

# XI NATIONAL INSTM CONFERENCE ON MATERIALS SCIENCE AND TECHNOLOGY

ISCHIA  
12<sup>th</sup>-15<sup>th</sup> JULY 2017



## BOOKS OF ABSTRACTS



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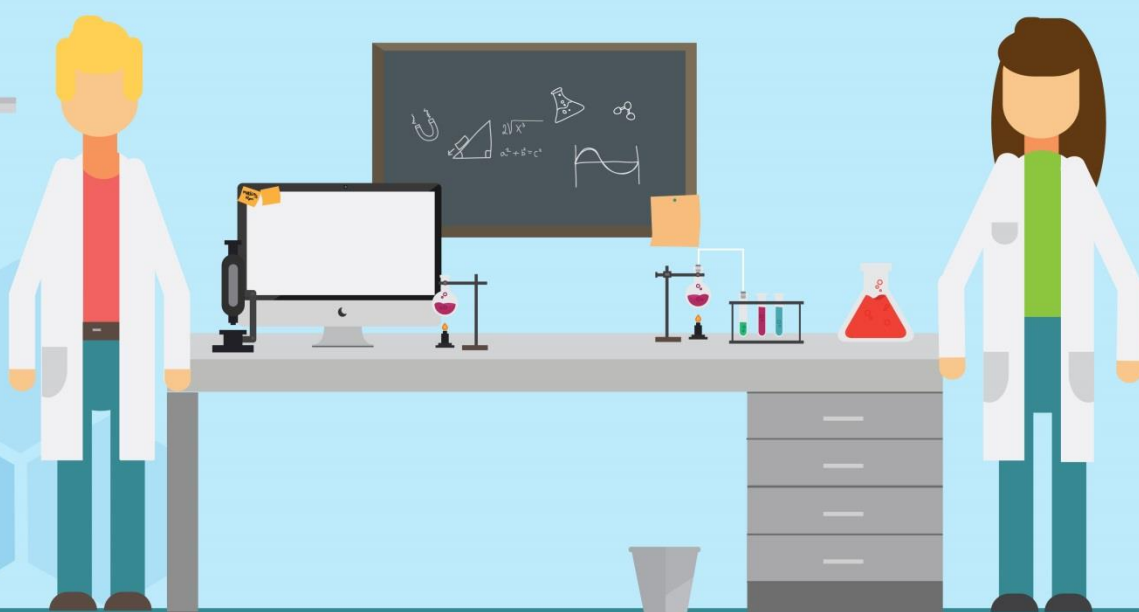
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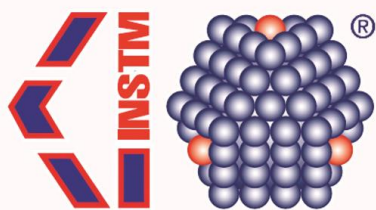
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**XI** NATIONAL INSTM  
C O N F E R E N C E  
O N M A T E R I A L S S C I E N C E  
A N D T E C H N O L O G Y

ISCHIA  
12<sup>th</sup>-15<sup>th</sup> JULY 2017



**BOOKS OF ABSTRACTS**





Plenary lecture - Invited lecture		
POLIMERI	ENERGIA	METALLI
LEGANTI	BENI CULTURALI AMBIENTE	BIOMATERIALI
SHORT ORAL		

# PROGRAMMA

	GIOVEDÌ 13 LUGLIO	VENERDÌ 14 LUGLIO	SABATO 15 LUGLIO
	<p>9.00-10.30</p> <p>Fredi Cicala Botta Scherillo Lanzara Fiore</p>	<p>9.00-10.30</p> <p>Ricciotti De Fazio Poggetti Molino Daniele Calabrese</p>	<p>9.00-10.30</p> <p>Auricchio Manfredi Salehi Kahrizsangj Pasqua Brenna Testa</p>
	<p>11.30 - 13.00</p> <p>Dintcheva Greco Esposito Corcione Dorigato Scarfato Masi Strehle</p>	<p>11.30 - 13.00</p> <p>Gastaldi Bolzoni Redaelli Coffetti Candamano Mavilia Coffetti</p>	<p>11.30 - 13.00</p> <p>Piselli Aversa Ormellese Pesenti Bucella Genova</p>
MERCOLEDÌ 12 LUGLIO	<p>Aperitivo offerto da Zwick Roell Italia</p>		<p>Chiusura del Convegno</p>
	<p>Pausa Pranzo</p>		<p>Pausa Pranzo</p>
15.00 - 17.15	<p>14.30 - 16.00</p> <p>Sciancalepore Cicala Cicogna Caradonna Scotti Mistretta</p>	<p>14.30 - 16.00</p> <p>Formisano Seghini Coppola Belli Donnini Di Mundo</p>	<p>14.30 - 16.00</p> <p>Sassoni Cappai Frontera Pepe Federici Giorgini</p>
	<p>Coffee Break offerto da Airlite by AM Technology Ltd</p>		<p>Coffee Break - Sessione Poster</p>
17.45 - 19.20	<p>16.45 - 18.30</p> <p>Sivula Punta Meroni D'Amore Demitri Bernardoni Pettinari</p>	<p>16.45 - 18.30</p> <p>Lavagna Giosuè Pia Motori Napolano</p>	<p>16.45 - 18.30</p> <p>Pierpaoli Macario De Gisi Bemporad Passalacqua</p>
	<p>Assemblea AIMAT</p>		
	<p>Cena sociale AIMAT - INSTM</p>		



**INVITED LECTURE**



# LUMINESCENT SILICON NANOCRYSTALS AND THEIR APPLICATIONS IN BIOIMAGING

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Silicon (Si) is a widely used semiconductor: it is abundant, widely available and essentially non-toxic. From the photophysical point of view, it exhibits weak light absorption and emission because it has an indirect bandgap nature. Conversely, Si nanocrystals (SiNCs) in the quantum size range (2-12 nm) can be made as viable light emitters with emission wavelength that can be tuned from the near-infrared (NIR) into the visible by decreasing their size. Covalent Si-to-carbon bonding also offers the possibility of integrating inorganic and organic components into robust structures. We studied the interaction of an inorganic silicon nanoparticle core with appended organic chromophores for the development of novel luminescent materials. H-terminated nanocrystals, produced by thermal disproportionation of silicon oxide, were used as a platform for co-passivation with dodecene and different organic chromophores, e.g. pyrene<sup>1,2</sup>, porphyrin<sup>3</sup>, or benzothiadiazole chromophores<sup>4</sup>. Excitation of the organic chromophores results in an efficient energy transfer to the nanocrystal core. To the best of our knowledge this is the first time in which highly efficient light harvesting from photoactive units to the silicon core have been demonstrated. This approach enabled us to circumvent the drawback of the low molar absorption coefficient of SiNCs. Moreover, we also demonstrated the possibility to couple two-photon excitation of the organic chromophores with sensitized emission of the SiNC in the NIR spectral region. The investigated hybrid material exhibits high quantum yield also in the NIR spectral region with lifetime in the  $\mu\text{s}$  range. This research has potential applications in bioimaging, taking advantage of time-gated luminescence microscopy to enhance image resolution.

<sup>1</sup>*J. Phys. Chem. Lett.* (2014), Vol.5, p.3325-3329.

<sup>2</sup>*Chem. Mater.* (2015), Vol.27, p.4390-4397.

<sup>3</sup>*Faraday Discussion* (2015), Vol.185, p.48-495.

<sup>4</sup>*Chem.* (2017), Vol.2, p.550-560.

# EUMELANINS: A BIOINSPIRED MATERIAL FOR ORGANIC ELECTRONICS AND BIOELECTRONICS

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Eumelanins are the black insoluble pigments of human skin, eyes and substantia nigra (neuromelanin), featuring unique assortment of chemical physical properties, i.e. broadband absorption in the UV-visible range, intrinsic free radical character, water-dependent hybrid ionic–electronic conductor behaviour<sup>1</sup>. These pigments, arising biogenetically from the aminoacid tyrosine via the oxidative polymerization of 5,6-dihydroxyindole (DHI) and/or 5,6-dihydroxyindole-2-carboxylic acid (DHICA)<sup>1</sup>, stand, today, as a unique source of inspiration for the design and implementation of soft biocompatible multifunctional materials for bio-optoelectronic devices. Interest in eumelanins stems from bioavailability, biocompatibility and their peculiar set of physicochemical properties, chiefly the electrical conductivity, which support optimistic feelings about a possible rise of eumelanin-mimics as innovative bioinspired solutions for organic bioelectronics. To date, a number of conceptual and technological gaps still hinder rapid progress of melanin-based organic electronics and bioelectronics, including in particular the limited contribution of electronic conductivity and current decay with time under biasing. Herein, we provide a concise overview of the structural and optoelectronic properties of melanins with a view to bringing to focus main issues and challenges en route to bioelectronic applications<sup>2</sup>. Basic structure-property function relationships, fundamental tailoring strategies, processing and the balance of ionic-electronic processes will be addressed along with representative examples of eumelanin-based hybrids to orient ongoing efforts toward efficient and competitive eumelanin-based technology.

<sup>1</sup> d'Ischia M., Wakamatsu K., Napolitano A., Briganti S., Garcia-Borron J. C. *et al.* (2013). *Pigmentcell & melanoma research*, Vol.26, p.616-633.

<sup>2</sup> Berggren M., and Richter-Dahlfors A. (2007). *Adv Mater*, Vol.19, p.3201-3213.

# ENGINEERING SEMICONDUCTING MATERIALS FOR DIRECT SOLAR FUEL PRODUCTION

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Developing routes to store solar energy as chemical fuels at a global scale is urgently needed for a carbon-neutral energy economy. High-efficiency direct solar-to-fuel energy conversion can be achieved using semiconductor liquid junctions in a photoelectrochemical device. However, the development of robust and inexpensive materials that operate with exceptional performance are needed to make this approach economically viable<sup>1</sup>. In this presentation our laboratory's progress in the development new materials will be discussed along with the application toward overall solar water splitting. Specifically, this talk will focus on the application of oxides such as CuFeO<sub>2</sub> as a photocathode<sup>2</sup>, organic semiconductors as photoanodes<sup>3</sup>, and solvent-exfoliated 2D semiconducting transition metal dichalcogenides (TMDs)<sup>4,5</sup>. Overcoming the challenges with charge transport, separation, recombination and water redox catalysis in these systems will be discussed with respect to the material preparation, nanostructure and defect passivation treatment. Overall it is shown that inexpensive and robust materials can offer promise for solar fuel production with advances in catalyst development and nanotechnology.

<sup>1</sup> *Nat. Rev. Mater.* (2016), Vol.1, p. 16010.

<sup>2</sup> *Chem. Mater.* (2017), Vol.29, p. 4952–4962.

<sup>3</sup> *J. Am. Chem. Soc.* (2015), Vol.137, p. 15338-41.

<sup>4</sup> *Nat. Commun.* (2015), Vol.6, p.7596.

<sup>5</sup> *ACS Energy Lett.* (2017), Vol.2, p.524-31.

## RESEARCH FIELDS, SKILLS AND COMPETENCES OF THE UNIVERSITY OF CAMERINO: THE 49<sup>th</sup> MEMBER OF THE INSTM CONSORTIUM

Pettinari C<sup>1,2</sup>

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Camerino and her university have expressed for almost 700 years a unique essence that can evolve and face the challenges of time, always remaining faithful to itself, to its values, to its long tradition. Research at UNICAM means innovation but also tradition, a stimulating creative environment, interdisciplinarity, investigation, new theories and ideas to gain a better knowledge of the world and its laws. Several research groups in UNICAM have been active in the innovative and/or functional materials sector for years. Here we will present the main lines of research and the outstanding results achieved in recent years. We will report about:

- 1) Fabrication of high efficiency organic PV devices
- 2) Advanced Composites
- 3) Bioplastics
- 4) Smart biopolymers for pharmaceutical and medical applications
- 5) Development of functional materials using advanced radiation sources
- 6) MOFs
- 7) Nanocomposite electrode materials for Li-ion batteries.



**ORAL**



# INNOVATIVE ACRYLATE-BASED SILVER NANOCOMPOSITE RESIN FOR 3D STEREO LITHOGRAPHY

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<sup>1</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

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## Introduction

The integration of nanomaterials into three-dimensional printing (3DP) offers huge potential and opportunities for the manufacturing of 3D engineered materials. For instance, due to their excellent conductivity and antibacterial activity, metallic silver nanoparticles (AgNPs) are increasingly used as nanofillers to fabricate polymer nanocomposites used in a wide range of applications ranging from sensing devices to biomedical field. Stereolithography (SLA) represents one of the most explored 3DP techniques used to build advanced resin structures. In this work, the simultaneous photo-reduction of metal precursors with the photo-polymerization of acrylate monomers for the preparation of 3DP nanocomposites is obtained by using the SLA technology.

## Material and Methods

3D acrylate-based silver nanocomposites were prepared by mixing silver acetate, AcAg, as silver salt (1.4 phr) into photocurable monomer formulation, based on a blend (3:1) of Ebecryl 7100, an amine functional acrylate, and PETIA pentaerythritol-triacrylate. Irgacure 819, bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, was chosen as suitable photoinitiator for 3D printing process and added to the photoreactive system (1 phr). In fact, working in the near UV spectrum, Irgacure 819 is responsive to the laser wavelength, used by 3D SLA printer. A commercial inverted SLA 3D Form 1+ printer (Formlabs Inc., USA) was used to print filled and pure resin samples.

## Results

The printed samples have dumbbell-shaped geometry and dimensions in agreement with the standard ISO 527-2 (Type 1BA), taken as reference. The 3D-printed samples were used for the subsequent characterizations, without further modification.

## Discussion

When the photoinitiator is irradiated, the homolytic photocleavage of the C-P bond in the Irgacure 819 molecules generates benzoyl and phosphonyl primary radicals, able to initiate both the photochemical synthesis of metal nanoparticles and the radical photopolymerization of acrylate monomers. During the layer-by-layer printing process, the focused UV laser beam of the printer was used to locally photo-induce the reduction of Ag<sup>+</sup> to Ag<sup>0</sup>, generating AgNPs, and at the same time photo-polymerize the acrylate monomers to solid resin, without any spurious reactions. The so obtained Ag nanocomposites showed improved functional and structural properties compared to the pristine resin, providing further rapid prototyping option to research and development of new products.

# MECHANICAL PROPERTIES OF PLASTIC BY FUSED DEPOSITION MODELLING (FDM): TESTING EFFICIENCY

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## Introduction

Additive manufacturing (AM) of plastic is gaining an increasing importance in industry. From being a just a rapid prototyping techniques AM is gaining wider acceptance as a production technique for functional parts. Among the different AM techniques FDM is the most important to produce functional components. However, in most cases the assessment of mechanical properties for FDM still rely on testing protocol derived from standards developed for plastics produced by traditional techniques. In the present paper a critical overview of the testing methods is reported and some statistical analysis of alternative techniques to characterize the mechanical properties of FDM parts is proposed. The present paper is the result of the experimental work carried out within the COMMAND project.

## Material and Methods

PEI and PC from Stratasys were used as main material for the present work. Most printing was carried out using the professional Fortus 400mc printer by Stratasys. Other under laboratory development materials were printed with a Roboze one 400+ machine. All the data were analyzed by the statistical software Minitab 17.

## Results

First test were aimed to evaluate the effect of specimen dimensions on the stability of testing. The ANOVA analysis revealed that only some specimen dimensions allows to obtain sound data. In addition to that, some thickness/bonding interlayer effects were found. This finding lead to the conclusion that interlaminar shear testing is relevant, despite being usually ignored, to really assess the true performances of FDM printed parts.

## Discussion

The obtained results demonstrated the need for specific testing standards for FDM parts in order to support further the material development in the field.

# PHOTOGRAFTING AS A TOOL TO MODIFY THE POLYMER SURFACE

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## Introduction

Polymer surface modification is a powerful method to impart new properties to polymeric materials without altering their bulk features. One method described in the literature to modify the polymer surface that gives good results in terms of reproducibility and efficiency, is the photografting polymerization. Indeed, the grafting polymerization of vinyl monomers onto polymeric surfaces can be successfully initiated by UV irradiation using a photoinitiator. In this work, the modification of polyethylene and polypropylene surfaces was carried out under UV irradiation by using methoxybenzophenone as a photoinitiator. TEMPO derivatives bearing functional groups or vinyl monomers substituted with polar groups were chosen as functionalizing agents to demonstrate the versatility of this procedure and to obtain functionalized materials.

## Results and discussion

The UV irradiation of a polymer surface in the presence of a photoinitiator produces macroradicals that can further react with different species. In this work, two approaches were compared to modify polymer surfaces. In the first case, TEMPO derivatives were used, since free radical TEMPO can react by coupling with macroradicals giving a covalent bond. Alternatively macroradicals can start the polymerization of different vinyl monomers leading to the modification of the polymer surface.

The grafting of TEMPO derivatives as well as the grafting polymerization of vinyl monomers was successfully carried out and confirmed by ATR-FTIR, UV-Vis and fluorescence emission analysis. Results confirmed that the nitroxide radical coupling reaction, already described for the functionalization of polyolefins and polyesters in the melt, was effective also under photografting conditions. Besides, the grafting of short polymeric chains onto the surface of PP spheres was exploited for obtaining modified polymeric particles useful in the wastewater treatment, because able to remove metal and dye ions from water.

# EFFECT OF GRAPHENE NANOPATELETS ON THE THERMAL CONDUCTIVITY OF POLYMER NANOCOMPOSITES

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## Introduction

In recent years, researchers have focused their attention on polymeric composite materials with enhanced thermal conductivity. Due to its outstanding conductive properties, graphene nanoplatelets (GNPs) is one of the most promising filler able to increase the thermal conductivity of polymers. Nowadays, researchers use GNPs with very different intrinsic properties, and for this reason it is difficult to compare the literature outcomes. In order to investigate the effect of different carbon-based fillers on the thermal conductivity of polymers, different thermoplastic and thermoset materials were filled with two commercially available graphene nanoplatelets and a natural flake graphite.

## Materials and methods

Graphene nanoplatelets were purchased from ABCR (6-8 nm thick and 5  $\mu\text{m}$  wide), and from Cheaptubes (GNPs Grade 4, <4 nm thick and 1-2  $\mu\text{m}$  wide). Natural flake graphite (Alfa Aesar) with size dimension ranging between 7 and 10  $\mu\text{m}$ . Thermoplastics (PP, ABS and TPU, from Basell, Sabic and Bayern respectively) and thermoset polymer (amine based epoxy resin, from Struers) were used as composite matrix.

## Results

On the basis of filler characterization, by means Raman, FE-SEM/EDS, TGA and XRD analysis, it was possible to attribute better intrinsic conductivity to GNPs Grade 4 with respect to the counterparts ABCR and/or graphite. In spite of this, the maximum increment of thermal conductivity of both thermoplastic and thermoset matrices was achieved by using GNPs ABCR. Moreover, surprisingly the composite containing natural flake graphite, generally showed better properties with respect to Grade 4 material.

## Discussion

The thermal conductivity of nanocomposites processed by using a filler with the higher thermal conductivity (as high quality GNPs) can be very similar to that achieved by using other carbonaceous materials. This can happen when the ratio between the intrinsic thermal conductivity of the carbonaceous fillers and that of the matrix is always over 100. This means that, for low amounts of filler, the intrinsic thermal conductivity and purity of the filler are not the key parameters which enhance the thermal conductivity of the nanocomposites. Otherwise, the thermal conductivity is mainly depending on the GNPs lateral size, but only slightly affected by the presence of impurities and defects inside GNPs.

# ZnO NANOPARTICLES ANCHORED TO SILICA FILLER AS CURING ACCELERATOR FOR RUBBER COMPOSITES

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## Introduction

Sulfur vulcanization is a consolidated process in tire industry to improve the rubber mechanical properties. ZnO is the most efficient activator currently worldwide employed in this process, in spite of its poor dispersion in rubber and partial reaction with the other curatives. Moreover, ZnO undergoes leaching during production, use and recycling of tires. Thus, the reduction of ZnO level in rubber is becoming an urgent issue. In this context, the present work aims at improving the efficiency of the curing process and, simultaneously, at reducing the amount of employed ZnO, by replacing it with a novel activator ZnO-NP@SiO<sub>2</sub>-NP, constituted by ZnO nanoparticles (NPs) anchored to silica, a common filler used in rubber composites for tires. ZnO-NP@SiO<sub>2</sub>-NP behaves at the same time as curing agent and reinforcing filler.

## Material and Methods

ZnO-NP@SiO<sub>2</sub>-NP was prepared by a sol-gel synthesis to anchor ZnO NPs (3-5nm) on the silica surface and characterized by X-Ray Diffraction, TEM Microscopy, Solid State NMR, IR and XPS spectroscopies. ZnO-NP@SiO<sub>2</sub>-NP were used to prepare cured polyisoprene (IR) nanocomposites with silica, by blending and compression molding. Curing rate was evaluated by the calculating the apparent activation energy in non-isothermal conditions using Differential Scanning Calorimetric measurements. The cross-linking products were investigated by a Model Compound Vulcanization approach. The composite dynamic-mechanical properties was assessed by Rubber Process Analyzer in a shear stress mode.

## Results

ZnO-NP@SiO<sub>2</sub>-NP showed higher curing efficiency in sulfur cross-linking of IR composites and the final cured materials presents improved dynamic-mechanical properties compared to those conventionally obtained by using higher amount of microcrystalline ZnO. This is due to the immobilization of ZnO NPs on silica surface, through covalent Si-O-Zn bonds, which minimizes the Zn leaching, provides a homogeneous dispersion of zinc in the rubber matrix and increases the accessibility of the curative reactants to Zn<sup>2+</sup> ions.

## Discussion

The higher curing efficiency of ZnO-NP@SiO<sub>2</sub>-NP was explained by its capability to accelerate two stages of the process: the formation of the sulfurating complexes at the beginning of reaction and of the mono- and di-sulfide cross-linking chains which account for the higher cross-linking density and mechanical properties of the final cured material.

# POLYSACCHARIDE-BASED NANOSTRUCTURED AEROGELS

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## Introduction

Polysaccharides, such as cellulose and galactomannans, are versatile building blocks derived from natural and renewable sources, which in the last decade have been widely investigated for the design of advanced functional materials with enhanced properties.

## Material and Methods

The selective oxidation of hydroxyl groups present on the polysaccharide backbone favours the introduction of functional moieties for further processing. Oxidation can be mediated by different nitroxyl organocatalysts (TEMO, NHPI) and by enzymes as well (laccase). A thermal cycle, consisting in freeze-drying the resulting milky polysaccharide suspension, eventually mixed with polyamine solutions, leads to organic aerogels whose mechanical and structural properties can be increased by heating up to 100 °C.

## Results

When applied to cotton or wood cellulose, the oxidation step promotes the partial conversion of alcoholic functions to carboxylic groups. As a consequence, the defibrillation of the bulk material occurs, leading to the formation of cellulose nanofibers (CNF). The freeze drying process in the presence of suitable cross-linkers favors the re-combination of CNF in macro-sized nanostructured porous aerogels, whose performances have been exploited in terms of adsorption and release activity. When a similar approach is applied to galactomannans, the resulting aerogel shows superb water absorption capability.

## Discussion

The new CNF-based aerogels were successfully tested as potential sorbent units for water remediation from heavy metals ( $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cr^{3+}$  and  $Cu^{2+}$ ) and organic contaminants (including pesticides and drugs). Moreover, after selective functionalization, the system can be easily modified, in order to introduce additional chemical properties, such as sensing for specific targets, or to enforce the mechanical and structural performances. These polysaccharide-based aerogels have been also investigated in terms of drug-delivery efficiency. Finally, these aerogels can also operate as suitable organic templates for further organic and inorganic coating, in order to differentiate the properties of the resulting structures (hydrophobicity, antioxidant or photocatalytic activity). This work has been sponsored and financed by Regione Toscana (POR FESR 2014-2020, Call RSI2014, Project NanoBonD) and Regione Lombardia (RL-INSTM Call20016, Project NAIADI).



# NANOCARRIERS BASED ON NANOMETRIC NATURAL AND SYNTHETIC OXIDES: THE ROLE OF THE LINKER-OXIDE INTERACTIONS

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## Introduction

Nanocarriers represent an emerging platform for the diagnosis and treatment of diseases such as cancer. Among them, oxide nanomaterials like halloysite nanotubes (HNTs) have recently emerged as promising candidates for drug delivery. HNTs are low-toxic and low-cost aluminosilicate clays with nanotubular structure, presenting a positively-charged  $\text{Al}(\text{OH})_3$  inner lumen and a negatively-charged  $\text{SiO}_2$  outer surface. While drug loading based on electrostatic interactions is generally adopted in the literature, this strategy leads to poor control over the release process. Stronger interactions can be used to improve the hybrid stability and to induce the site-specific delivery of bioactive molecules using a physicochemical trigger.

## Material and Methods

Several oxides were adopted as substrates for surface functionalization. Commercially available HNTs were pretreated to tailor surface hydration. Alumina and silica nanoparticles, as models of the two HNT surfaces, were synthesized by precipitation and modified Stöber methods, respectively. Titania nanoparticles were also synthesized by sol-gel synthesis as model parallel system, on the grounds of our previous experience. Surface functionalization was carried out with both commercial and lab-synthesized compounds (alkylsilane, phosphonic acid and isocyanate derivatives).

## Results

An extensive characterization of the functionalization degree and adsorption modes was carried out by combining contact angle measurements, FTIR, zeta-potential, XPS and NEXAFS analyses. Kinetics and reversibility aspects were studied, finding notable differences among the investigated oxides. Adsorption isotherms were obtained for each substrate by controlling the electrification features of the oxide and the dissociation degree of the adsorbates, particularly in the case of phosphonic acid derivatives. Preliminary *in vitro* tests were carried out to evaluate cell toxicity.

## Discussion

HNTs represents promising nanocarrier systems as shown by the limited toxicity in *in vitro* cell toxicity tests. Silane derivatives show high affinity for both silica and alumina surfaces and are thus not suitable for the selective loading of a single HNT surface. Phosphonic acids proved the most interesting moiety for the selective functionalization of the inner lumen of HNTs, due to the lability of their interactions with silica. Surface functionalization with isocyanates was instead hindered by competition with physisorbed water. Possible mechanisms of controlled release using physicochemical triggers (light, pH) were determined.

# HIGH-SPEED NANOINDENTATION: A NOVEL TOOL FOR MECHANICAL CHARACTERIZATION OF HIGHLY HETEROGENEOUS MATERIALS AND SURFACE PATTERNING

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## **Introduction**

Instrumented Indentation Testing represents a well-established and widely used standard technique for the characterization of mechanical properties (elastic modulus and hardness). Nevertheless, new nanoindentation methods were recently introduced, opening the way to a new not-standard application. The introduction of the High-Speed nanoindentation technique, which allows to realize one complete indentation cycle per second, dramatically reduced the time needed for high time-consuming tests. Two High-Speed nanoindentation applications are presented: an innovative tool for the mechanical characterization and high resolution mapping of high heterogeneous materials and a new technique for the surface patterning (N.I.H.L., Nanoindentation High-Speed Lithography).

## **Material and Methods**

In the first one, two different and very high heterogeneous materials (LiMn<sub>2</sub>O<sub>4</sub> polymer battery cathodes and cement pastes) were characterized combining Standard CSM and High-Speed Nanoindentation tests with FIB microscopy and SEM-EDS maps. In the second application, two different nanoindenter tips, realized by F.I.B. nanomachining, were used to nano-print surface patterns on two different substrates.

## **Results**

High resolution mechanical maps for highly heterogeneous materials, phases analysis obtained by the statistical deconvolution of the results, surface patterning on both hard and soft materials and measurement of the adhesive properties with the same equipment.

## **Discussion**

Regarding the first application, the obtained results were post processed obtaining mechanical maps in good agreement with SEM micrographs and EDS analysis; a physical phases analysis based on the statistical study of the results deconvolution allowed the discrimination of all the phases contained in the tested materials. For the second application it was possible to modify the surface morphology over large areas, with the benefits of the pattern control on a nano-scale. A very large pattern was realized on bulk PMMA, highlighting macroscopic effects on the free surface energy, characterized by the contact angle technique. The obtained results open a new way to the I.I.T. exploiting, raising its importance in the most advanced industrial applications.

# BIOCOMPOSITES BASED ON POLYESTERS AND NATURAL FIBRES

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## Introduction

The use of “bio-polymers” for the production of “bio-plastic” and “Bio based composites” has become worldwide an assessed priority with the aim of reducing dependence from petro sources, and handle the concern for disposal of waste generated from not degradable plastics. Their use has attracted interest of various application sectors ranging from packaging to automotive components and other high value applications, and has been from many year a main topic of research activity in our unit, bound to several related European and Regional projects (PHA- ARFAS 2007-2013). Advantages of natural fibres on conventional reinforcements such as glass and aramid fibres are their relative cheapness, ability to recycle, and competition with them in terms of strength per weight of material. However the strength of the bond between fibres and matrix is substantial for the best mechanical performances of a composite. Many factors interacting with each other affect the complex process of the fibre/matrix adhesion.

## Material and Methods

Bio-polyesters such as polylactic acid and polhydroxyalkanoates (PHAs) have been addressed as polymeric matrices for the production of biobased composites with natural fibres such as wood, ramie, cellulose, wheat, potato, peas, and posidonia oceanica. Materials were processed both in laboratory and in industrial scale and extensively studied for morphological, thermal and mechanical properties. Degradation in different environment (compost, soil, marine water) was also addressed coupled with study of products environmental sustainability by Life Cycle Assessment.

## Results and discussion

Composites based on PLA or PHAs and different natural fibres up to 30% by weight was achieved on industrial scale with increasing of elastic modulus and impact energy-absorbing capability related to increasing the fibres content. Several mathematical models were applied to fit the experimental trends as a function of composition. Degradability in compost, soil, and in the case of PHAs based composites also in marine water, was promoted by natural fibres presence. Sustainability is also improved by carbon balance due to the use of biobased polymers and bio based natural fibres, as well additives introduced in the materials, such as plasticizers were selected giving preference to biodegradable and bio-based products.

# TUNING THE BEHAVIOR OF CARBON/Mg(OH)<sub>2</sub> MATERIALS FOR THERMOCHEMICAL HEAT STORAGE

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## Introduction

Referring to the Energy Efficiency Directive, waste heat storage represents a key issue for helping EU to reach 20% energy efficiency target by 2020. A growing interest matured on MgO/H<sub>2</sub>O/Mg(OH)<sub>2</sub> thermochemical system that stores heat (200-400°C) through the dehydration of Mg(OH)<sub>2</sub> and releases stored heat when required by reversible hydration of MgO in presence of water vapour. For the future development of this technology, the improvement of the active medium performances is a key issue. In this study, exfoliated graphite (EG)-Mg(OH)<sub>2</sub> hybrid materials are synthesized by two preparation methods: Deposition-Precipitation (DP) and Reverse Deposition-Precipitation (RDP).

## Material and Methods

DP reaction consists in the gradual addition of a solution containing Mg precursor (Mg(NO<sub>3</sub>)<sub>2</sub>) to a NH<sub>4</sub>OH solution (1.3M) containing a specified amount of EG. RDP reaction, contrarily, is carried out through the gradual addition of the precipitating agent (1.3 M NH<sub>4</sub>OH solution) into the solution containing the Mg salt and the EG. The effect of the variation of some reaction conditions (i.e. temperature, precipitating-agent feeding rate) on morphology, crystal structure and thermochemical behaviour of the developed samples have been investigated by means of Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and ThermoGravimetric (TG) analysis.

## Results

It was observed that the preparation method strongly influences the Mg(OH)<sub>2</sub> coverage on EG surface. Specifically, by DP method thin Mg(OH)<sub>2</sub> layers uniformly covers EG surface, while for RDP a worsening of coverage degree is observed. Moreover, varying RDP synthesis conditions a difference in Mg(OH)<sub>2</sub> particle size was evidenced. The smaller is the particle size, the higher is the capacity of the active medium to dehydrate/hydrate.

## Discussion

It can be argued that the mean Mg(OH)<sub>2</sub> particle size is strictly correlated to the achievement rate of a supersaturation degree, which depends from the synthesis conditions: the rapid achievement of the supersaturation degree during the hydroxide precipitation favors the formation of a larger number of smaller Mg(OH)<sub>2</sub> crystals. Moreover, the smaller is the Mg(OH)<sub>2</sub> particle size the better is the dispersion over the carbonaceous support and the higher are the reaction conversions in the hydration/dehydration process. A linear correlation between particle size and dehydration/hydration conversion was observed.

# AB-INITIO MODELLING OF THE ARRANGMENT OF OXYGEN VACANCIES AND THEIR EVOLUTION UNDER HEATING AND ELECTRIC FIELD IN HfO<sub>2</sub>-RRAM

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## Introduction

Researching new architectures and storage mechanisms has been attracting great attention and investment from the main electronics-companies whose aim is improving memory-devices in terms of speed and dimension. Metal-Oxide Resistive random access memories RRAM based on 'filamentary switching' represent a very promising candidate for the future market of memory devices in which the extreme device downscaling still remains compatible with excellent attainable performances and good industrial compatibility. Although the presence of a less resistive filament has been observed by TEM and C-AFM, it is still unclear how shape, growth and local composition of the filament evolves during the electrical operation leading to the switching.

## Material and Methods

We performed Ab-Initio Molecular Dynamics (AIMD) on a 5x5x5 supercell of monoclinic m-HfO<sub>2</sub> in which oxygen atoms were extracted to design Oxygen Vacancies (OV) based filaments. Temperatures from 1000 to 4000 K were considered to estimate the oxygen diffusion barrier heights, and their dependence on the charge state and electric field.

## Results

The evolution of the filament shape and composition due to the re-organization of the OV during the switching operation were studied to unravel the role of the temperature and external electric fields in modulating the electrical properties, endurance and data retention of sub-stoichiometric HfO<sub>2</sub> based RRAM.

## Discussion

We demonstrate that oxygen vacancy filaments are energetically more stable than randomly distributed defects. Furthermore, the stability of the filaments increases with the number of confined oxygen vacancies. Energetic and structural analyses show that bonds between neighboring coordinative unsaturated Hf atoms promote the filament stability and that electron trapping, due to electron injection, increases the cohesive energy until the injection is moderate. The highly oxygen deficient configuration of the filaments leads to a substantial lowering of the HfOx band gap, which locally increases the conductivity of the system. Charge injection and electric fields modify the oxygen ions' mobility in the proximity of the filament. The simulations suggest that oxygen ion diffusions can lead to an asymmetric reduction of the filament thickness and thus to its progressive disruption where the vacancy cohesion energy is lower.

# CONTROLLED CRYSTALLIZATION IN $\text{CuO-V}_2\text{O}_5\text{-TeO}_2$ GLASSES: CORRELATION BETWEEN STRUCTURE AND ELECTRONIC CONDUCTIVITY

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## Introduction

Transition metals (TMs) containing glasses represent very promising materials in the design of new-generation solid state batteries. In particular, the addition of  $\text{V}_2\text{O}_5$  to a tellurite glass matrix has attracted significant attention due to the relatively higher electronic conductivity reached by these systems with respect to other vanadium containing oxide glasses such as phosphates, borates, and silicates ones. In order to guarantee electronic conduction, the TM ion should exist in more than one valence state thus promoting electron transfer from ions in a lower valence state to those in a higher one. Moreover, the electronic conduction can be further enhanced through nano-crystallization of the material as a consequence of the creation of defective regions. The aim of this work is the development and characterization of vanadium tellurite glasses containing vanadium oxide crystalline grains of nano-or submicrometer sizes with the goal of enhancing the electrical conductivity of the starting glasses.

## Material and Methods

Glasses belonging to  $\text{CuO-V}_2\text{O}_5\text{-TeO}_2$  system were synthesized by melt-quenching method and thermally treated at different temperatures and times, in order to promote a controlled crystallization. The as synthesised glasses were characterized by means of thermal analysis, physical and electrical properties, X-Ray diffraction, Raman spectroscopy and FEG-scanning electron microscopy in order to correlate the structure with the conductivity results.

## Results

Different values of conductivity were obtained as a function of vanadium content, temperature and time of the heating treatments. Particularly, samples treated at the onset crystallization temperature showed higher conductivity and lower activation energy with respect to the starting glass and the other treated samples. The FEG-SEM images of these samples showed crystals of 10-50  $\mu\text{m}$  immersed in glass matrix.

## Discussion

The conductivity enhancement of the appropriately thermally treated glasses is closely related to the microstructure of these materials. Indeed, the enhanced electronic conductivity of the samples treated at the onset crystallization temperature was attributed to a substantial role of the interfacial regions around newly formed micro-grains, which creates the favorable conditions for the electric charge transport. In these defective regions, an increased concentration of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  centers, responsible of the electron hopping, can be hypothesized.

# Co AND (Co,Ni) NANOPARTICLES: EFFECT OF PREPARATION PROCEDURE ON CATALYTIC ACTIVITY IN ETHANOL STEAM REFORMING AND CO<sub>2</sub> METHANATION

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## Introduction

Hydrogen production through bioethanol steam reforming is a very promising way for low temperature production (523-773 K). Up to now, the catalyst formulation is still not optimized, even if Nickel and Cobalt were identified as active phase for this process, being more robust and cheaper than noble metal based catalysts.

## Material and Methods

The synthesis of Cobalt based nanopowders has been carried out following different preparation pathways, i.e. reduction in aqueous solution or thermal degradation, starting from different metals precursors. This in order to study the effect of the residual counter ions on catalysts activity, structure and performances. The complexity of the system is increased for bimetallic NPs [(Ni,Co) NPs] that, at the present, have been prepared using reduction method in aqueous solution. All the NPs were fully characterized by XRD, IR, XPS, DC-SQUID, FE-SEM, HR-TEM with EELS spectroscopy. Catalytic activity tests have been carried out with a complete characterization of catalysts before and after catalytic runs.

## Results

Co and bimetallic catalysts have been tested in ESR and CO<sub>2</sub> methanation. Concerning ESR, all the materials result to be active in conversion of ethanol in presence of steam. Unsupported Co NPs were active in complete reforming with high selectivity to CO<sub>2</sub> at 773K, showing a high hydrogen yield (90%) while bimetallic NPs demonstrate an intermediate behavior in between that of the two metals.

## Discussion

All the three catalysts have been successfully prepared, characterized and tested in ESR showing promising performances. The effect of the synthetic procedure and the possible preparation residuals will be discussed because they might strongly affect both catalytic activity and catalysts stability.

# ELECTROLESS PURE NICKEL DEPOSITION ON CARBON MICROFIBERS FOR ENHANCED INTERFACE ALUMINUM MATRIX COMPOSITES

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## Introduction

Electroless Nickel-Phosphorous Plating (ENP) is one of the most promising plating technique in the field of micro or nanostructured reinforcement. This is due to its versatility in terms of complex substrate-shapes (the coating is deposited without using electrical current) and homogeneity of coating. Despite of those advantages, the introduction of a reactive element in the matrix (P) can be deleterious for composite's properties (for example mechanical fracturing caused by formation of phosphorous anhydrides even at low temperature). In this work a new Electroless Nickel Pure Plating (ENP<sup>2</sup>) technique was proposed to modify the interface of a carbon reinforcement without introducing any reactive element in the coating.

## Material and Methods

Electroless nickel pure plating was carried out using hydrazine monohydrate ( $N_2H_2 \times H_2O$ ) as reducing agent. Lactic acid and disodium EDTA were used as complexing agents in different concentrations. Micrograf HT carbon microfibers (CMFs) were produced by PROCHIMA (Italy) and used without any further purifications. First, the as-received CMFs were added in deionized water and dispersed with assistance of both ultrasonication and mechanical stirring for approximately 30 min. Then, a quantity of hot plating solution was added. Influence of temperature and plating ratio (volume solution/mass of MCF - ml/g) was studied at different temperatures.

## Results

XRD diffraction and EDS analysis have confirmed that the fibers were covered by pure nickel. SEM micrographies have shown the influence of plating ratio and plating temperature on the homogeneity of coating.

## Discussion

The surface functionalization of CMFs with pure nickel coating has allowed to investigate the mechanism of plating. The nickel grows in macro domains onto the surface with a speed that change with the plating parameters.



# DEVELOPMENT OF HYDROGEL FIBROUS PATCHES FOR CELL DELIVERY

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## Introduction

Three-dimensional networks made from natural polymers have attracted considerable attention as platforms for cell delivery. Due to low toxicity and extremely mild gelation, alginate-based hydrogels appear as ideal choice for cell encapsulation. High cell viability can be maintained in the process and biologically active molecules can be blended-in to overcome alginate lack of biological cues. Here, we developed a system for cell encapsulation into continuous alginate-based fibers, to prepare hydrogel patches for cell delivery.

## Material and Methods

Alginate microfibers were prepared using a purpose-designed system. A syringe pump was used to inject alginate/cell suspension in a coaxial flow of CaCl<sub>2</sub> solution. The extruded fibers were collected in a strainer and post-treated with higher concentration of CaCl<sub>2</sub>. Microfibers were morphological characterized by optical microscopy and aged in PBS at 37°C to assess their stability. Different materials were evaluated: pure alginate, alginate/Type A gelatin (1.5 % w/v) and alginate/Hyaluronan (0.2% w/v) blends. Mouse fibroblasts L929 were encapsulated and process effectiveness was evaluated after encapsulation by live/dead assay and by Alamar Blue assay up to 10 days.

## Results

After optimization of processing parameters, homogeneous microfibers were obtained. Microfibers diameter (60 - 400 μm) was found to depend on alginate solution flow rate, low molarity of CaCl<sub>2</sub> solution (0,035 M) and its high flow rate (3850 ml/min). Microfibers stability in PBS was dependent on blend composition and Hyaluronan blends were found to maintain their integrity longer than other two formulations (up to 15 days). The system resulted efficient in cells encapsulation (about 70% viable cells). Cell release was observed on all materials and after initial latency cell colonization of plate wells begun at day 5 and Alamar Blue values increased.

## Discussion

The system developed was found to enable dimensional and compositional control of microfibers and maximize encapsulated cell viability and proliferation. Blending with biologically instructive molecules was also demonstrated to be an effective strategy.

# EFFECT OF INJECTABLE CALCIUM PHOSPHATES ON MACROPHAGE/OSTEOBLAST COCULTURE MODEL

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## Introduction

Calcium phosphate (CaP) materials are widely used as bone substitutes for their properties close to those of the mineral phase of bones. Nevertheless, after several months, CaP-based materials release particles that may be phagocytosed by monocytes, leading to an inflammatory reaction. Strontium is well known for osteoporosis treatment for its role as inhibitor of resorption and also as stimulus of bone formation. Furthermore, previous study demonstrated that the integration of phosphoserine-tethered poly( $\epsilon$ -lysine) dendrons (G3-K PS) in CaP gels increases the proliferation of hMSC and enhanced their long-term ALP and OCN activity. On this basis, the purpose of this work was to study the effect of injectable strontium-modified CaP materials (Sr-CaP) with and w/o G3-K PS on the inflammatory reaction.

## Material and Methods

Strontium-modified CaP gels with and w/o G3-K PS were prepared at room temperature by sol gel-approach. The effect of gel materials on inflammatory response was evaluated in macrophage/osteoblast indirect co-culture method. For macrophage culture, intracellular and extracellular ILs levels were evaluated by RT-PCR and ELISA kit, respectively. Meanwhile for MC3T3 osteoblasts the effect of conditioned media on the expression of specific markers involved in osteogenesis was analyzed by RT-PCR.

## Results

The biological studies demonstrated that the cytokine genes were suppressed for all modified materials. The addition of Strontium in CaP and CaP/G3KPS may decrease secretion of inflammation-related cytokines by macrophages. Moreover, CaP/G3KPS and Sr-CaP/G3KPS showed the highest cell viability, followed by CaP-HA. Different conditioned medium not only have an effect on cell proliferation, but also modifying gene expressions.

## Discussion

We have demonstrated that CaP-G3KPS and Sr-CaP/G3KPS can upregulate the early and later marker of osteogenesis and may further enhance bone forming functions of the cells. This study was supported by PNR-CNR Aging Program 2012-2014.

# EFFECT OF ION DOPING ON ZIRCONIA MESOPOROUS COATINGS AND THEIR POTENTIAL BIOMEDICAL APPLICATION

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## Introduction

Zirconia has different biomedical application since it is a non-toxic material with outstanding mechanical properties and high chemical stability and it is assuming increasing importance in dental implant production. The surface modification of fully-zirconia dental restoration may allow for the improvement of osseointegration and antibacterial activity.

## Material and Methods

Pure and doped zirconia mesoporous coatings were obtained through the self-assembly method mixing  $ZrCl_4$  and Pluronic F127 as soft template agent in ethanol. The required amount of nitrate precursor was added to the initial mixture to produce Ca/Ga-modified  $ZrO_2$  coatings (11% and 25% mol.). Template removal process was performed at 400-600 °C. The prepared solution was spin coated on cover glasses for following chemical-physical characterization (contact angle, XRD and TEM) and biological tests (Alamar blue assay and SEM). [SAOS-2] line of human osteoblast-like cells were employed for biological characterization.

## Results

A ordered mesoporous structure was observed by TEM, showing pores around 5-10 nm both for pure and doped  $ZrO_2$  surfaces. By XRD observation tetragonal phase was found stable until 600 °C for pure zirconia coatings and up to 800 °C for both stabilized samples. The presence of ion further increased the thermal resistance of mesoporous structure. Surface hydrophilicity increases along with temperature and decreases adding Ca-dopant. Generally, higher viability values were reported for meso-structured zirconia samples in comparison with tested non porous surfaces.

## Discussion

The presence of dopant allowed imparting more thermal resistance to the mesoporous structure in comparison with the undoped one affecting the sample phase transition alongside. Surface nanopatterning and chemical composition can be easily modified to impart specific functionality to the substrate by doping meso-structured zirconia samples.

# SYNTHESIS OF CNT FOAMS FOR OIL RECOVERY

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## Introduction

The use of sorbents in common oil spill treatment is considered the most ideal solution because it can remove oil from the sea. Synthetic organic sorbents such as polymeric foams are the most commonly used commercial sorbents in oil spill recovery. But they adsorb not only oil but also water, decreasing the sorption efficiency. In this work a silicone foam comprising carbon nanotubes (CNT) is synthesized. Pristine and functionalized CNT are used. The foam filled with pristine CNT shows a higher oil sorption capacity and an optimal maneuverability and reusability.

## Material and Methods

CNT are prepared by Chemical Vapor Deposition of  $i\text{-C}_4\text{H}_{10}$  on 17 wt.% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst. CNT are then functionalized by exposure to nitric acid vapors. Degree of chemical oxidation process was tested by measuring the mass loss ( $\Delta m$ ) in Thermo Gravimetric Analysis. Three kinds of CNT samples are used, pristine, functionalized for 2h ( $\Delta m=22$  wt.%) and functionalized for 4h ( $\Delta m=36$  wt.%). The CNT silicone foams are obtained by foaming a solution of a silicone matrix with CNT filler (5.6 wt. %) in presence of a Sn-based catalyst. Absorption tests are carried out at room temperature with different oils (virgin naphtha, kerosene, pump oil and crude oil) under stirring. Oil absorption capacity is evaluated as the percentage ratio between the weight of the absorbed oil (after saturation) and the initial weight of the foam.

## Results and Discussion

The foam morphology is a porous structure of relatively spherical cells with interconnected pores. Absorption tests evidence that all the obtained foams absorb effectively oils. The efficiency increases in low density oils, in which pristine CNT foam reaches about 700 wt.% and 830 wt.% respectively in kerosene and virgin naphtha. Furthermore, analyzing the absorption performances in water, oil selectivity of the composite foams can be obtained. The unfilled silicone foam evidences a low selectivity to oil/water recovery. The addition of CNT filler on silicone matrix significantly reduces the water absorption, slightly enhancing the oils absorption. Consequently, this class of composite foam evidences a high oil/water recovery selectivity. Based on these promising results their use in industrial field could be forecasted.

# MAGIC SPHERES FOR BIOSPHERE: CAPTURE, MONITORING AND REMOVAL OF PERSISTENT POLLUTANTS

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## Introduction

Sensitive detection and efficient removal of micropollutants are challenging tasks in environmental remediation. In the last years, we have developed photocatalytic core/shell microspheres that are able to exploit the combination of multiple light scattering and evanescent fields to enhance the sensitivity of the Raman response, allowing the detection of different analytes with unprecedented reproducibility. In parallel, the photocatalytic efficiency of these materials is crucial for the selective removal of organic pollutants. The same spheres are excellent low-background matrices for laser desorption/ionization mass spectrometry, which enabled the development of multi-modal analytical platforms for monitoring adsorption and degradation of the pollutants. Here we extend this approach to the production of a new class of adaptive materials that can efficiently capture and remove various micropollutants, including drugs, persistent organic pollutants and inorganic species like hexavalent chromium and arsenite/arsenate ions. The micropollutants are captured by receptors obtained by either raw or waste materials and their removal efficiency was tested in real working conditions.

## Materials and Methods

The core/shell SiO<sub>2</sub>/TiO<sub>2</sub> microspheres were obtained by coating monodisperse silica beads with a conformal shell layer through atomic layer deposition. The alginate/TiO<sub>2</sub> macrobeads were obtained through ionotropic gelation of anatase nanoparticles, using Ca<sup>2+</sup> ions for cross-linking. The functionalization of both micro- and macrospheres with organic acids was monitored by FTIR and microRaman. The analysis of micropollutants was carried out by combining UV-Vis, x-ray fluorescence, mass spectrometry and Raman microspectroscopy.

## Results

The adsorption/removal capabilities of cellulose-based filters activated with “magic spheres” were tested against different samples of water contaminated with several hazardous pollutants, including Cr(VI), As(V)/As(III), textile dyes (MB, MO...), polychlorinated biphenyls and drugs, showing very high efficiency for both processes. Moreover, the “magic spheres” exhibited enhanced sensitivity in Raman sensing.

## Discussion

The unique combination of macro- and microspheres functionalized with different organic acids that can be obtained from raw materials enables the efficient capture, analysis and removal of both organic and inorganic micropollutants, opening exciting perspective for technology transfer. This work has been sponsored and financed by Regione Lombardia (RL-INSTM Call20016, Project MI ADATTI E L'ABBATTI).

# GREEN TOOLS FOR IMPROVING PHAs EXTRACTION FROM MICROBIAL SLURRY

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## Introduction

The availability of green and cheap technologies for recovery of polyhydroxyalkanoates (PHA) from microbial biomass is fundamental for the development of a reliable and sustainable productive chain. While major research efforts have been addressed to the development of Mixed Microbial Cultures able to improve the PHA storage capacity of the bacteria, possibly using cheap wastes and feedstock as carbon source. The downstream costs, ranging around 50% of the overall processing costs, are mainly related to extraction and separation from the bacterial biomass, and presently none of the adopted procedures complies with green chemistry requirements.

## Material and Methods

PHA containing biomasses were conveniently pretreated (thermally, mechanically and/or chemically) and extracted with green solvents. The obtained PHA were analyzed via elemental analysis, GPC and Thermogravimetric Analysis to provide the quality of the extracted polymers.

## Results

We propose alternative extraction approaches, based on green components and with good efficiency, which also maintain the very high average molecular weight typical of the bacterial PHAs. Switching anionic surfactants (SAS) were applied without any pre-treatment of the biomass before the extraction of PHB for microbial slurry. Alternatively, dimethylcarbonate (DMC) was used, once again without any pre-treatment of the biomass before the extraction, to recover both Poly(hydroxybutyrate) or its copolymers, separating them from bacterial residues. The PHA recovery and purity were very high, and its thermophysical characteristics were excellent, thanks to the low extraction temperature necessary for achieving these good extraction performances.

## Discussion

Both the use of SAS as well as the application of DMC proved to be efficient methods for the extraction in terms of yields and purity. Moreover, the latter appears suitable for application to MMCs, which are particularly resistant to cell hydrolysis and disruption. Good results are obtained, comparable to those achieved by use of the chlorinated solvents. Moreover, the results achieved in terms of purity and average molecular weight of the obtained PHAs are well comparable with those obtained using single strains cultures. Finally, all the applied chemicals do not represent an environmental concern, since they can be both easily recycled and reused, or they can be readily biodegraded.

# ELECTROCATALYTIC BEHAVIOR OF SUB-NANO Cu CLUSTERS IN THE CO<sub>2</sub> REDUCTION REACTION

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## Introduction

Copper is a peculiar element in the electrocatalytic reduction of CO<sub>2</sub>, an area of growing relevance. Sub-nano Cu clusters have been suggested by computational studies to be good candidate for CO<sub>2</sub> reduction, being able to lower the overpotential in the reaction. However, there is no clear evidence on how these sub-nano copper particles behave during electrocatalytic conditions. Here, we report an electrochemical investigation of two size-controlled Cu nanoclusters, prepared by a deposition method developed at the Argonne National Laboratory (ANL). The absence of organic ligands or capping agents in the resulting clusters, even at the level of contamination (which cannot be avoided in conventional wet techniques) makes these materials very interesting for electrocatalytic studies.

## Material and Methods

The samples were fabricated by using size-selected cluster deposition, a technique which enables mass selection with atomic precision. The clusters were soft landed on the support (glassy carbon tips - GC) and neutralized upon landing with a picoamperimeter used for biasing the support. The samples were properly modified to allow the electrochemical testing by square wave voltammetry (SWV) and cyclic voltammetry (CV).

## Results

The electrochemical investigations evidence that the coordination of CO<sub>2</sub> influences the electrocatalytic behavior of sub-nano Cu clusters.

## Discussion

Cu<sub>5</sub> and Cu<sub>20</sub> clusters were chosen being representative of a planar-type cluster configuration and of a 3D-type (double icosahedron) structure, respectively. Grazing-incidence X-ray absorption near edge structure measurements were used to determine the valence state and chemical composition of Cu in the as fabricated samples. The electrochemical study of naked Cu<sub>5</sub> and Cu<sub>20</sub> nanoclusters evidences some relevant results regarding the redox behavior of these sub-nanometre size copper particles and the effect of CO<sub>2</sub>. Cu<sub>20</sub> nanoclusters show anodic redox processes occurring at much lower potential with respect to Cu<sub>5</sub> nanoclusters, which behave relatively similar to much larger Cu particles. However, Cu<sub>5</sub> nanoclusters coordinate effectively CO<sub>2</sub> (hydrogen carbonate) in solution differently from Cu<sub>20</sub> nanoclusters and larger Cu particles. This effect, rather than the redox behavior, is connected to the ability of Cu<sub>5</sub> nanoclusters to reduce CO<sub>2</sub> under cathodic conditions at low overpotential.

# MECHANICAL PROPERTIES OF THERMALLY-TREATED BASALT FIBRES

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## Introduction

Glass fibre reinforced thermoset composites account for about 90 % of all the composites currently produced. Land-fill is the most common way of disposal for these composite materials with serious consequences for the environment. Various methods have been proposed to recycle composites, being thermal recycling by pyrolysis the most preferred technique. Because of the high temperatures reached during pyrolysis, recovered glass fibres are unusable as reinforcement in new polymer matrix composites. In this regard basalt fibres are claimed to exhibit better high temperature resistance compared to E-glass fibres, therefore suggesting better prospects to survive an end-of-life composite thermal recycling process. The present work is an experimental investigation about the effects of temperature and atmosphere on the tensile behaviour of single basalt fibres.

## Material and Methods

The heating conditions investigated reproduce those used in thermal recycling of polymer matrix composite materials. The effects of temperature and atmosphere on fibre properties were studied using basalt fibres sized with an epoxy and polypropylene compatible sizing. The variation of properties is investigated by performing tensile tests on fibres heat-treated for 1 h up to 600 °C in air and in inert atmosphere. After testing, the fracture surfaces of the fibres were examined using scanning electron microscopy. To identify the crystalline phases and their growth and development, X-ray diffraction analysis of annealed fibres was performed.

## Results

The tensile strength and modulus of thermally-treated basalt fibres were affected by both temperature and atmosphere. In particular, a loss in fibre strength and an increase in modulus were found.

## Discussion

A marked strength loss occurred under heating conditions normally used for high temperature incineration of polymer composites. The modulus of thermally-treated basalt fibres increased linearly with conditioning temperature. These effects can be interpreted in terms of decomposition of the organic sizing and structural relaxation during thermal annealing. XRD analysis led to the exclusion of the effect of incipient crystallization on the mechanical behaviour of the fibres. Scanning electron microscopy revealed a failure dominated by a single population of defects mostly originating on fibre surface.



# EFFECT OF FUNTIONALIZATION OF MACRO, MICRO AND NANOMATERIAL ON THE MECHANICAL PROPERTIES OF CEMENT-BASE COMPOSITES

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## Introduction

Different materials can be used as fillers/reinforcements in cement or concrete for civil infrastructure or oil&gas applications. The introduction of fillers reduces the cement porosity leading to stronger and more durable products, moreover the high surface area of nano-materials makes them efficient in controlling the propagation of cracks. However, in the case of carbon-based materials (carbon nanotubes, graphene, carbon fibers, non-polar polymers), the main issue is related to the poor interaction between matrix and filler. To improve the composite properties, functionalization of the fillers was performed, with the aim to enhance their direct dispersion in water and their interaction with the cement paste.

## Material and Methods

Carbon fibers TOHO-Tenax (6 mm length), carbon nanotubes Nanocyl 7000 and recycled tyres rubber were chemically oxidized with various chemicals: sulfuric acid, nitric acid, hydrogen peroxide, sodium hydroxide. Graphene-based materials were purchased with different oxygen content from Cheaptubes and Graphenea. An oil-well cement Class G was used, curable at 85 °C. The composites were mechanically characterized by three-point flexural tests in CMOD mode.

## Results

Surface composition and size of filler showed to have an important role in the interaction with cement. In fact, different types of chemical oxidation bring to different mechanical behavior. The results obtained shown that a strong oxidation of nano and micro-material allow a better dispersion in water and a good interaction with cement. On the other hand, an oxidation at low concentration of acid enhance the mechanical properties of rubber-cement composites.

## Discussion

The optimization of the oxidative treatment has a strong effect on the interaction and adhesion of fillers with cement. In particular for carbon fibers a treatment with piranha solution enhance the surface wettability and enhance the bridging effect in the composites. For carbon nanotubes the oxidation with sulfonitric acid improve the dispersion in aqueous media and the dispersion in the cement matrix. For rubber is better a slight oxidation with piranha solution, a too strong treatment damages the surface and create defects that do not guarantee the proper interaction with cement paste. Flexural, compressive strength and toughness all increase when materials are properly surface treated.



**SHORT ORAL**



# DREAM: DRIVING UP RELIABILITY AND EFFICIENCY OF ADDITIVE MANUFACTURING

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## Introduction

The DREAM project, financed by the EU Commission (H2020, Work program: FOF-13-2016: Photonics Laser-based production, grant agreement no. 723699) is an end-user driven action which aligns the research and development of Additive Manufacturing (AM) technologies to the specific needs of its three industrial end users, Ferrari SpA, Adler Ortho France SARL, and RB Srl. The aim of DREAM is to significantly improve the performance of laser PBF of titanium, aluminium and steel components in terms of speed, costs, material use and reliability, also using a LCA/LCC approach, whilst producing work pieces with controlled and significantly increased fatigue life, as well with higher strength-to-weight ratios.

## Material and Methods

To reach the needed productivity and to bridge the gap between the demonstrated possibilities of AM processes and their exploitation as business opportunities it is necessary to work interdisciplinary on the following three main challenges: (i) part modeling and topology optimization; (ii) raw material improvement to avoid powder contamination; (iii) process and software optimization to enable high throughput production. This approach has been used in the DREAM project on three different materials, representative of the three different application fields of the involved end users: titanium for prosthetic, aluminium for automotive and steel for mould-making applications. The first obtained results are related to the effect of powder recycling on the mechanical properties of Ti6Al4V printed samples.

## Results

Tensile strength proved to be between 1100 and 1200 MPa, and yield strength between 1050 and 1150 MPa. No evident detriment was observed proceeding with the powder aging. A slight decrease of elongation at break and of part density was obtained with prolonging powder reuse. Further analyses are ongoing aimed at appraising the statistical significance of such result.

## Discussion

The powder global aging doesn't seem provoking negative effects on final mechanical properties of additive manufactured components. The only exceptions seem to be the elongation at break and density.



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# EFFECT OF THE NATURE OF THE $\pi$ -DELOCALIZED MOIETY TO TUNE THE SECOND ORDER NLO RESPONSE OF NOVEL CYCLOMETALATED Pt(II)-COMPLEXES

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## Introduction

Organometallic chromophores with both luminescent and second-order nonlinear optical (NLO) properties are of growing interest as new molecular multifunctional materials, since they offer additional flexibility, when compared to organic chromophores, by introducing NLO active electronic charge-transfer transitions between the metal and the ligand tunable by virtue of the nature, oxidation state and coordination sphere of the metal centre. In the last few years it appeared that N<sup>4</sup>C<sup>4</sup>N-coordinated cyclometalated dipyriddybenzene Pt complexes are very emissive compounds characterized by high second-order NLO properties. This observation prompted us to study new members of this appealing family.

## Material and Methods

We prepared variously substituted 1,3-di(2-pyridyl)benzene Pt(II) complexes, by reaction of K<sub>2</sub>PtCl<sub>4</sub> with the related ligand at reflux in CH<sub>3</sub>CN/H<sub>2</sub>O under argon for 18h. Their second-order non linear properties were determined in DMF solution with the electric-field-induced second-harmonic generation (EFISH) technique, working with a non resonant incident wavelength of 1.907  $\mu$ m.

## Results

We obtained new Pt(II) terdentate complexes with different  $\pi$ -delocalized substituents at the central 5-position of the phenyl ring of the N<sup>4</sup>C<sup>4</sup>N ligand and we found a strong effect of the nature of the  $\pi$ -delocalized moiety on the second-order NLO properties, determined by the EFISH technique. Of particularly relevance is the nature of the linker between the  $\pi$ -delocalized donor moiety and the 1,3-di(2-pyridyl)benzene system.

## Discussion

Some of our new Pt(II)-complexes are characterized by a  $\mu\beta_{1.907}$  value much higher than that of Disperse Red One, an NLO chromophore currently used in electro-optics polymers. Their NLO response is strictly correlated to the nature of the  $\pi$ -delocalized system on the 5 position of the central benzene ring. Remarkably, it appeared that a thiophene moiety is better than a double or triple bond to optimize the nonlinear optical response. In conclusion some of the new Pt (II) complexes prepared in this work are particularly appealing for NLO applications.

# INNOVATIVE COMPOSITES FOR ADDITIVE MANUFACTURING

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## Introduction

Additive Manufacturing techniques, in particular Fused Deposition Modelling (FDM), represent the nowadays approach for the realization of functional components or product with specific design. Among possible materials under study as filaments, the aim of the present work is to assess the development of new formulations to be used as a novel soluble material, named Poly-paper (patent co-owned by the Politecnico di Milano and NextMaterials srl), for FDM processing.

## Material and Methods

For the matrix, a formulation based on water-soluble PVA with degree of hydrolysis between 75% and 90%, average molecular weight between 75 and 150 kDa and a polydispersity index between 2.5 and 4.3 was selected. For the filler, different percentage of cellulose were investigated (from 0% up to 60% w/w). Filament extrusion was performed and the obtained samples were characterized by tensile test, thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) to investigate, respectively, the real cellulose content and the thermal transition together with the  $E'$ ,  $E''$  and  $\tan \delta$  trend in the temperature range 10 – 250°C.

## Results

Mechanical tests exhibited a good correlation between cellulose content in PVA matrix and tensile properties. In particular, elastic modulus showed an increase of three folds from 10 to 30% w/w cellulose filler. At the same time, a slighter increase in stress at break (from  $9.78 \pm 0.13$  MPa to  $11.94 \pm 0.67$  MPa) together with a significant reduction in elongation at break was detected (from  $276.1 \pm 17.0\%$  to  $57.7 \pm 2.5\%$ ). In addition, different degradation kinetics is expected for the considered composite materials here described. TGA-DTA and DMA analysis are under evaluation.

## Discussion

The obtained results demonstrated the possibility to extrude filament with different properties depending on the cellulose filler in PVA matrix. Financial support: Funding was received from the Bando Congiunto INSTM, Regione Lombardia 2016, Project IN-RL11 COMMAND, Materials for Additive Manufacturing.

# ULTRALIGHT MAGNESIUM ALLOY FILLED WITH MICRO AND NANO CARBON STRUCTURE

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## Introduction

Magnesium is the lightest structural metal with a very low density (1.74 g/cm<sup>3</sup>) and low melting temperature (650 °C). In recent years, it has been increasingly used in different industrial sectors: automotive, aeronautic and nautical industries. However, it is interesting to improve its technological properties. In this work, micro and nano fillers were added to magnesium alloy with a centrifugal casting process directly in the metal. In particular, carbon microfibers (CMFs) and carbon nanoplates (CNPs) were chosen as reinforcement. In this work it was studied the influence of the dispersion of different carbon fillers by measuring the mechanical properties of magnesium micro and nano composites.

## Material and Methods

Magnesium alloy shavings (AZ63) and carbon nanoplates (M grade with 15 µm of diameter) were provided by COMETOX (Italy). Micrograf HT carbon microfibers were produced by PROCHIMA (Italy). Two different composites were prepared by mixing magnesium alloy shavings directly with fillers in a mortar. Acetone was used to promote the dispersion procedure. Melting and casting were carried out in a Neutor Digital induction furnace with a centrifugal casting made by F.lli Manfredi (Italy) in a controlled atmosphere (Ar). The dispersion rate of fillers (at different wt %) and the microstructure were evaluated by optical microscopy for CMFs samples. For CNPs samples, microstructural characterizations were conducted with a FE-SEM Zeiss-Auriga. Flexural strength and Young modulus were evaluated with a Zwick Roell Z2.5 and correlated with the different percentage of fillers.

## Results

Microstructural characterization has shown the presence and dispersion of the fillers in AZ63 specimens in both cases but was observed defectiveness in the matrix due to wettability of the fillers with the molten metals. Negligible increasing of Young modulus measured with flexural test confirmed the microstructural characterization data.

## Discussion

To increase wettability suitable metal deposition on carbon filler could be a way. Tests will be presented in future works.



# CERAMIC NANO-PARTICLES INFLUENCE ON PROPERTIES OF PHENOLIC RESIN COMPOSITES

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## Introduction

Phenolic resins have been widely employed for their good mechanical properties, high thermal stability (300-350°C) and their easy manufacturing process. Different kinds of phenolic resins can be obtained thanks to the different combination of phenol and formaldehyde and the choice of a basic or acidic catalysis. Resole phenolic resins are thermosetting polymers with high mechanical resistance and, according to their compositions, an high char yield. The mechanical performance of phenolic resins can be enhanced with the addition of nano-fillers. Furthermore at inert atmosphere and for temperature higher than 300°C a pyrolysis reaction occurs and the kinetic can change according to the amount and nature of the nano-particles.

## Material and Methods

Nano-composite materials were obtained by mixing different nano-fillers with a commercial phenolic resin (Durite SC1008). Two different manufacturing processes were carried out in order to obtain samples suitable for bending tests (according to ASTM Standards D7265/D7264M-07) and for thermogravimetric analysis (from RT to 1000°C in inert atmosphere). In particular, in the first case 1-propanol was selected as resin solvent in order to minimize the porosity of the samples, in the second case ethylene-glycole was selected to obtain a gel phase and cured porous samples which can be easily reduced to powder. The samples were manufactured with different ceramic nano-fillers (ZrO<sub>2</sub>, MgO, SiC) with the same granulometry (~50 nm). An ultrasonic bath and a sonicator probe were employed to optimize the dispersion of nano-particles in the solvent. After the manufacturing all samples were cured in an oven at the higher temperature of 180°C. The microstructure of the samples were evaluated by SEM analysis.

## Results

Nano-composites with a phenolic resin matrix and ceramic nano-fillers show enhanced mechanical properties compared with pure phenolic resin. For example, with addition of nano-ZrO<sub>2</sub> the mechanical resistance is incremented of about 50%. The thermogravimetric data enlighten some difference in the pyrolysis reaction depending on the nano-filler addition.

## Discussion

The manufactured nano-composites show the possibility to optimize the behavior of the resin during the pyrolysis reaction. The addition of nano-particles can be useful to modify or improve the mechanical characteristics of a phenolic resin.

# PAPER FIBER AND WOOD FLOWER SURFACE SOAKING ATTACK. A PREVIOUS STUDY FOR WPC MATERIALS IMPROVEMENT

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## Introduction

During last decades, natural fillers additions to polymeric matrixes have been developed, in particular Wood Plastic Composites achieved great importance thanks to their properties and possibility to use waste material for their production. Another source of waste product is paper, potentially useful as filler in polymeric matrixes. In order to improve fillers-matrix interface many efforts have been done, among which the use of surface modification is one of the most used. Chemical treatment with NaOH, has been used in this work, analysing the effect of several soaking time on different natural fillers.

## Material and Methods

Wood flour of hardwood beech was provided by La.So.Le Est Srl-Italy. Wood particles have medium diameters of 250µm. Cellulosic recycled papers were derived from a common industrial product used as self-adhesive labels. We have obtained through micronization fibres with diameters of about 15-20 microns and lengths of the order of 250-500 micron. Sodium hydroxide treatments were performed with 1M concentration of NaOH at room temperature. We performed treatments of 30,60,120 and 240 minutes. Contact angles and SEM analysis have been performed.

## Results

All fillers treated have displayed evident effects of different soaking time period, considering if the attack has been performed or not. Contact angle at zero time was reduced by 30 minutes soaking time, suggesting hydrophobic elements removal on natural fillers. Increasing soaking period affected both contact angles and water absorption speeds. SEM analyses displayed sodium hydroxide effects.

## Discussion

Interesting results have been obtained by sodium hydroxide treatments, with possible modification of interfaces and properties of resulting composites. In this work, we changed soaking time, but NaOH concentration and temperature could be also analysed. Different kind of analyses could be performed, such as infrared spectroscopy, thermogravimetric analyses, and crystallinity evaluation through X-ray diffraction. Moreover, different treatments could be considered, such as ionic liquid treatments.

# WATER BASED POLYURETHANE ADHESIVES FOR FLEXOGRAPHIC PRINTING

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## Introduction

Water-based polyurethane adhesives are a promising alternative to solvent-based polyurethane adhesives typically used in different academic and industrial research fields, in particular as waterborne adhesives for metals, e.g. flexographic printing bars. With the aim of developing innovative and eco-friendly water-based adhesives for metal substrates, different aqueous polyurethane formulations were prepared via the "pre-polymer mixing process", characterized by three synthetic steps: I) reaction of isocyanates, aliphatic and aromatic, with polyols having high molecular weights to enhance cold-adhesive properties; II) reaction of polyurethanes with amines in order to improve the macromolecular properties and adhesive stiffness; III) preparation of water-based polyurethane emulsions.

## Material and Methods

The polyurethane formulations were prepared by reaction of aliphatic and aromatic isocyanates – hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate and diphenylmethane diisocyanate – with high molecular weight polyols – polyethylene glycols and polypropylene ethers -, short chain amines and a comonomer with an acid group as emulsion promoter. The resulting polyurethanes were analyzed via NMR spectroscopy, Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analyses (DMTA).

## Results

Different waterborne polyurethane formulations were successfully synthesized via the pre-polymer mixing process; adhesive films were prepared via solvent casting deposition using polyethylene terephthalate films as carrier substrates. Polyurethanes macromolecular structure were determined via <sup>1</sup>H NMR spectra and their thermal features were assessed via DSC measurements. DMTA analyses were performed on industrial polyurethane adhesives in order to determine reference adhesion and rheological parameters.

## Discussion

A preliminary study on polyurethane water-based adhesive formulations for metal flexographic printing bars was performed. The pre-polymer mixing process allows permits a good control over the soft and hard phases of prepared polyurethane samples, modulating the adhesive and the rheological behavior of the resulting polymer films obtained via solvent casting deposition. The work is continuing with an emphasis placed on the study of adhesive and rheological features, related to the microstructural properties, compared with the ones measured for industrial solvent-based samples. Sticker prototypes based on waterborne polyurethane emulsions will be prepared via Mayer bar deposition technique. This work was performed within the project "GreenStickers" founded by Consortium of Materials Science and Technology (INSTM) and Regione Lombardia.

# DISTANT NANOSTRUCTURES INTERACTING UPON AN EXTERNAL STIMULUS

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## Introduction

Transport phenomena have profoundly been influenced by the development of nanotechnology. We have investigated a system comprising of two discrete covalently surface-confined monolayers, in which one of them can supply an important component to the other, by exposing to a mass transport phenomenon their external surfaces.

## Material and Methods

In a glove box under a N<sub>2</sub> atmosphere some SiO<sub>2</sub> and Si(100) freshly cleaned substrates were covalently coated with a trichloro[4-(chloromethyl)phenyl]silane monolayer. Then some monolayer were reacted with a solution of 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphyrine, H<sub>2</sub>THPP, and some others with a solution of 4-(2-pyridylazo)resorcinol, PAR. Then the PAR\_SAMs molecules were quantitatively complexed with Cu<sup>2+</sup> ions in a 1:1 ratio. The covalently immobilized monolayers were characterized by XPS, AFM and UV-vis.

## Results

Two H<sub>2</sub>THPP\_SAM and Cu\_PAR\_SAM<sup>+</sup> monolayers were fixed in a particular Teflon set-up, put in a cuvette and covered with an acidic solution (starting pH=1.88). Then successive aliquots of a NaOH solution have been added. There are UV-vis evidences that the -OH ions activated a controlled Cu<sup>2+</sup> mass transfer from the Cu\_PAR\_SAM<sup>+</sup> to the H<sub>2</sub>THPP\_SAM.

## Discussion

The monolayers setup exhibits many optically active states. We have shown that these systems can communicate among themselves and exchange mass upon a precise external input. Therefore, for the first time it has been reported a guided transfer of Cu<sup>2+</sup> cations between two molecular interfaces, specifically from a Cu\_PAR\_SAM<sup>+</sup> to a H<sub>2</sub>THPP\_SAM. This transfer was carried out in an aqueous environment and driven by a fine tuning of an external trigger (-OH<sup>-</sup>). It has been possible to read the physical states of the overall system that, in turn, represent the answer (output) to the chemical OH<sup>-</sup> stimulus. For the first time, the protonation and complexation equilibria of monolayers have been described. Moreover, we trust that this archetypal setup may represent the platform for the development of advanced interfacial communication systems based on optically active monolayers.

# BIOCOMPATIBLE HYBRID MAGNETIC NANOPARTICLE FOR THERANOSTIC APPLICATION

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## Introduction

Magnetic nanoparticles, (MNP), are fundamental building-blocks for developing innovative nanodevices with multi-fold therapeutic and diagnostic activities, including magnetic fluid hyperthermia, (MFH), Magnetic Resonance Imaging, (MRI) and targeting of tumor cells. Combining MNPs with the human protein H chain ferritin, HfT, is an interesting way to achieve this goal as they offer multiple advantages. MNPs of iron oxide could be mineralized within the inner cavity of HfT, however, their size is not large enough to produce a significant MFH efficiency. In this work we propose an approach based on connecting large, chemically synthesized, magnetite MNPs of 15-18 nm with apo-HfT, thus conjugating a high MFH efficiency with the drug carrier and targeting functions of apo-HfT. Moreover we demonstrate how the same system can be used as carrier for the chemotherapeutic drug doxorubicin.

## Material and Methods

Highly monodisperse superparamagnetic MNPs were been synthesized with thermodecomposition of metalorganic precursor in high boiling solvent in the presence of surfactant and chemically, physically and magnetically characterized. The junction with apo-HfT was realized by a hetero-bifunctional PEG and was verified by Gel electrophoresis and Atomic Force Microscopy. In vitro tests were conducted on PC3: human prostate cancer cells line. The cell samples were incubated in the presence of decreasing concentration of MNP-HfT, and then exposed to an alternating magnetic field of intensity and frequency below the threshold of clinical application.

## Results

In vitro tests showed that the MNP-HfT system was highly biocompatible and confocal microscopy demonstrated a good level of cell internalization. Calorimetric measurements showed high Specific Absorption Rate. The MTT viability showed that using a concentration of MNP that increases temperature above 41°C, the MNP-HfT system is able to eliminate almost all cancer cells, while at lower concentration the effect is significantly reduced. Moreover, relaxometric measurements indicated this nanosystem had a good capability of enhancing the contrast in MRI.

## Discussion

All tests show that this system has promising applications as theranostic device for nanomedicine. These encouraging results, led us to use the HfT hollow core as carrier for the chemotherapeutic drug doxorubicin, and improve the effectiveness of the device, which is currently under investigation.

# OXIDATION EFFECTS ON THE SERS RESPONSE OF SILVER NANOPRISM ARRAYS

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## Introduction

Silver nanostructures are widely employed for Surface Enhanced Raman Scattering (SERS) characterizations owing to their excellent properties of field confinement in plasmonic resonances. However, the strong tendency to oxidation at room temperature of these substrates may represent a major limitation to their performances.

## Material and Methods

In the present work, we investigated in detail the effects of oxidation on the SERS response of a peculiar kind of Ag nanostructured substrates, i.e., bi-dimensional ordered arrangements of Ag nanoprisms synthesized by nanosphere lithography. Particularly, wavelength-scanned SERS measurements were performed on Ag nanoprism arrays (NPA) with a different level of oxidation to determine the SERS enhancement curves as a function of the excitation wavelength around the dipolar plasmonic resonance of the arrays. The experimental results were compared with those obtained by finite elements method simulations. With this approach, we were able to decouple the effects of spectral shift and decrease of the maximum value of the SERS enhancement observed for the different oxidation conditions.

## Results

From a practical standpoint we can state that the tendency of silver towards oxidation does not preclude the use of Ag NPAs as platforms for SERS sensing with thiol- terminated molecules. Benzenethiol was found to effectively bind to the oxidized NPA surface as it does to the metallic NPAs: the SERS enhancement reduction demonstrated in the oxidized samples amounts only to a factor of 2.5 and therefore does not alter significantly the NPA performances required for applications.

# NEW SOL GEL APPROACH FOR THE SYNTHESIS OF Ln<sup>3+</sup> DOPED NaYF<sub>4</sub> THIN FILMS: ANALYSIS OF PHASE STABILITY AND LUMINESCENCE PROPERTIES

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## Introduction

Luminescent trivalent lanthanide (Ln<sup>3+</sup>) activated fluoride materials have attracted great attention for a wide variety of technological applications, ranging in microelectronics, optics, photovoltaic devices and for biomedical assays. In particular, the NaYF<sub>4</sub> host has been studied for doping with Ln<sup>3+</sup> ions, such as Eu<sup>3+</sup>, Yb<sup>3+</sup>, Er<sup>3+</sup>, Yb<sup>3+</sup>, Tm<sup>3+</sup>, to achieve optimal photoluminescence properties through upconversion (UC) or downconversion (DC) processes. These forms of spectral conversion have been considered as a solution in the area of photovoltaics for the most widely used silicon based solar cells, to harvest the extra-bandgap photons that are lost in the common solar devices. In the present study, a new sol-gel preparation route to nanostructured Yb<sup>3+</sup>, Er<sup>3+</sup> and Yb<sup>3+</sup>, Tm<sup>3+</sup> co-doped β-NaYF<sub>4</sub> thin films has been optimized through an accurate control of the synthesis parameters, such as molar ratio, times of aging, technique of deposition and annealing temperature.

## Material and Methods

The fluorinated β-diketonate compounds, Na(hfa)tetraglyme and Ln(hfa)<sub>3</sub>diglyme (Ln = Y, Er, Tm, Yb,) have been applied as single precursors of the metals and fluoride ion. A combined sol-gel and spin-coating approach has been applied to grow Yb<sup>3+</sup>, Er<sup>3+</sup> and Yb<sup>3+</sup>, Tm<sup>3+</sup> co-doped β-NaYF<sub>4</sub> films. X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX) have been used to characterize the deposited films.

## Results and discussion

A systematic study has been implemented to optimize the formation of single hexagonal β-NaYF<sub>4</sub> phase, much more efficient than the cubic α-NaYF<sub>4</sub> phase with respect to the UC properties. Structural, morphological and compositional characterization of the films, carried out through XRD, FE-SEM and EDX, respectively, show the formation of polycrystalline β-NaYF<sub>4</sub> films with the correct doping ratio and a very homogeneous surface. Strong emissions in the visible and near infrared regions upon 980 nm laser excitation indicate that efficient UC processes are present. The proposed sol gel approach has the potential advantage of being a tunable and scaling up method for the production of upconverting β-NaYF<sub>4</sub> thin films with high homogeneity in thickness and composition.





**POSTER**



## FOR TECHNOLOGICAL APPLICATIONS

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### Introduction

In the recent years, the research and development of magnetic materials with improved properties for several technological applications (e.g., medicine, data storage, refrigeration, electronics, optics, catalysis, sensors) has been focused on nanomaterials that have unique physical and chemical properties with respect to the corresponding bulk materials. However, despite of the promising properties, the final application of nanomaterials still remains an open challenge and considerable efforts are required to develop technological procedures for the exploitation of nanostructured magnetic materials in real devices. In this contribution we discuss the synthesis of nanostructured hard and soft magnetic materials specifically tailored to realize rare earth free permanent magnets and low power loss transformers, respectively.

### Materials and Methods

Soft ( $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ) and hard ( $\text{SrFe}_{12}\text{O}_{19}$ ) ferrite nanoparticles (NPs) were synthesized by two different approaches: the first by co-precipitation of metal chlorides in a basic aqueous solution, while hard NPs by low-temperature solid-state reaction using metal chlorides and sodium hydroxide. The obtained powders were sintered at different temperature ranging from 600 to 1200 °C under different conditions. Pristine and sintered products were characterized by transmission electron microscopy, scanning electron microscopy, X-ray powder diffractometry and inductively coupled plasma. Magnetic (saturation magnetization (Ms), coercivity (Hc)) and electronic properties (AC initial permeability and AC power losses at 2 MHz) were also evaluated.

### Results

High crystalline ferrite nanoparticles were successfully obtained by the two different synthetic strategies both for the soft and for the hard magnetic material. The magnetic and electronic properties (AC initial permeability and AC power losses) of the synthesized materials allowed to identify the conditions to obtain materials with the best performances for the desired applications. These synthetic strategies present many advantages such as easiness of scale-up to industrial production, low cost, high yields and low environmental impact (water or no solvent).

### Discussion

This work was focused on the synthesis of soft and hard magnetic materials by two different synthetic strategies. The obtained nanopowders present a high degree of crystallinity and magnetic properties suitable for the desired applications (low power loss devices and production of rare earth free permanent magnets with a high energy product). Research supported by EU- H2020 AMPHIBIAN Project n. 720853

# TRIBOLOGICAL BEHAVIOR AND MICROSTRUCTURAL ANALYSIS OF SELF-LUBRICATING COMPOSITE COATINGS DEPOSITED BY PLASMA TRANSFERRED ARC

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## Introduction

Stellite coatings are a class of cobalt-based alloys, often deposited by Plasma Transferred Arc (PTA) and used in components operating in harsh environments because of their good resistance to wear and corrosion. The present study aims to assess whether and how the tribological properties of a Stellite alloy may be improved by adding solid lubricant and hard ceramic compounds. Modified Stellite coatings were tested, and their properties were compared to those of plain Stellite.

## Materials and Methods

A Stellite 12 alloy deposited on steel by PTA was used; CaF<sub>2</sub> and MoS<sub>2</sub> were selected as lubricant compounds, while TiC was added as a reinforcement. The microstructure of the modified coatings was analyzed by scanning electron microscopy (SEM), and element and phase analyses were performed through energy dispersion spectrometry (EDS) and X-ray diffraction analysis (XRD) respectively. Vickers microhardness tests were carried out (ASTM E-384-89). Wear tests at room temperature were performed with an inverted block-on-ring configuration (ASTM G77). Volume losses were calculated by profilometric analysis, and weight variations were evaluated too.

## Results

The addition of lubricant and reinforcing phases did not affect the Stellite 12's microstructure and density; both EDS and XRD analyses confirmed the presence of the additive compounds. When compared with simple Stellite, the modified coating experienced a 13% decrease in Vickers microhardness, and an increase in material loss after wear test; the friction coefficient and the block temperature were slightly lower.

## Discussion

The modification of Stellite 12 with self-lubricant and reinforcing phases affected the tribological behavior by providing a lubricating effect. Nonetheless, the self-lubricating coating was softer than the conventional one and underwent more mass loss post-wear test. More studies will be needed to optimize the process and the material.

# EFFECT OF PROCESSING ROUTES ON THERMOELECTRIC PROPERTIES OF $\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$ COMPOUND

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## Introduction

Among thermoelectric materials, used for direct electrical power conversion of waste heat sources, skutterudites show great potential. In fact, electron and phonon contributions to thermal conductivity can be decoupled through insertion of interstitial atoms, such as lanthanides or alkaline earth metals, in the cubic structure, leading to improved conversion efficiency.

## Material and Methods

Powders of n-type skutterudite  $\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$  were prepared by grinding bulk ingots obtained by melt solidification, followed by annealing (P1), and ribbons obtained by rapid solidification, followed by annealing (P2) and without annealing (P3). Powders were sintered in bulk form by Open Die Pressing (ODP1, ODP2 and ODP3).

## Results

X-Ray Diffraction and Scanning Electron Microscopy evidenced that P1 and P2 are composed by  $\text{CoSb}_3$  single phase, while in P3,  $\text{CoSb}_2$  and Sb phases were also observed. ODP2 and ODP3 are denser than ODP1, as a consequence of a more efficient packing of the corresponding P2 and P3 starting powders, which are characterized by a larger size distribution with respect to P1. ODP2 and ODP3 showed a lattice parameter of 9.0548 Å and 9.0446 Å, respectively, suggesting a greater solubilization of Yb inside the elementary cell in ODP2 with respect to ODP3. ODP2 and ODP3 showed microhardness values around 560-580 HV. Indents showed radial and lateral cracks. The occurrence of chipping suggests that cracks propagate by clivage.

## Discussion

ODP2 and ODP3 present similar values of Seebeck coefficients and electrical conductivity, despite the observed differences in microstructure. Conversely, ODP2 presents a lower thermal diffusivity with respect to ODP3, due to the larger solubilization of Yb inside the elementary cell. The dimensionless ZT figure of merit was calculated, obtaining a value of about 1 for ODP2 around 450 °C, which turns out promising for thermoelectrical applications.

# EFFECTS OF UNCONVENTIONAL FILLERS ON THE PERFORMANCES OF COMMERCIAL PAINTS FOR INDOOR APPLICATIONS

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## Introduction

The effect of using unconventional fillers, both as addition or as total replacement of a conventional calcareous filler, on the ability of commercial paints to improve IAQ, for the comfort and health of occupants, has been tested.

## Material and Methods

Two different types of commercial paints are considered (A and B paints). A is an acrylic paint for indoor applications, B is an acrylic paint for outdoor applications. In the case of paint B, two different types of unconventional fillers (F1, F2), characterized by high porosity and specific surface area, are added in the commercial formulations as it is or as total replacement in volume of the conventional filler. Paints are tested and compared in terms of inhibition of mold growth (UNI EN 15457:2008), water vapour permeability (UNI EN 1015-19:2007 - UNI 7783:2013), moisture buffering capacity (NORDTEST) and depolluting properties as ability of removal a known quantity of Methylethylketon in a closed box. Paints are applied and tested on two different substrates: real substrate where paints are applied (pre-mixed mortar commercially available), and inert substrate.

## Results

There are no evidences of moulds growth for all paints. Paint A gives the lowest value of  $\mu$  both if applied on inert substrate or pre-mixed mortar. The addition of unconventional fillers in paint B is very effective in reducing  $\mu$  factor, in both cases, up to 60 %. Again, regarding the moisture buffering value (MBV), with the simple addition of unconventional filler F1, the performance of paint B is increased 3 times, when applied on the inert support, and of about 30% when applied on the mortar substrate. The addition of unconventional fillers permits to improve the depolluting capacity of paint B of about 15%.

## Discussion

The application of paint A on the mortar substrate does not imply substantial changes in the substrate properties. The addition of unconventional fillers permits to enhance the ability of paints B to positively affects IAQ. The high porosity and polarity of unconventional fillers enhance the transpirability, the MBV and depolluting ability of this paint and, consequentially, of the whole system mortar + paint.

# OXIDATION OF g-C<sub>3</sub>N<sub>4</sub> AS VIABLE ROUTES TO IMPROVE THE PHOTOCATALYTIC PERFORMANCE

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## Introduction

Global energy shortages and the environmental damage caused by the combustion of fossil fuels have limited the sustainable evolution of human society. Research and development of renewable, clean and carbon-neutral alternative energy sources is, thus, urgently required to reduce our dependence on fossil fuel. Among the numerous energy carriers, hydrogen is one of the ideal alternative candidates.

## Material and Methods

Graphitic carbon nitride is an exemplar material for metal-free photocatalytic hydrogen production, essential to drive the change to a greener economy. Nonetheless, improvements on the crystal configuration and optimization of electronic structure and microstructure of g-C<sub>3</sub>N<sub>4</sub> for high performing visible-light photocatalysis is still challenging and expected. Oxidation is an effective means to introduce structural distortion to semiconductors which can dramatically modify their electronic structures, resulting in efficient separation of electron–hole pairs and achieving high photocatalytic activity of catalysts. The samples have been synthesized starting from melamine polymerization and characterized for their structure, surface area, IR spectra, electronic structure (XPS) and photocatalytic hydrogen production.

## Results

Oxidation is an effective means to introduce structural distortion to semiconductors which can dramatically modify their electronic structures, resulting in efficient separation of electron–hole pairs and achieving high photocatalytic activity of catalysts.

## Discussion

The optimization of the photocatalytic performances of this material has been carried out by its gradual oxidation in an analogous approach as done for other nanostructured carbon-containing materials. The oxidation make it possible to extend the response of g-C<sub>3</sub>N<sub>4</sub> to visible light and to insert electron withdrawing character which play a significant role in improving its photocatalytic performances. In addition, by oxidation it is possible to introduce C=O and –OH groups which play a role in chemical reactions catalized by g-C<sub>3</sub>N<sub>4</sub>.

# BIOPOLYMERIC BILAYER FILMS FOR PACKAGING APPLICATIONS PREPARED BY CO-EXTRUSION FILM BLOWING

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## Introduction

The requirements for reducing packaging waste drove academic efforts to search compostable bio-sourced polymeric materials. Multilayer systems can represent a suitable strategy to obtain the required properties and to improve biopolymer performance. Thus, the aim of the current work is the preparation by co-extrusion film blowing of a bio-based bilayer film with the purpose to overcome the drawbacks of the individual components.

## Material and Methods

The two biopolymers used in this work are a film grade MaterBi<sup>®</sup>, which is a mixture of biodegradable polyesters of proprietary composition produced by Novamont, and a film grade polylactic acid (PLA). Monolayer films of Mater-Bi and of PLA were prepared by film blowing in a single screw extruder equipped with a film blowing die head. The bilayer film PLA/MaterBi was prepared by using a co-extrusion system. The thickness of the produced films varied in the range 40-70  $\mu\text{m}$ . The morphology of the films was evaluated using a scanning electron microscope (SEM). The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry was performed, and tensile tests and dart impact tests of the films were carried out.

## Results

In the ATR-FTIR characterization of both sides of the PLA/MaterBi bilayer film were obtained spectra with different characteristics for each side, in which the specific bands of the pure compounds can be observed. The SEM micrographs of the bilayer revealed that the respective thicknesses of PLA and MaterBi layers were comparable, i.e. around 30  $\mu\text{m}$ . As regards the mechanical properties, in bilayer film the presence of PLA produced a marked increase in Young's modulus, a decrease in elongation at break and in toughness; however, the tensile strength remained unaltered in comparison with MaterBi monolayer.

## Discussion

It was found that the two polymers did not mix each other during the preparation, since the spectra obtained from each layer corresponded to the pure component spectra. Morphological observation showed that co-extrusion film blowing is a performing technique to prepare film with very good adhesion and balanced mutual thicknesses. The mechanical results of the bilayer revealed that the material becomes more resistant and less deformable respect to MaterBi.



# POLYLACTIC ACID FIBROUS MATS LOADED WITH NANOCRYSTALLINE CELLULOSE AND DECORATED WITH SILVER NANOPARTICLES BY ELECTROSPINNING TECHNIQUE

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## Introduction

Electrospun membranes present outstanding applications in several fields, including filtration, tissue regeneration, drug delivery, functional and active packaging. In recent years, a lot of attention has been dedicated to the formulation of multifunctional systems with improved mechanical, thermal, and antimicrobial properties. In the present work, poly(lactic acid) (PLA) fibrous mats, loaded with cellulose nanocrystals (CNCs) and decorated with silver nanoparticles (NPs), were produced by electrospinning. PLA is the most widely used biopolymer, due to its interesting properties, such as biocompatibility, transparency, stiffness and thermoformability. CNCs were selected as reinforcing fillers and silver nanoparticles as antimicrobial agents.

## Material and Methods

CNCs (5%wt), both pristine (p-CNCs) and surfactant modified (s-CNCs), were disagglomerated in CHCl<sub>3</sub>:DMF (67:33, in volume ratio) by ultrasonication. Then PLA pellets (15%wt/v) were added to the suspensions. Prepared suspensions were electrospun under the following conditions: applied voltage 12kV, flow rate 0.5ml/h, needle-target distance 15cm. As a reference, neat PLA mat was also produced. The silver nanoparticles were physisorbed on the PLA fibers surface, starting from a stable Ag nanoparticles suspension (0.5mg/ml). As a reference, the PLA fibers were also loaded with 1%wt of Ag NPs, to compare the antimicrobial efficiency of the nanoparticles entrapped within the fibers and exposed on their surface.

## Results

The obtained mats were composed of randomly oriented submicrometric fibers (average diameter ~500nm). A good s-CNCs dispersion within polymeric fibers was confirmed by scanning electron microscopy, differential scanning calorimetry and dynamic mechanical thermal analysis. More interestingly, s-CNCs allowed to obtain a superficial honeycomb-like layer, composed of fibers bundles. A decrement of the mechanical properties was recorded in the case of s-CNCs loaded samples, whereas p-CNCs loaded fibers showed a slight improvement. Finally, the effective antimicrobial action of the silver nanoparticles immobilized on the polymeric fibers was demonstrated by antimicrobial tests against *Amp<sup>r</sup> E.coli strain BL21*.

## Discussion

On the basis of the collected results, the obtained fibrous mats can be considered promising systems for potential applications in the filtration and packaging sector, due to the double simultaneous action as filter to entrap non-desirable micro-organisms and as carrier of antimicrobial/antioxidant agents, and also in biomedical sector as biomaterial for tissue repair.

# MECHANICAL CHARACTERIZATION OF HIGH PERFORMANCE CEMENT-BASED MATERIALS FOR 3D PRINTING

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## Introduction

A high-performance printing concrete has been developed for an innovative freeform construction concrete-printing process. The concrete used some advantages of self-compacting concrete and sprayed concrete for optimization of the mix proportions to suit the innovative process. The concrete printing process uses an additive, layer-based, manufacturing technique to build complex geometrical shapes without formwork and thus has a unique advantage over conventional construction methods. This paper presents the hardened properties of a high-performance fiber-reinforced fine-aggregate concrete extruded through a 12-mm diameter nozzle to build layer-by-layer structural components in a printing process. The effects of the layering process on density, compressive strength and flexural strength are presented together with the implication for mix proportions.

## Materials and Methods

Different mixture were studied prepared by using Portland cement type 52.5 R (650-750 kg/m<sup>3</sup>), carbonatic aggregate with maximum size of 0.6 mm (1150-1250 kg/m<sup>3</sup>), silica fume (120-150 kg/m<sup>3</sup>), superplasticizer (3.5-4 kg/m<sup>3</sup>), shrinkage reducing admixture (3-5 kg/m<sup>3</sup>), water (265-275 kg/m<sup>3</sup>), expansive agent (either 0 or 30 kg/m<sup>3</sup>), polypropylene fibers (1 kg/m<sup>3</sup>). Mechanical properties have been evaluated after 1, 7, 28 days of air curing by three-point bending tests and compressive tests.

## Results

Compressive strength was in the range 26-28 MPa after 1 day of curing, in the range 55-58 MPa after 7 days, and in the range 60-63 MPa after 28 days. Flexural strength ranged from 5 MPa after 1 day of curing up to 9.5 MPa after 28 days of curing. Density ranged from 2050 to 2150 kg/m<sup>3</sup>, indicating that a degree of compaction of about 0.89-0.93 was achieved in absence of any vibration.

## Discussion

The degree of compaction strongly affected mechanical performance. The bond strength between the layers of printed concrete is perhaps the critical mechanical property of material produced by an additive manufacturing process, creating potential flaws between extrusions that induce stress concentrations. The optimized mix contained appropriate proportions of superplasticizer and shrinkage reducing admixture. The experimental work will demonstrate the potential of concrete printing as a viable new production process that can introduce greater geometric freedom into the design process as well as offering a novel means of manufacture.

# DESIGN AND ASSESSMENT OF POLYURETHANE FOAMS AS 3D IN VITRO MODEL FOR BONE METASTASIS

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## Introduction

Breast cancer represents the majority of cancer cases in women, with bone metastasis occurring in 70% of cases. *In vitro* 3D models, compared to *in vivo* and 2D *in vitro* studies, gained great interest in cancer research thanks to their reproducibility, 3D spatial cues and reduced costs. This work aims at mimicking the 3D bone microenvironment by a polyurethane foam, loaded (PU\_L) or not (PU) with tricalcium phosphates, to investigate bone cells - metastatic cells from breast cancer interactions.

## Material and Methods

The PU foam was synthesised by reacting a poly-ether-polyol mixture with diisocyanate MDI prepolymer, using water as expanding agent and Fe-Acetyl-Acetonate as catalyst; tricalcium phosphates (40%  $w_{CaP}/w_{polyol}$ ) were added during the synthesis to obtain PU\_L. Foams morphology was assessed by SEM, mechanical properties by compression tests. Adipose derived stem cells (ADSCs) were seeded on the foams, differentiated in osteoblasts using osteogenic medium and subsequently co-cultured with human breast cancer stem cells (BrCSCs). Inorganic ECM deposition was checked by Alizarin Red; cell morphology and the competition between deposited inorganic ECM and BrCSCs proliferation was investigated by SEM/EDX and histological analysis. Data were compared by ANOVA.

## Results

PU and PU\_L foams showed a porous structure; the presence of CaPs didn't affect the material morphology. Mechanical properties (in particular E,  $\sigma_{max}$ ) of PU\_L were significantly higher compared to PU foams, confirming the reinforcement role of CaP. ADSCs were successfully differentiated in osteoblasts and subsequently co-cultured with BrCSCs: BrCSCs aggregates on differentiated ADSCs were observed by SEM and E-cadhering staining.

## Discussion

PU foams suitability as 3D bone metastasis microenvironment model was proved. ADSCs adhered to the scaffold, depositing inorganic ECM, and BrCSCs formed aggregates on pre-cultured ADSCs. Future tests will quantitatively investigate the interactions between healthy and cancer cells.

# PULSED LASER DEPOSITION OF AN INNOVATIVE GLASS-CERAMIC FOR THE COATING OF BONE-RELATED IMPLANTS

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## Introduction

Bioactive glasses and glass-ceramics are an important class of biomaterials capable of bonding the bone, therefore they can be used to bone tissues repair. Since the first 45S5 Bioglass<sup>®</sup>, several other glass and glass-ceramic have been investigated for biomedical applications. In this context, RKKP is a glass-ceramic material, recently deposited by Pulsed Laser Deposition (PLD) on Ti substrate, with the aim to coat bone-related implants. Thanks to its significant role in the metabolism of both muscle and bone, manganese oxides have been added in the RKKP composition (RRKP\_Mn). In this work films of RKKP\_Mn have been prepared using PLD. It presents several advantages compared to the other deposition procedures: it is possible to control the growth kinetics, thickness, roughness and the crystallinity of the coatings.

## Material and Methods

PLD experiment has been performed in a vacuum chamber with a frequency doubled Nd:YAG laser source (532 nm emission wavelength, 10 Hz repetition rate, 7 ns pulse duration). The experimental parameters have been optimized to prepare films with properties suitable to coat the bone-related implant and the obtained films have been characterized by several spectroscopic and microscopic techniques.

## Results

RKKP\_Mn presents good biocompatibility; XRD analysis shows the presence of different silicate and phosphate crystalline phases. The FT-IR and Raman spectra of the bulk materials and the deposited films show the typical signals of phosphate and silicate vibrations. The films morphology is characterized by spherical nanoparticles superimposed on a dense background.

## Discussion

Thin films of RKKP\_Mn bioactive glass-ceramic have been deposited by nanosecond PLD. The phase and morphology investigations of the deposited films are suitable to coat bone-related implants. It has been showed that the PLD deposited films present compact microstructure and surface roughness suitable for cell adhesion.

## 2.5D PATTERNING USING FOCUSED ION BEAM AND INDENTATION LITHOGRAPHY

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### Introduction

The ability to prepare patterns and structures with small dimensions has been crucial for the development of many modern technologies. Over the last two decades, different lithographic techniques have been used to fabricate complex 3D structures based on electron, laser and ion irradiation. Focused Ion Beam (FIB) technology combined with an electron column offers promising advantages such as simplification of sample preparation, small processing times enabling imaging, milling and deposition in a single instrument over a wide range of materials. One of the main peculiarity is the "Direct-Writing" that locally enables the control of ion dose for 3D pattern production with high shape factor and reliability, without applying resist and mask. In this work, a new methodology is proposed to generate a stream file capable of producing both micro-and-nano scale patterns with improved quality and the possibility to replicate them on large area using both ion lithography and through a master fabrication for Indentation-lithography (IndL)

### Material and Methods

The instrument used for ion lithography is FEG-FIB microscope. A nano-indenter, generally employed for surface nano-hardness test was preferred for indentation-lithography. Materials used are silicon and PMMA for different mechanical behaviour comparison under the indenter load. Furthermore, a diamond tip for nanoindentation was patterned to fabricate a master for IndL.

### Results

Development of a new approach to compile a stream file to use as input to mill complex patterns. The process is optimized with a software interface to manage process parameters. Based on the pattern geometry and dimension, the method defines a new beam scan strategy different from the usual raster scan with the advantage of redeposition reduction. A script was assembled for automatic replication of the pattern.

### Discussion

The possibility to control pixel-by-pixel scan movement allows one to prepare customized scan strategies that follows the geometrical contours of the pattern allowing control at micro- and nano scales. The technique is useful for producing multifaceted shapes and method has the potential to produce large patterns with sub-100nm resolution.

# THERMO-RESPONSIVE MAGNETIC NANOCOMPOSITE AS MULTIFUNCTIONAL HEAT AND CARGO DELIVERY VEHICLES

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## Introduction

Thermoresponsive polymer-coated magnetic nanoparticles loaded with anti-cancer drugs are of considerable interest for novel multi-modal cancer therapies. Such nanocomposite can be used for effective drug delivery followed by simultaneous hyperthermia and controlled drug release when they undergo reversible structural changes from a swollen to a collapsed state due to the response to the internal stimulus such as magnetically induced heating in the case of superparamagnetic core. In this project magnetic nanocomposite (MNC), used as magnetic hyperthermia-mediated drug release agent, consisted of Fe<sub>3</sub>O<sub>4</sub> core and the thermoresponsive copolymer poly-n-vinylcaprolactam-copolyvinylpyrrolidone shell subsequently loaded with anticancer drug-5-Fluorouracil to evaluate controlled drug release and hyperthermia behavior of MNC.

## Material and Methods

(MNP) were synthesized by polyol method in DEG. The crystal structure, size, morphology, and magnetic properties of the synthesized samples were characterized by XRD, DLS, TEM, and SQUID. Heat capacity of MNP was calculated by calorimetric method. MNP coated with thermo- copolymer by solvent evaporation method. Subsequently, a solution of 5-FU in buffer phosphate (PBS, pH=7.4) was loaded into MNC. Simultaneous hyperthermia and *in vitro* drug release of 5-FU loaded MNC at temperatures below and above the LCST of copolymer ~ 41°C was measured by HPLC.

## Results and Discussion

MNP with average size of 37 nm with high monodispersity were synthesized. The SAR was calculated to be 167 W g<sup>-1</sup> for the 37 nm MNP at 183 kHz, 17 kAm<sup>-1</sup> AMF and the M<sub>s</sub> value was 76 emu g<sup>-1</sup>. Thermo-copolymer with LCST of ~41 °C was synthesized via radical polymerization. Then, the copolymer was applied for encapsulation of MNP and subsequently 5-FU was loaded on MNC by solvent evaporation method. Simultaneous hyperthermia and *in vitro* drug release, which were considered by MNC dispersed in (PBS) below and above the LCST of copolymer, indicated increased drug release rate at above LCST.

# NEW CURCUMINOID Ir(III) COMPLEXES WITH ANTITUMORAL PROPERTIES

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## Introduction

Curcumin is an active polyphenolic compound derived from the root of turmeric (*Curcuma longa*), toxic to cancerous cells and cytoprotective to healthy cells. Clinical application of curcumin as such is severely limited due to its poor bioavailability, pharmacokinetic profile resulting from its hydrolytic instability under physiological conditions, associated skin sensitivity and intestinal disorders, taken in its native form in high doses. The hydrolytic instability is due to the presence of a highly reactive  $\beta$ -diketone moiety. Binding this  $\beta$ -diketone moiety to a metal centre increases the stability of curcumin, and the resulting complexes show remarkable cytotoxic or photocytotoxic activity.

## Material and Methods

Surprisingly no curcumin Ir complex has been reported up to now although it is known that Ir(III) complexes can generate  $^1\text{O}_2$  and can also be luminescent, an important aspect for bio-imaging. For this reason, we prepared and fully characterized two Ir(III) complexes, bearing two phenylpyridine and curcumin, or its reduced form (tetrahydrocurcumin).

## Results

The Ir(III) complex with curcumin is not luminescent in solution at room temperature due to an isomerization *trans-cis* of the olefinic double bond. At low temperature, on the other hand, it emits very nice in the red region of the spectrum. Contrarily the complex with tetrahydrocurcumin, which is anticancer too, shows good emission properties also at r.t. Their cytotoxicity and phototoxicity were investigated in collaboration with IFOM Institut, our preliminary studies seem very promising.

## Discussion

The Cyclometallated iridium(III) complexes enter the cells and are selectively localized at the mitochondria. The complexes have been tested for cytotoxicity in standard culture conditions through MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay and no defect in viability was evident even after 96 hours of continuous treatment. Taking advance of time-lapse microscopy, we irradiated cells with a wavelength of 495 nm for 2 seconds, and then we monitored cells for 48 hours. Treated and irradiated cells underwent apoptosis, whilst neighbor cells in which the compounds weren't activated were perfectly viable. These results are exceptionally promising for photodynamic therapy, also because the time of light exposure is dramatically reduced and the dosage is very low, compared to existing photosensitizers.

# GRAPHENE-ENRICHED NITROGEN-DOPED CARBON FIBRES FOR ELECTROCHEMICAL WATER DESALINATION

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## Introduction

The ever-increasing demand of fresh water has promoted the development of a variety of desalting techniques of seawater. The capacitive deionization (CDI) method, based on the formation of electrical double layers inside the pores of the electrode material, is one of the most attractive among them. CDI is an environmentally friendly technology since no secondary contaminant is released during the process. In addition, operating at low DC potential (1.0–1.2 V), CDI can be of great help in remote areas. Different high surface area nanocarbons, such as carbon nanotubes, carbon aerogel, mesoporous carbon, graphene (G), and activated carbon, have been successfully utilised to fabricate the electrodes in CDI cells. This contribution deals with synthesis, analysis and testing, as electrode materials in CDI cells, of G-enriched C fibers (GCFs), and C fibers (CFs) as a reference.

## Material and Methods

GCFs and CFs are prepared via electro-spinning (ES). ES is carried out using polyacrylonitrile and N,N-dimethylformamide respectively as polymer and solvent, and adding graphene oxide to the spinnable solution in the case of GCFs. After stabilization and carbonization, N-doped fibres with 360 nm average diameters are obtained. The electrochemical behaviour of the as-prepared samples is evaluated by cyclic voltammetry. A three-electrode cell is used for this purpose, with graphite, standard Ag/AgCl and (CFs- or) GCFs-based electrodes acting as counter, reference and working electrodes, respectively.

## Results

Data collected in 0.1mol/l NaCl solution, in the potential range from –1 to 0.5 V, demonstrate that specific capacitances between 106 and 18F/g are obtained with the CFs-based working electrode for 5–100 mV/s scan rates. Under the same conditions, GCFs exhibit better electrochemical performances.

## Discussion

The nitrogen doping, favours the wettability of the fibres by the electrolyte, playing a crucial role in determining the outstanding electro-sorption capacities of the fibers. It allows to fully utilize the volume of pores in graphene-enriched fibers, obtaining greater conductivity and capacity, to reach unprecedented electro-sorption activity through an extremely simple synthesis process, without need for activation treatments.



# CHARACTERIZATION OF BRICKS AND MORTARS USED IN QUANG TRI CITADEL – VIETNAM

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## Introduction

To design a suitable restoration, the mortars and bricks of the masonry of Quang Tri Citadel in Vietnam, built in '800, have been characterized to identify the type of binder and of clay/firing temperature in bricks.

## Material and Methods

Representative samples of the different materials were collected: 8 samples of bricks (3, 4, 5, 6, 8, 9, 10, 11), 2 samples of mortars (rendering and bedding) and analysed by mercury intrusion porosimetry, X-ray diffraction and ion chromatography (for water-soluble ions).

## Results

Total porosity of bricks is generally typical for handmade bricks (24-43%). In 3, 6, 10 samples, high presence of pores with  $d \leq 1 \mu\text{m}$  is detected. In these samples hillite and calcite are mainly found. Hematite is in 4, 5, 8 reddish bricks where the pore sizes distribution is shifted towards higher diameter (especially in 8). Samples 9, brownish, and 11, reddish with lighter stripes, are quite different with very low porosity, 4% and 7%, respectively. For mortars, the total volume of pores is 22% with no gel pores. The principal mineralogical phase is calcite with traces of gehlenite and a not perfectly straight baseline at  $2\theta$  about  $35^\circ$ . The aggregate of mortars is composed by quartz and feldspar of near river sand. Soluble ions are 1% and 3% in bricks and mortars, respectively.

## Discussion

The wide differences in colours, microstructures and chemical compositions suggests that bricks with different origins have been adopted during the maintenance works carried out in different ages. Samples 9 and 11 are probably rocks; 3, 6 and 10 are manufactured with carbonate rich raw materials and firing temperatures lower than  $800^\circ\text{C}$ ; 4 and 5 have firing temperatures of  $900^\circ\text{C}$  and sample 8 of  $1000^\circ\text{C}$ . The aspect of sample 9 and 10 suggests that probably they are rocks rather than bricks. By the evidences, the mortar is hydraulic but not cementitious. The presence of gehlenite confirms a firing temperature higher than  $800^\circ\text{C}$  but lower than  $1000^\circ\text{C}$ . The low content of soluble ions indicates that masonry has not been submitted to chemical degradation.

# POLYMERIC NANOCOMPOSITE SYSTEMS AS PROTECTIVE MATERIALS FOR CULTURAL HERITAGE

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## Introduction

Aim of this work is to develop organic/inorganic polymer networks and thermoplastic polymeric nanocomposite systems as protective materials for cultural heritage. Indeed, these materials can show a reduced permeability to vapor and oxygen, gas that can deteriorate the stones.

## Material and Methods

The materials used in this work were and PLA. Mechanical characterization of the materials was carried out with a universal testing machine on samples (90x10x0.5 mm). Protective films, about 200 nm thickness, were produced by compression molding. The adhesion tests were carried out by placing the protective film on the surface of the stones. The film was heated at a temperature of about 50°C so as to adhere to the surface. For the realization of these materials, EVA with a vinyl acetate content of 28% was initially used as polymer matrix. The polymer matrix was subsequently loaded with organomodified clay nanoparticles. Protective films were also made using the solvent casting method. In this case PLA was used as matrix and chloroform and acetone as solvents.

## Results

Mechanical tests show that films containing organomodified clays have a higher modulus than that made with the pure polymer. The films made by compression molding adhere to the top of the stones although after the cooling there is a slight debonding. The materials made by solvent casting and then brushed on stone, show better adhesion.

## Discussion

The preliminary characterizations show that these films can adhere on the surface of the selected stones and this is a necessary condition for a good protection from vapor and gas. The work is in progress to measure the permeability values and the effect on the degradation.

# SURFACE MODIFICATION OF DIATOMITE TAILORED FOR RUBBER COMPOUNDS

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## Introduction

In this work an hydrophobic diatomite (fossil material composed of porous siliceous cell walls of diatoms), often used in rubber compounds as processing aid or diluent, was modified by introduction of a limited content of surface silanol groups and successively silanized with a sulfur-containing silane coupling agent for rubber applications.

## Material and Methods

Silanol groups were introduced on the surface of an hydrophobic diatomite (D) as follows: 1g of D was added to 250 ml of a solution of H<sub>2</sub>O:NaOH (40 wt% aqueous solution): H<sub>2</sub>O<sub>2</sub> (30% v/v aqueous solution) = 2:1:1(volume ratio). The system was stirred at 85°C for 2 h. The powder was then collected by filtration, washed and dried. The modified diatomite is referred to as D-OH. Silanization was carried as follows: 1 g of D-OH was dispersed in 50 ml of ethyl alcohol by sonication, bis(triethoxysilylpropyl) disulfide (TESPD) (0.126 ml) was then added and the mixture was heated at 100°C until the complete ethyl alcohol evaporation. Finally, the powder was heated in air at 120°C for 2 h. The silanized diatomite is referred to as DS. D, D-OH and DS were characterized by SEM/EDS, FTIR and XPS.

## Results

Both D and DS are constituted of micrometric frustules with pore sizes in the range 25 nm-1 µm. FTIR spectrum of D-OH shows absorption bands associated to silanol group vibration modes, that were not detected for D. XPS analysis performed on DS proved the effectiveness of silanization process: the deconvoluted high resolution Si 2p and O 1s spectra show components coming from silicon and oxygen atoms of TESPD, respectively, and the S 2p region exhibits one peak corresponding to sulfur atoms of TESPD.

## Discussion

DS could be used in rubber compounds as semi-reinforcing filler due to the potential capability of chemical linking to rubber molecules in vulcanization process.

# PEI BLENDS FOR ADVANCED APPLICATIONS

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## Introduction

Polymer blending is a well-established technique to develop novel formulations with tailored properties with short time to market compared to novel synthesis. In many cases, polymer blending allows to overcome thermal or mechanical limitations of one polymer. However, this approach can also be used when better processing is required. The present paper will address the development of some PEI based blends with reference not only to their compounding but also to their application in FDM (Fused Deposition Modelling).

## Material and Methods

Polyetherimide (PEI) from commercial sources was selected. For comparison purposes Ultem 9085 by GE was considered as the commercial reference for our testing. Different types of blends were prepared both by static mixers and compounding in a twin extruder. The blends were obtained by the addition of polycarbonate (PC) or other novel polymers.

## Results

Rheological testing revealed that adding only 10wt% of PC can influence the viscosity of the PEI helping its processing. At the same time the immiscible PEI/PC blends do not show, by DMA, significant Tg reduction when PC content is kept low. By contrast, ULTEM 9085 showed a lower Tg of 185 °C which is about 216 °C for the unmodified PEI used in this study. TGA-DTA, SEM and tensile analysis are under evaluation but cost predictions allow to forecast that blending is quite advantageous from the economic point of view. Alternative polymers as processing aids were also tested. Filament processable by FDM were produced out of the blends and tested successfully by FDM.

## Discussion

The obtained results demonstrated the possibility to melt compound out of PEI which can enhance its processability in FDM while reducing its cost.

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# AMINO ACID-DERIVING CHIRAL POLYMERS WITH POTENTIAL FOR BIOTECHNOLOGICAL APPLICATIONS

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## Introduction

Polyamidoamines (PAAs) represent a well-known family of soluble synthetic functional polymers with a recognized potential for biotechnological applications. PAAs are obtained by the stepwise polyaddition of *prim*-monoamines or *sec*-diamines with bisacrylamides. The reaction occurs at room temperature in pH = 8-9 aqueous solutions. By using  $\alpha$ -amino acids as monomers, poly(amidoaminoacid)s (PAACs) are obtained. PAACs maintain the chirality and the amphoteric properties of the starting monomers. In previous works, the PAAC obtained from the reaction of L-arginine and N,N'-methylenebisacrylamide, proved highly citycompatible with  $IC_{50} \geq 8$  mg/mL. Cell internalization studies demonstrated its localization in the perinuclear region.

## Material and Methods

(D)-, (L)- and (D,L)-arginine were added under stirring to an aqueous mixture of N,N'-methylenebisacrylamide and lithium hydroxide. The reaction mixtures were maintained at 50°C for 5 days, acidified to pH = 4, ultrafiltered through 100 and 3kDa membranes and finally freeze-dried. The acid-base properties of the resulting polymers were evaluated by potentiometric titration in 0.1 M NaCl solutions at 25°C under nitrogen. Their secondary structures in aqueous solutions were investigated by circular dichroism (CD) spectroscopy carried out at 25°C in the pH range 3.0 - 10.0.

## Results

Amphoteric PAAC isomers, named (D)-, (L)- and (D,L)-ARGO7, were obtained with 58% yield,  $M_n = 8500$  and  $PDI = 1.40$ . Their  $\beta$  corrected  $pK_{a1}$  (COOH) and  $pK_{a2}$  (main chain *tert*-amine) values were evaluated using the modified Henderson-Hasselbach equation. L-ARGO7 species distribution indicated isoelectric point  $\approx 10$  and +0.25 net average charges per repeating unit at pH 7.4. Circular dichroism (CD) spectra showed pH-dependent bands in the 200-340 nm region with maximum values at 280 nm and strong absorption at pH > 6.5. The (D)- and (L)- isomers had mirror-like CD spectra.

## Discussion

(D)-, (L)- and (D,L)-ARGO7 were obtained with yield and  $M_n$  comparable to those observed in  $Ca^{2+}$  catalyzed synthesis. Their  $pK_{a1}$  values resembled that of arginine, whereas  $pK_{a2}$  decreased by two units due to the acrylamide electron withdrawing effect. Both  $\beta$  constants indicate deviation from the ideal behaviour, more pronounced for the carboxyl group. The pH-dependent conformation and the high cytocompatibility of ARGO7 polymers let envisage a potential for stereochemical-governed intracellular localization and interactions with biocell components.

# ENHANCING WETTABILITY OF PLA ELECTROSPUN MEMBRANES FOR IMMOBILIZATION AND ACTINORHODIN PRODUCTION INTENSIFICATION OF *STREPTOMYCES COELICOLOR* CULTIVATIONS

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## Introduction

The immobilization of actinomycetes on suitable porous supports may prevent mycelial cell-cell aggregation, resulting in an improved biosynthetic capability. In this work, electrospun polylactic acid (PLA) membranes, subjected or not to O<sub>2</sub>-plasma treatment (PLA-plasma) were used as support for immobilized-cell submerged cultivations of *Streptomyces coelicolor* M145. This strain produces different bioactive compounds, including the blue-pigmented actinorhodin (ACT).

## Material and Methods

PLA solution was electrospun and collected on a grounded rotary drum. PLA electrospun membrane was then treated in a plasma reactor at 50 W for 30 seconds. Wet contact angles (WCA) and X-ray photoelectron spectroscopy (XPS) were performed on PLA and PLA-plasma electrospun membranes. The morphology of the membranes were carried out through SEM analysis. ACT production yields were assayed at 3, 5 and 7 days of incubation by applying the procedures described by Kieser et al., with minor modifications.

## Results

WCA measurements revealed that the O<sub>2</sub>-plasma treatment enhanced wettability of PLA electrospun membranes. XPS analysis confirmed that the increased wettability can be ascribed to the introduction of oxygenated functionalities. SEM analysis highlighted that plasma treatment do not modify the morphology of the PLA membranes. ACT productions were approximately 5 and 10 fold increased in immobilized-cell cultures on PLA and PLA-plasma membranes in comparison to free-cell cultures, respectively.

## Discussion

Both membranes showed a similar narrow distribution of diameters centered at 0,9 μm indicating that plasma treatment did not induce significant changes in the PLA nanofiber morphology. Furthermore, the spores inoculated into the growth medium were able to germinate and adhere to both the membranes. The increase in ACT production can be ascribed to the nature and characteristics of ACT, a diffusible water-soluble compound which resulted absorbed on PLA membranes. Moreover, the modified membrane could activate specific cellular signals.

# NANOCARBON-BASED BIOMATERIALS FOR PRESSURE SENSING

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## Introduction

Graphene oxide (GO) is a promising filler for advanced nanocomposites. In fact, its piezoelectric properties and large specific surface area make it suitable for preparing high performance sensors with high sensitivity, selectivity and stability. The possibility to integrate GO lamellae into biopolymers could be promising to realize transducers for biomedical applications.

## Material and Methods

GO was synthesized by oxidizing graphite in an acidic mixture, in the presence of  $\text{KMnO}_4$ . Prior to be mixed with polylactic acid (PLA), GO was pre-dispersed with polyethylene glycol (PEG) in water and successively freeze-dried. The materials were melt processed and the specimens were achieved by compression-molding. The stability of PLA-PEG blends in presence or absence of GO was assessed by monitoring structure-property relationship upon time. The I-V characteristics upon compression and temperature variation were measured using laboratory-designed fixtures and data acquisition system.

## Results

PLA-PEG blends displayed metastable miscibility and were found to be prone to unmixing after a certain time interval. The presence of amphiphilic GO, mainly located at the PLA-PEG interface, enhanced the stability of the blend and endowed the ternary materials with electric properties that were found to be dependent on the pressure applied to the specimens. A current increase was observed upon pressure increasing and the obtained differential resistivity, resistance, conductivity were correlated with the applied pressure in order to evaluate the sensitivity of sensors. The conductive behavior of such samples was investigated by comparing the I-V characteristics with existing experimental data and mathematical models.

## Discussion

The results obtained are in a good agreement with the reversible dielectric breakdown theory caused by Zener effect, probably occurring inside the composites at low macroscopic field strengths. The high sensitiveness of these sensors can be ascribed to the presence of PEG, since this latter provides a higher mobility of PLA macromolecules, thus enabling tunneling phenomena and the formation of a GO network throughout the matrix.

# Dy<sup>3+</sup>-DOPED MULTIFERROIC BiFeO<sub>3</sub> FILMS: MOCVD FABRICATION AND PIEZORESPONSE FORCE MICROSCOPY CHARACTERIZATION

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## Introduction

Bismuth ferrite (BiFeO<sub>3</sub>) materials have been the subject of intense research activity in the last two decades. The great interest arises from the BiFeO<sub>3</sub> being one of the rare multiferroic compounds in which ferroelectricity and magnetism coexist at room temperature. To improve these properties several studies have been reported on the doping at the A and/or B sites of the BiFeO<sub>3</sub> perovskite structure. In the present study, a simple metal-organic chemical vapor deposition (MOCVD) route is reported for the deposition of Dy-doped BiFeO<sub>3</sub> films on SrTiO<sub>3</sub> (100) and SrTiO<sub>3</sub>:Nb (100) substrates.

## Material and Methods

Films were deposited through an in situ one step approach using a multi-metal source mixture composed by the Bi(phenyl)<sub>3</sub> and the Fe(tmhd)<sub>3</sub> (phenyl = -C<sub>6</sub>H<sub>5</sub>; H-tmhd = 2,2,6,6-tetramethyl-3,5-heptandione). The Dy-doped films are deposited using a mixed tri-metallic source mixture consisting, in addition to the Bi(phenyl)<sub>3</sub> and Fe(tmhd)<sub>3</sub> complexes, of the Dy(hfa)<sub>3</sub>diglyme precursor (Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, diglyme = 1-Methoxy-2-(2-methoxyethoxy) ethane). X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDX) and piezoresponse force microscopy (PFM) have been used to characterize the deposited films.

## Results and discussion

The structural characterization of the BiFeO<sub>3</sub> films shows peaks associated with 00ℓ reflections, in addition to the substrate peaks, which point to the formation of a highly oriented film. The deposited BiFeO<sub>3</sub> films have an out of plane cell parameter  $a = 3.966 \text{ \AA}$ , in excellent agreement with the reported  $3.965 \text{ \AA}$  value. In the case of Dy<sup>3+</sup> doping, the 00ℓ peaks are only slightly shifted to higher angles, giving rise to an out-of-plane a-axis parameter of  $3.962 \text{ \AA}$ . The similar values of a-axes parameters of BiFeO<sub>3</sub> and Bi<sub>(1-x)</sub>Dy<sub>x</sub>FeO<sub>3</sub> films reflect the small difference in the ionic radius of the Dy<sup>3+</sup> ( $r_{6\text{-coord}} = 0.912 \text{ \AA}$ ) with respect to the Bi<sup>3+</sup> ( $r_{6\text{-coord}} = 1.03 \text{ \AA}$ ). This study assesses the applicability of a simple MOCVD approach to the deposition of perovskite multiferroic BiFeO<sub>3</sub> films with an appropriate Dy<sup>3+</sup> doping at the A site. A correlation between the nanostructure/composition and piezoelectric properties has been highlighted.

<sup>#</sup> G. S. is currently a PhD student at the School of Chemistry, Trinity College, Dublin, Ireland.



## EUMELANIN-PEDOT:PSS INTEGRATION FOR AN ITO-FREE ORGANIC LIGHT EMITTING DIODE

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The scope of organic bioelectronics is largely dictated by the chemical nature of the materials that transduce signals across the biotic/abiotic interfaces<sup>1</sup>. Bioinspired materials are attracting increasing interest for the fabrication of functional biocompatible interfaces and, in this scenario, the human pigment eumelanin is currently gaining a leading role. This black insoluble pigment, present in the human skin, hair, eyes and nigral neurons (neuromelanin)<sup>2</sup> arises biogenetically from the amino acid tyrosine via the formation and the oxidative polymerization of 5,6-dihydroxyindole (DHI) and/or 5,6-dihydroxyindole-2-carboxylic acid (DHICA)<sup>2,3</sup>.

Eumelanins feature unique assortment of chemical physical properties<sup>3</sup>, including a semiconducting behavior and a permanent radical signal, which are at the root of the interest towards these pigments. Indeed, two main obstacles hampered a full exploitation of eumelanin based devices: (i) the actual eumelanin insolubility in any solvents, preventing easy processability of the pigment as well as the devices fabrication; (ii) its low conductivity, limiting both the range of possible working potential and functional applications. To improve the electrical performances of the eumelanin thin films, a clear-cut approach lies in the hybridization with a suitable conductive counterpart. In this view,  $\pi$ -conjugated molecules featuring conductive pathways appear a key choice in the production of new organic materials for electronic (nano)devices.

Here, we present the first (at the best of our knowledge) preparation of an eumelanin-PEDOT:PSS blend, featuring valuable functional and processing properties, like easy films preparation, high adhesion, good electrical conductivity and biocompatibility. The hybrid was characterized by chemical, physical, electrical and morphological analysis.

As a proof of concepts an OLED featuring an eumelanin-PEDOT anode was fabricated and characterized.

<sup>1</sup> Berggren M., and Richter-Dahlfors A. (2007). *Adv Mater*, Vol.19, p.3201-3213.

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# PHOTOOXIDATION BEHAVIOR OF POLYPROPYLENE NANOCOMPOSITES WITH MODIFIED HALLOYSITE

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## Introduction

The photooxidation behaviour of polymer nanocomposites depends on the photooxidation of the matrix, but also on the possible interactions with the nanoparticles. In this work, the effect of halloysite modified nanoparticles on the photooxidation of a polypropylene matrix has been investigated.

## Material and Methods

The materials used in this work were a polypropylene sample (PP), a cycloaliphatic hydrocarbon resin (A), a halloysite modified with A (B) and with trimethylolpropane trimethacrylate (C). The samples, PP with 10% of A, PP with 3% of B and PP with 1% of C, were prepared in a twin-screw extruder. Photooxidation was carried out in a QUV at 60 °C with a solar/condensation cycle of 8/4 hr. Mechanical properties were measured with an Instron machine.

## Results

The mechanical properties as a function of the irradiation time show two different behaviors: tensile strength and elongation at break decrease, while the modulus increases. As for the effect of the nanoparticles, no significant effect is shown by the sample with halloysite modified by C, while the photooxidation kinetics seems more pronounced for the sample modified by A and, but in less extent, by B.

## Discussion

The increase of the modulus can be attributed to the increase of the crystallinity due to the decrease of the molecular weight. For the same reason the ultimate properties decrease. The slight increase of the photooxidation kinetics of polypropylene in presence of hydrocarbons and – in less extent - with the nanoparticles modified with the hydrocarbons can be attributed to interactions of the PP macromolecules with the hydrocarbon molecules. Radicals of these molecules can be produced during irradiation and, inducing the production of PP radicals, increase the photooxidation of the matrix.

# MODIFICATION OF THE MECHANICAL PROPERTIES OF BIODEGRADABLE FIBERS BY COLD DRAWING OPERATIONS

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## Introduction

The importance of biodegradable polymers in new technological applications is continuously increasing. Among the possible applications, fibers are of particular interest but, at the same time, it is difficult to tailor their mechanical properties on the basis of the desired use. In fact, this can be done basically by controlling the orientation or the crystallinity, but the latter can be modified during processing only to a limited extent. Therefore, it is important to focus on controlling the orientation degree, by means of hot or cold drawing operations. In this work, the influence of cold drawing on the mechanical and thermomechanical properties of biodegradable fibers was investigated.

## Material and Methods

The biodegradable polymer systems used were a Mater-Bi and a Bioflex grade. For comparison, a PET sample was also used. Fibers were produced by extruding the molten polymer in a capillary rheometer, and cold stretching was performed in tensile mode, at different cold draw ratios. Mechanical and dynamic-mechanical analysis was performed on the fibers.

## Results

The main results showed that the cold drawing significantly improved the elastic modulus, tensile strength and thermomechanical resistance of the fibers, if compared to the hot-drawn fibers. The moduli of the fibers underwent higher increment rates on increasing the draw ratio; on average, Bioflex fibers showed slightly higher increments.

## Discussion

The improvement in thermomechanical resistance of the fibers was evaluated by considering the temperature at which the modulus of the cold-drawn fibers showed the same values as those of the hot-drawn fibers, measured at room temperature. Cold stretching significantly improved the elastic modulus and the tensile strength on increasing the cold draw ratio, while the elongation at break significantly worsened. Furthermore, on increasing draw ratio, higher increment rates of the elastic modulus were found and explained by considering the higher mobility and lower degree of already achieved orientation of the macromolecules.

# THEORETICAL APPROACH FOR THE INVESTIGATION OF SINGLE-SITE SUPPORTED CATALYSTS

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## Introduction

The development of the catalytic science has been extensively justified by the great industrial importance of catalytic processes. In this perspective, understanding structure-reactivity relationships in catalytic systems is a fundamental issue for the realization of efficient new catalysts. These reasons help to explain the success of homogeneous catalysts which offer the possibility of precise molecular structure control. By contrast, heterogeneous catalysts are widely used in chemical industry because they are easy to handle, separate, and recycle. The last three decades have witnessed attempts to transfer homogeneous molecular approaches to heterogeneous catalysis. In this context, analogues of well-defined homogeneous catalytic structures have been obtained for heterogeneous catalysis by the direct grafting of organometallic complexes on metal oxide surfaces. Today, single-site supported catalysts have attracted interest for both fundamental scientific and technological reasons, due to the molecular level control of catalyst-substrate interactions and selectivity that they afford. Although experimental results argue that such adsorbate complexes play a significant role in the surface and catalytic chemistry, many important kinetic and mechanistic details of such catalytic processes remain to be elucidated. In this context, theoretical investigations represent a powerful tool for understanding in detail, important aspects of both complex/surface interactions as well as operative catalytic mechanisms.

## Computational Details

DFT-based simulations were performed with the CP2K/Quickstep package, using a hybrid Gaussian and plane wave method. DZVP and TZPV Gaussian basis set were employed. The GTH pseudopotentials were used with the PBE functional, and vdW forces are taken in account with the Grimme D3 Method.

## Results and Discussion

The present contribution focuses on the DFT modeling capabilities in the explanation of the peculiar catalytic behavior of the single-site supported catalyst. In particular, analysis focused on the interaction of prototypical complexes with suited surfaces. Moreover, the individuation of the catalytic mechanism as the preferred reaction path is investigated for the most representative adsorbate species chemisorbed on the surface. The model of the solid support is driven by the wide experimental use in many studies related to heterogeneous catalysis and by the pronounced Lewis or Brønsted acid chemistry that allows direct comparison with analogous homogeneous catalytic systems.

# ACTIVATED CARBON CLOTH AS AGGREGATE FOR SPECIAL MORTARS

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## Introduction

Activated Carbon Cloth (ACC) is an adsorbent for the removal of micropollutants from the gaseous and aqueous phase, characterized by its woven fabric structure. Once exhausted, these materials are disposed as CER 150203 or as CER 150202\* depending the presence of hazardous substances. In our study a non-hazardous ACC waste was used as a partial replacement of the aggregate in special mortars, both to meet the EU priority in waste management, both to obtain lighter mortars with special characteristics.

## Material and Methods

For this purpose, mortars with water/cement equal to 0.45 by weight and aggregate/cement equal to 2.5 by volume were considered. The cement used was a CEM II/A-LL 42,5R. Different mixes with different percentages of ACC substituted (50%, 75%, 90%, 100%) to the fine sand (passing through a sieve with 850 µm openings) were prepared. Compressive strength was evaluated up to 7 days of curing according to UNI EN 1015-11:2007. Additional tests as the measurement of shrinkage (UNI EN 6687:1973), the water vapour permeability (UNI EN 1015-19:2008) and the Volatile Organic Compound (VOC) adsorption were evaluated for the specimens.

## Results

Replacing part of the aggregate with the ACC, the compressive strength is negatively affected and the specific weight is also reduced, while the shrinkage is not very influenced by it. By replacing the sand with 75% of ACC, a good compromise between the reduction of mechanical strength (from 39.0 to 15.4 N/mm<sup>2</sup>) and the decrease of specific weight (from 2.07 to 1.58 kg/l) was achieved. Moreover, the obtained mortar, shows an higher water vapor and VOC adsorbent capacity.

## Discussion

The most valuable result is the reuse of the waste product, in order to the reduce the density of the mortar. Leaching tests and VOC desorptive tests are intended for evaluating the potential release of adsorbed species from the ACC in the mortar. Moreover, the addition of a photocatalyst will be taken into consideration to study the environmental effect.

# Co/SiO<sub>2</sub> BASED CATALYSTS: EFFECT OF PREPARATION PROCEDURE ON CATALYTIC ACTIVITY IN ETHANOL STEAM REFORMING AND CO<sub>2</sub> METHANATION

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## Introduction

Cobalt based catalysts have been recognized as promising materials for hydrogen production through bioethanol steam reforming at low temperature production (523-773 K) and are currently under investigation for Fischer Tröpsch synthesis through CO<sub>2</sub> hydrogenation. However, catalyst formulation is still not optimized for these processes and the effect of preparation procedure is fundamental.

## Material and Methods

A commercial silica gel (Carlo Erba) have been used as catalyst support after calcination at 823 K for 3 h. The synthesis of Cobalt based catalysts has been carried out by wet impregnation starting from different metals precursors (Co(NO<sub>3</sub>)<sub>2</sub>\*6H<sub>2</sub>O, CoCl<sub>2</sub>\*6H<sub>2</sub>O and Co(CH<sub>3</sub>COO)<sub>2</sub>\*4H<sub>2</sub>O) aqueous solution, keeping a total Co loading of 20%. All the catalysts were fully characterized by XRD, IR, FE-SEM, UV-vis. Catalytic activity tests have been carried out both in ethanol steam reforming and CO<sub>2</sub> methanation with a complete characterization of catalysts before and after catalytic runs.

## Results

Co dispersion on silica support displayed a strong effect as a function of precursor used. After calcination dispersion is decreased in the order Co/SiO<sub>2</sub> (nitrate)> Co/SiO<sub>2</sub> (chloride)> Co/SiO<sub>2</sub> (acetate). All the materials have been tested both in ethanol steam reforming and CO<sub>2</sub> methanation. In CO<sub>2</sub> methanation, preliminary results show a strong effect of Co dispersion on both methane production and catalyst deactivation.

## Discussion

All the catalysts have been successfully prepared, characterized and tested in ethanol steam reforming and CO<sub>2</sub> methanation. The effect of the synthetic procedure and consequently on cobalt dispersion will be discussed because they might strongly affect both catalytic activity and catalysts stability.

# SILICA AS A GREEN EXFOLIANT AGENT FOR GRAPHENE OXIDE-POLYMER NANOCOMPOSITES PREPARED IN THE MELT

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## Introduction

For the first time, solid state exfoliant agents were used to hinder the re-aggregation of graphene oxide (GO) during melt processing with polyamide 6 (PA6). This technique drastically reduces the time and difficulty related to solvent (removal, disposal, etc.), and avoids water consumption, since in this case 150 mL of water under mild operative conditions are enough to prepare the amount of GOS necessary for the realization of almost 100 grams of PA6-GOS nanocomposites with outstanding ultimate properties.

## Material and Methods

Graphene oxide-silica nanohybrids (GOS) were synthesized in water, by heating the GO/silica dispersion at T=120 °C for about 30 minutes at atmospheric pressure. GOS displayed a lasagna-like structure, with the silica layers intercalated between GO lamellae. GOS was added to PA6 and melt- mixed. All the materials were fully characterized by FTIR/ATR, XPS, EDX, NMR, tensile and IZOD tests, SEM, AFM, XRD and DSC.

## Results

The green route herein proposed does not involve any toxic solvent nor time-consuming protocols, and allows achieving remarkable improvements in stiffening (up to +180%), strengthening (up to +210%) and toughening (up to +210%) at extremely low filler contents (0.25% or 0.5%) with respect to neat polymer.

## Discussion

The remarkable improvements achieved in terms of both mechanical and thermo-mechanical properties are mainly due to the concomitance of an extended and strong interphase. In fact, PA6-GOS materials displayed a broadened loss factor plot with respect to neat PA6 and PA6-GO nanocomposites. Furthermore, the spectroscopic and morphological analysis of interphase extracted by HCOOH put into evidence that a significant aliquot of PA6 remains anchored to GOS even after solvent extraction, thus suggesting the formation of a chemical interphase.

# NOVEL GRAPHENE-BASED NANOCOMPOSITE FILMS FOR MONITORING UV RADIATION EFFECTS ON SPACE STRUCTURES

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## Introduction

A new hybrid nanocomposite material was developed to monitor the effects of UV-C radiation on space-grade structures. Ultraviolet radiation represents one of the most critical limitations for human space exploration and survival. In particular, the UV-C band with shorter wavelengths (100-280 nm) can severely damage materials and life in space. Ultraviolet sensing films were realized using graphene nanoplatelets (GNPs) as signal transducer and DNA as biological sensitive component. Hybrid GNP/DNA nanoparticles were dispersed into a conductive polymer matrix of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) to improve the adhesion of the sensing film on space-grade structures based on epoxy resins.

## Materials and Methods

Graphene nanoplatelets (thickness about 60 nm and lateral size 3-7  $\mu\text{m}$ ) were dispersed in aqueous solutions of double-stranded DNA (ratio of 1:1 by weight) using sonication. PEDOT:PSS was added to the GNP/DNA solutions at different percentages. The sensing films were prepared by drop cast deposition followed by drying in oven overnight. Space-grade advanced laminates made of carbon fiber fabric and RTM6 epoxy resin were used as substrates for the nanocomposite films. Electrical properties of the films before and after UV-C irradiation were analyzed by electrical impedance spectroscopy (EIS) and tomography techniques. Film morphology was investigated by SEM.

## Results

The nanocomposite films containing GNP/DNA elements show purely resistive behavior (frequency range 10 Hz-1 MHz). The surface electrical resistivity can be tuned by the amount of PEDOT:PSS in the nanocomposite mixture. After irradiation, the impedance values decrease for all films as a result of the dose of radiation received. SEM investigations on the GNP/DNA hybrid films highlight the degradation effects caused by UV-C radiation, in particular its effect in the smoothing of nanoparticle edges. Using an additional layer of PEDOT:PSS between nanocomposite film and substrate enhances the stability of the coating on resin-based laminates, while increasing its electrical conductivity.

## Discussion

Sensing materials realized using GNP/DNA hybrid elements dispersed into a conductive polymer matrix can be effectively used to monitor material degradation induced by the energetic UV-C radiation. These nanocomposite films are particularly well adapted to space missions due to their characteristics like lightness and real-time UV detection, and low power supply requirements.



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