bars are galvanized or stainless steel bars, or polymer composites with carbon fiber, glass fiber or basalt.

Basalt fibers are becoming competitive in civil engineering, with advantages that are 89% lighter than steel and less susceptible to alkaline degradation (concrete) that carbon fibers, making it an alternative especially in regions high seismic risk.

This experimental work performs a characterization study of Polymer reinforced with basalt fiber bars (BFRP) supplied by two different companies, as well as analyzed and compared.the fibers and the resin used in the respective manufacture.

To obtain the type and quality of the resin, the thermal characterization was done by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The size and distribution of the fibers is observed by optical microscopy, scanning electron microscopy (SEM) and field emission microscopy (FESEM). From the microscopies were also obtained the percentage, shape, distribution and chemical analysis of the fibers.

The elastic modulus and hardness of the fibers and resin have been obtained through nanoindentation tests.

The results show that between the two types of bars analyzed there are significant differences in the distribution and size of the fibers, as well as in the curing of the applied resins, and this affects the tensile strength of the bars. Also, the obtained results allow to establish which bars can have better mechanical properties for the commissioning.

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Piezoresponse and Kelvin probe force microscopy studies to assess local switching on polycrystalline ferroelectric coatings

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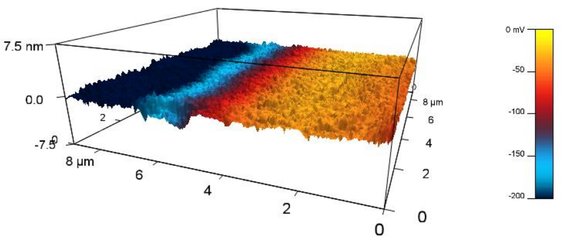
Functional perovskite oxides, such as piezoelectrics, ferroelectrics, semiconductors, are an important class of materials that serve key components in a wide spectrum of applications. Within this family there is a particular group of the so-called lead-free piezoelectrics, and among them alkali niobates and tantalates play an important role in contemporary technical ceramics, mainly owing to their outstanding electrical properties. Several tantalates possess ferroelectric properties, and are used in several applications, notably in the field of electro optics. Among the best-known tantalates is lithium tantalate ($LiTaO_3$) with highly distorted perovskite-like structure. The displacement of the Ta ion within the oxygen octahedron gives rise to unique electro-optical, pyroelectric and piezoelectric properties combined with good mechanical and chemical stability. This makes $LiTaO_3$ well suited for numerous applications including electro-optical modulators, pyroelectric point detectors, optical waveguide and surface acoustic wave (SAW) substrates, piezoelectric transducers, etc. Ferroelectric and piezoelectric perovskite oxides also seem to have a great potential for a new sort of bio-MEMS. In this work, polycrystalline ferroelectric $LiTaO_3$ thin films, coating metallic 316L-type stainless steel substrates, are assessed These platforms can be electrically functionalized as a whole or locally patterned according to the intended application. Regardless of the application the local characterization, and manipulation, of the electrical behavior are imperative. Therefore, there is a need for much deeper and systematic studies of these polycrystalline $LiTaO_3$ surfaces. The use of two different scanning probe microscopy techniques: Piezoresponse Force Microscopy (PFM) and Kelvin Probe Force Microscopy (KPFM), present a suitable approach to map the local switching induced changes and the local surface potential distribution, allowing to image surface electronic properties with nanometer scale resolution.



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Microstructural Characterization of ZrN/CrN Nanoscale Multilayer

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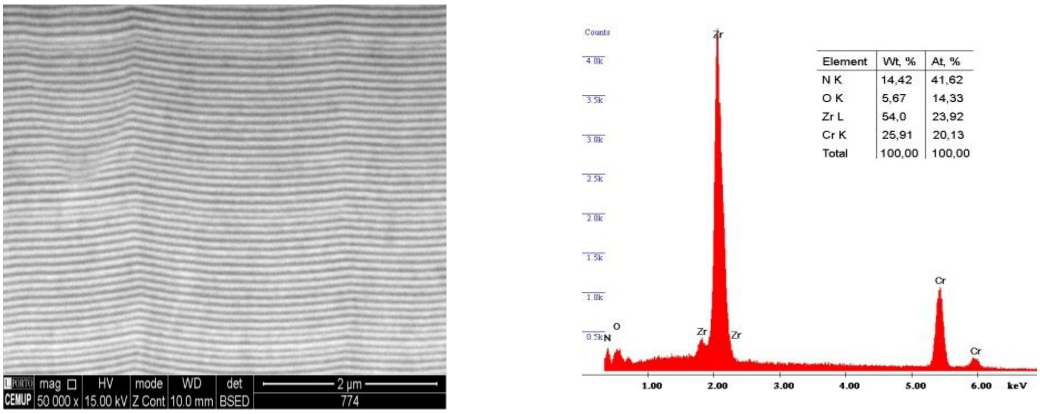
Transition metal nitride coatings, based on zirconium and chromium, are used as protective coatings that increase the life of the elements coated by them. Nanoscale multilayer ZrN/CrN coatings with bilayer thicknesses ranging from 105 to 148 nm were prepared by vacuum arc deposition techniques. The total thickness of the coatings ranges from 9 to 12 μm. ZrN/CrN samples were obtained under the following conditions: arc current was 100 A, nitrogen pressure (P_N) in the chamber was varied from $6{,}2\times10^{-4}$ to 3.2×10^{-3} Torr and negative bias potential U_s = -70 V and -150 V. Microstructural characterization of the thin films was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The systematical investigations demonstrate that the chemical composition and microstructure of the coatings intimately depend on the deposition parameters (pressure of working gas and substrate bias). Morphology investigations show that even for the great number of thinner layers it is observed good planarity. SEM observations revealed that the coatings are characterized by the high continuity and the lack of heterogeneity in the form of droplet phase. Fig 1(a) shows the SEM image where it is possible identify the layers of ZrN (bright layers) and CrN (dark layers) and with a bilayer thickness of 105nm. The chemical composition of the coatings was obtained by EDX analysis. An example of an EDX spectrum for a ZrN/CrN coating (I_A=100°, $P_N=6.2\times10^{-4}$, U_s = -150 V) is given in Fig. 1(b).



Element	Wt, %	At, %
N K	14,42	41,62
O K	5,67	14,33
Zr L	54,0	23,92
Cr K	25,91	20,13
Total	100,00	100,00

(a) (b)

Fig. 1. (a) Cross-sectional SEM image and (b) EDX spectrum and elemental chemical composition of the ZrN/CrN multilayer coatings.

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Materials modelling (Advanced atomistic algorithms, computer simulations) (D4)

Growth and Stability of a Model Catalyst on Oxides

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The dynamic process of the formation of the system Pd /thin MgO (100) surface is investigated by developing many programs using Fortran software. This simulation is based on rate equations and includes processes of nucleation, surface diffusion of adatoms, growth and coalescence of islands in the case of thin films growth in Volmer–Weber mode. The nucleation kinetics is interpreted according to the theory of random nucleation. It shows a good agreement with the experimental result time dependencies of island density. The phenomenon of coalescence is explained via island migration process. It is essentially described by surface atom diffusion and the surface coverage. It is important to notice the influence of the deposition temperature, which modifies the clusters coalescence time. It is clearly seen that the coalescence occurs more rapidly when the substrate temperature is high.

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Influence of granular material characteristics in the behavior of “Bouregreg Valley” soft ground improved with stone columns

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The use of finite element analysis has become widespread in geotechnical practice as means of optimizing engineering tasks; it can be easily applied to the treated areas by stone columns, which are a method of improving the soil having low geotechnical properties and likely to deform significantly under load action, by incorporating granular material (commonly called ballast) compacted by remounting passes. However the characteristics of this granular material influence the behavior of soft soils treated by the stone columns technique, especially: the friction angle, the cohesion, the modular ratio and the constitutive model. The choice of the constitutive model depends on many factors but, in general, it is related to the type of analysis that we intend to perform.

Numerical modeling must consider the diversity of the materials nature, the complex geometry of structures- land and the behavior of materials generally nonlinear (permanent deformation).
It is a simple and effective alternative to approach the real behavior of soils reinforced by stone columns and the influence of materials characteristics, it allows settlement analysis, lateral deformation, vertical and horizontal stresses in order to understand the behavior of columns and soil. It also has the advantage of integrating the settlements of the underlying layers.

This paper aims to study the mechanisms of functioning and interactions of stone columns with the surrounding ground, and vis-à-vis the various parameters characterizing the granular material "ballast" and the surrounding soil, which influence the behavior of the improved soil, so the parametric study was carried out varying several properties especially granular material properties.

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Analysis of the statistical significance of factors in the tensile strength optimization of thermoplastic cassava starch nanocomposites with modified clay

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In this study, the factors that significantly influenced the optimization of the mechanical properties of cassava starch nanocomposites were investigated by complete factorial planning 2^3. The factors to be investigated were cassava starch (A), glycerol (B) and modified clay (C) contents. Bentonite clay was used as a filling material of the biofilm, and had its surface modified by an ion exchange in the presence of a quaternary ammonium salt. Glycerol was the plasticizer used to thermoplasticize cassava starch. The factorial analysis suggested a regression model capable of predicting the optimal mechanical property of the cassava starch biofilm from the maximization of the tensile strength. The reliability of the regression model was tested by the correlation established with the experimental data through the following statistical analyzes: student t test, analysis of variance (ANOVA), Pareto graph, normal probability graph and dispersion graph. Student t test determined the significance of the correlation coefficients of the effects. The analysis of variance performed the regression test to ensure an appropriate model. The Pareto graph showed which of the individual factors analyzed, as well as their interactions, contributed significantly to the response. To identify whether the effects found are "real" or "random", a normal probability graph was used. The scatter graph showed how closely the set of observed values followed the theoretical distribution. All factors and their interactions were considered significant to the response variable, except for the interaction between the three factors (ABC) at 95% confidence. The sequence of the degree of statistical significance on the tensile strength in relation to the effects investigated is therefore C> B> A> BC> AC> AB. The modified clay was the factor of bigger statistical significance on the tensile strength observed, being the one that most contributed for the improvement of the mechanical property of the starch biofilm. The factorial experiments showed that the interaction of glycerol with both modified clay and cassava starch was significant for the reduction of biofilm ductility. Modified clay and cassava starch contributed to the maximization of biofilm ductility, while glycerol to the minimization.

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The influence of geometric discontinuity on the fatigue behavior of aluminum alloy 7075-T6 and 6082-T6.

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This study allowed us to see the influence of geometric discontinuity namely defects or cracks in the aluminum alloys (7075-T6 and 6082-T6), on the fatigue behavior, in other words life using the criteria of fracture mechanics using Ansys finite element code. This discontinuity has multiple internal or external origins resulting from improper design, imperfect implementation or from misuse. This work was performed by simulations on uninterrupted, hole and cracked specimens. Thereafter, the study has allowed to characterize the singularity of the stress field on crack tip by calculating the J-Integral.

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Macro Approach to Molecular Modelling of Linear Polymers Applied to Estimation of Tensile Modulus for New Materials Development

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The typical design of new materials has been empirical (formulation, assembling, synthesis, processing, and testing). At present, there has been much progress in the knowledge of relationships between the molecular structure of a material and its properties that lead to the ability to predict material properties previous synthesis. In this way, it could be obtained important reductions in time and cost. However, it is not easy to achieve these predictions for polymers since the involved variables are very complex because of high molecular weight (MW) and polydispersity (PDI). To the best of our knowledge, this is one of the first attempts to investigate the possibility of predicting tensile properties for polymers by using Quantitative Structure-Property Relationship (QSPR) techniques and considering real average MW of polymers (see dataset range in Table), instead of synthetic molecular models (monomer).

Property	Mn	PDI	CHS (20-25°C)	Tensile Modulus
Range	4700-765000 g/mol	1.15-5.6	1-100 mm/min	4.00-0.13 GPa

At present work, main problems for modeling real polymeric materials are described and innovative solutions are proposed. Representing (2D) high MW polymeric molecules cannot be done with available software. We recently developed an informatics tool based on SMILES code that reaches $1x10^7$ g/mol and more. On the other hand, QSPR technique requires calculating molecular descriptors which is also not possible with available software. In this stage, we have worked with different packages of the R programming language, and many of classic descriptors have been calculated. Once these problems were solved, we applied methodology used for micro approach [1], consisting of 3 steps: A- Feature Selection (DELPHOS [2]), B- Computational Model (VIDEAN, WEKA) including statistical metrics and C- Physic-chemical interpretation. The obtained results are promising and the models look more robust than micro approach ones.

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Numerical study of retaining wall backfilled with sand-tire shred mixture

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The use of scrap tires in geotechnical applications has ground in the last decades. The main objective of this paper is to evaluate numerically a retaining wall backfilled in the first case with sand alone and in the second case with tire shred-sand mixtures, using ROCSCIENCE software. Properties of sand-shred tire mixture are computed using homogenization techniques. The results show that lateral pressures on the wall is reduced considerably when tire shred-sand mixture is used. This allows a gain in the concrete of the retaining wall.

Keywords : Retaining wall, Sand-tire shred mixture, numerical analysis.

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Smart Vehicle Lighting System using a-SiCH Technology

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We propose the use of Visible Light Communication (VLC) for vehicle safety applications, creating a smart vehicle lighting system that combines the functions of illumination, signaling, communications, and positioning.

We use the nonlinear property of SiC multilayer devices under UV irradiation to design an optical processor uniquely positioned to help to develop automated vehicle technologies, that lets cars talk to the 'environment' around them. The 'environment' around a car could be other cars and trucks, traffic lights, roadworks or even pedestrians and cyclists. By utilizing Visible Light Communication (VLC) between vehicles, drivers are given a clearer knowledge of the preceding and nearby vehicles status. These aspects can significantly reduce the chance of traffic accidents.

The system is a self-positioning system in which the measuring units are mobile. Each vehicle is assumed to be equipped with two headlamp transmitters, two side light mirrors transmitters, and two taillight transmitters. Distance receivers are assumed to be placed at the front, at the back and at each of the two side mirrors. Trichromatic Red-Green-Blue LEDs (RGB-LED) are used together for illumination proposes and individually, each chip, to transmit the channel location and data information. The chips of the RGB-LEDs can be switched on and off individually, in a desired bit sequence to transmit the information. The receivers consist of two stacked amorphous cells [p(SiC:H)/i(SiC:H)/n(SiC:H)/p(SiC:H)/i(Si:H)/n(Si:H)] sandwich between conductive transparent contacts. The receiver and the transmitters are characterized through spectral response, I-V characteristics and transmittance measurements under different optical bias. The spectral sensitivity of the receiver as a function of the distance from the transmitters is analyzed.

The receivers join the simultaneous demultiplexing operation with the photodetection and self-amplification. The information and the code position of each LED are transmitted simultaneously through the RGB pulsed transmitted channels. A violet LED is used for error control. Free space is the transmission medium. An on-off code is used to transmit data. A visible multilateration method estimates the position of the device by using the decoded information received from several, non-collinear transmitters. To improve the transmission rate, parallelized communication will be analysed by using multiple emitters and receivers.

The proposed coding is based on SiC technology. Furthermore, we present a way to achieve vehicular communication using the parity bits and a navigation syndrome. A representation with a 4 bit original string color message and the transmitted 7 bit string, the accurate positional information encoding/decoding and the design of SiC navigation syndrome generators are discussed and tested.

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Materials for Non-Pneumatic Tyres (NPTs): a New Concept

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This work aims to address a new concept for tyres: the non-pneumatic tyres (NPTs). First, the objectives for the use of a tyre are presented, as well as the requirements they must meet.

Then, it will present the history of the NPTs, the motivation for the creation of the concept for a non-pneumatic tyre. It examines the different tyres used in according to the initial lunar applications, mainly requirements, as well as applied solutions. Some existing concepts for NPTs are presented, including the concepts of Michelin and Bridgestone companies, as well as details related to their different structures.

Also, a more detailed analysis of the structure (different types of flexible structures) and of the materials used (mainly to polyurethane) is made. New approaches to the NPTs are considered, at the geometry level of the tyre, more specifically, a tyre characterized by its behavioral continuity during its rotation.

On the basis of these approaches, simulations are made (in SOLIDWORKS and ABAQUS CAE). A simulation was made to an integrated model, consisting of steel, aluminum and polyurethane. For the simulations of the new concept, it was used: 1) an epoxy-fiberglass composite; 2) polyurethane. Radial rigidity optimizations were made by varying the thickness of the tyre.

Experimental work was done using test pieces manufactured with polyurethane matrices, reinforced with glass fiber, polypropylene and carbon fibre. Based on the properties obtained experimentally, the simulations carried out previously were reviewed and optimized, once again, for radial rigidity.

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Ductile tear under monotone loading by XFEM method

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This work consists in a development of a numerical code by the implementation of the Extended Finite Element Method (X-FEM) using the criteria of the mechanics of rupture of cracked structures, which serves to follow the path of the crack under a monotonic loading. In this regard, several applications will be processed in order to show the validity of the generated code.

The extended finite element method (X-FEM) has been implemented in the ANSYS APDL calculation code. This numerical method makes it possible to successfully perform efficient simulations of arbitrary crack propagation in a varied application domain: fatigue [1] and [2], fragile fracture in elasto-dynamics [3], multi-cracking [4] and [5].

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The theoretical evaluation of the saccharin electrochemical detection, based on specifically modified polypyrrole in neutral solution

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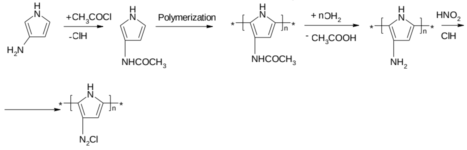
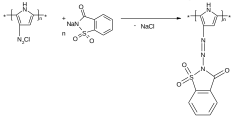
The use of chemically modified electrodes has become a useful and modern tool in electrochemical analysis, being capable to provide the rapid, cheap, sensitive, precise and exact quatification of different substances [1], along with their affinity to the analyte.

On the other hand, the saccharin [2] is an artificial sweetener with a vast specter of use. It is about 500 times sweeter than sucrose and does not possess any caloric value. Nevertheless, it contains toxicophore groups, and, thus, its use is linked with side effects like altering gut microbiota, allergic reaction, [3] and even with carcinogen influences. Thus, a development of a method, capable to detect its concentration precisely and exactly, remains an actual problem, and the electrode coverage with conducting polymers would serve as an interesting solution for it

An interesting technique may employ saccharine azo-coupling with specific conducting polymers in neutral solution. The polymer, in this case, has to be prepared by the procedure:



and the coupling, to be realized by:



In this work, the described technique, capable to be used either in electroanalytics, or in conducting polymer modification for different purposes, has been evaluated from the theoretical mechanistic point of view. The mathematical model, describing this system´s behavior in neutral solution was developed and analyzed. It was derived that the system´s electroanalytical and electrosynthetical efficiency will strongly depend on solution composition and temperature, although the stable steady-state is easy to maintain. The process is expected to be diffusion or reaction controlled. The oscillatory and monotonic instabilities for this system are more probable, than for the common case of the conducting polymer-based electrochemical sensing.

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Grain growth Kinetic during austenitization of 100Cr6 and X20Cr13: numerical study

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A numerical investigation of effect of austenitization on kinetic grain growth of 100Cr6 steel grade is performed based on an empirical model. The austenitization temperatures used in this investigation were 900 ° C., 950 ° C., 1000 ° C., 1050 ° C., 1100 ° C. and 1200 ° C. with three holding times of 10 min, 30 min and 60 min to study the effect of the austenitization temperature and the holding time on the grain growth. The results shows that the austenite grain size increases with austenitizing temperature and holding time with different rate. Experimental results of ERIK PERSSON are used in order to compare them with the numerical results obtained. the predicted grain sizes by the model are in good agreement with exiperimental results.

On the other hand, this model has been applied to the X20Cr13 steel and compared with100Cr6 steel to show the effect of the alloying elements on the austenitic grain growth.

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Design and fabrication of phantoms to study electromagnetic effects

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This work describes the design techniques and manufacturing of phantoms to study the electromagnetic (EM) radiation wireless equipment near the human body. The digital 3D was also used for numerical simulations with COMSOL Multiphysics software [1].

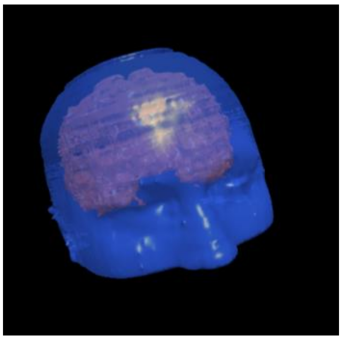

Figure 1 – 3D model of the head reconstructed form a CT dataset.

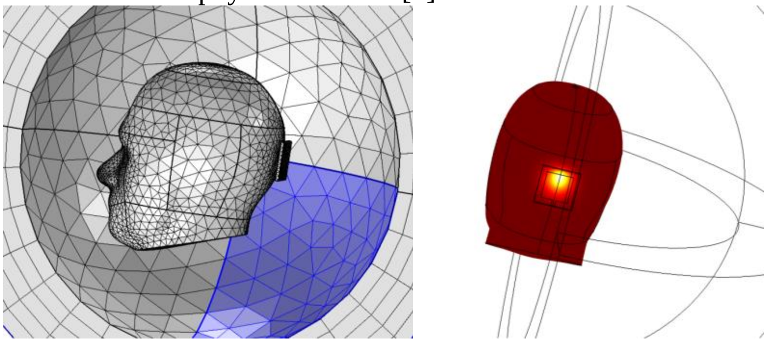

Figure 2 – (a) On left, the geometry of the 3D head and of the RF emitter. (b) On the right, the level of absorbed energy inside the head.

The rapid prototyping techniques and the numerical simulations both need a three-dimensional digital model. In order to do so, we reconstructed a 3D model of a human head, as shown in Fig.1, based in medical images obtained by Computer Tomography (CT). The CT dataset used was from the Visible Human Project [2].

The phantoms were constructed to inquire about the need to be sufficient to have an overall homogeneous medium, as used in some SAR evaluation studies, or there is the need to unravel the various means constituting the human head and the effects of interfaces between them to test the effects of electromagnetic waves. The materials employed in prototyping based on characteristics and properties of materials used in other phantoms works [3].

In our numerical simulations the emitter was placed near the head (Fig.2 - (a)) as the purpose of work was to evaluate the effects of electromagnetic radiation of implantable wireless devices for medical use, especially neural implants. In (Fig.2 - (b)) is shown a preliminary result of the absorbed energy rate with a homogeneous model. The emitter position was choose to mimic the implantable wireless device for a bionic eye direct to the brain [4].

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Ferromagnetism in the half-heusler XBaB Compounds from first-principles calculations (X=K, Rb)

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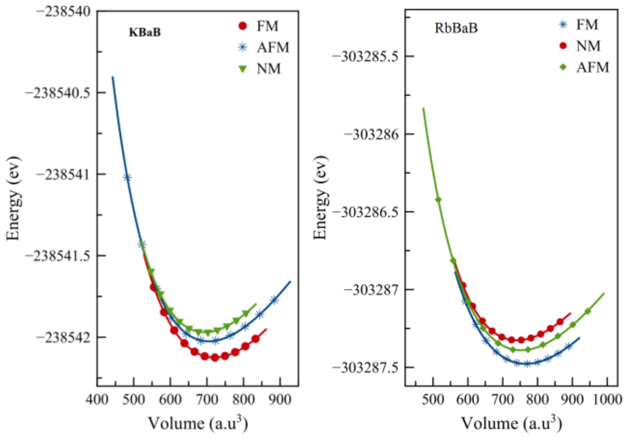
In this work, first principles calculation of structural, electronic and magnetic properties of the half-metallic ferromagnetic Half-Heusler compound KBaB and RbBaB are presented. We have applied the full-potential linearized augmented plane waves plus local orbitals (FP-LAPW+lo) method based on the density functional theory (DFT). For the exchange and correlation potential generalized-gradient approximation (GGA) is used.

We found that the KBaB and RbBaB in the ferromagnetic state are more favorable than the antiferromagnetic state and they exhibits half-metallic ferromagnetism, the computed equilibrium lattice parameters agree well with the available theoretical and experimental data. The calculated total magnetization of 1 μB is in excellent agreement with recent experiments.

We give also a comparison between the standard generalized gradient approximation (GGA) and the modified Becke–Johnson exchange potential approximation (mBJ–GGA) on the electronic and magnetic properties.



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Ab-silico thermodynamics of (giant) magnetocaloric materials

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All magnetic materials present the magnetocaloric effect (MCE), by which a reversible temperature change occurs when the material is subject to an applied magnetic field. In high-performance materials, the MCE is large enough to serve as the basis of efficient energy conversion devices, including heat pumps. Magnetic refrigeration is particularly attractive since it is a vapor-free, highly efficient technology, nowadays in its starting steps of commercialization. There is an on-going search for new, efficient, sustainable and cheap magnetocaloric materials. Traditionally, this search is based on empirical approaches, namely synthesizing new samples by exploring elemental substitutions and a subsequent experimental evaluation of the material's properties. As MCE materials families have a huge range of elemental substitutions to explore, computer-based materials screening/prediction approaches are naturally sought.

A computational approach to predict the performance of a given magnetocaloric material would need to start at the atomic scale, exploring the effects of chemical substitution on magnetic interactions, electronic degrees of freedom and structure. A thermodynamic approach would be required to predict the field and temperature dependence of relevant properties. We here explore a two-step process, where the microscopic properties of a given magnetic material are determined at 0 K via adequate ab-initio Density Functional Theory calculations, and thermodynamic properties are calculated via a recently reported monte-carlo method [1] applied to solving an Hamiltonian that includes coupled magnetic and structural terms.

We show that our approach is able to reproduce the giant MCE [2,3], presenting estimates of our predictive approach using real materials for comparison and validation. We find an excellent agreement on the magnetic, structural and magnetocaloric properties of metallic Gd. We present preliminary studies on Fe_2P and MnAs-based families of materials and explore the vast potential of elemental substitutions and subsequent performance impact in cubic Heusler alloys [4].

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Molecular Dynamics Investigation of the Stern Layer for Water–Silica Interfaces

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We investigate the Stern layer of charged silica-water interfaces by calculating the ion-surface interaction from biased molecular dynamics such as “Umbrella-Sampling” [1] thereby allowing to determine the ions interaction profiles with surfaces where from ensue association constants. We varied hydrophilicity of silica surface by varying the number of silanols on the surface. Each modeled surface has a single charge on deprotonated oxygen: qOc= -1 e
It is noted that the lithium is more strongly bounded than the cesium due to its small size. These results are evidenced by the values of association constants which can be made with the PMF. Lithium adsorption is favorised by the hydrophilicity of the surface, in contrast to cesium [2]. This ion specific result is confirmed by experiment at high pH. Association constant are equilibrium data. The PMF profiles allow the determination of dynamic values, namely the Mean Residence Time (MRT) [3]. We find that MRT for lithium can be as high as one second.
Our calculations show that the Stern layer can be conceived as the set of counter-ions placed near the charged surface atoms, more precisely in the first well of the observable PMF on Figure 1.

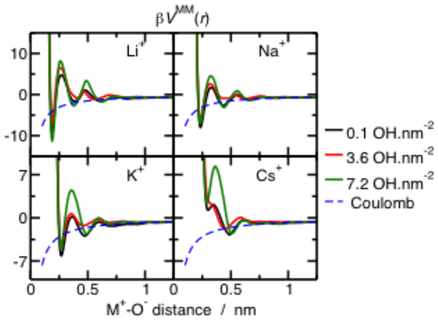

Figure 1: McMillan Mayer potential between Oxygen of silanolates on cation with O_c= -1e local net charge on the surface

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