

## Abstracts from the X INSTM National Conference on Materials Science and Technology “KE-MAT! Key Enabling Material” Favignana (TP), Italy | 28 June-1 July 2015

### β-PYRROLIC SUBSTITUTED PORPHYRINS IN DYE SENSITIZED SOLAR CELLS: SYNTHETIC BENEFITS, PROPERTIES AND FUTURE PERSPECTIVES

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**Concept:** The facile synthesis of β-substituted porphyrins and their photoelectrochemical properties make this class of dyes very promising for application in Dye Sensitized Solar Cells (DSSCs).

**Motivations and objectives:** Porphyrins are one of the most widely investigated classes of molecules in chemistry due to their chemical stability, catalytic activities, interesting optical and photophysical properties. Today, the best performance in a porphyrin-sensitized solar cell has been reached by a well-engineered meso disubstituted push-pull Zn<sup>II</sup>-porphyrinate. Nevertheless such class of porphyrins can be obtained only by multistep and uneconomical synthetic routes. On the contrary β-substituted Zn<sup>II</sup>-porphyrinates are of great interest because they can easily be obtained with remarkable yields using facile synthetic procedures. In addition they are featured by a significant steric hindrance which guarantees a decrease of π-stacking aggregation on TiO<sub>2</sub> photoanode resulting highly beneficial to DSSC performances.

**Results and discussion:** Our investigation has shown that β-substituted Zn<sup>II</sup>-porphyrinates are capable of serving as effective dyes in DSSCs, showing performances comparable to the most commonly used meso substituted push-pull Zn<sup>II</sup>-porphyrinates. An in-depth EIS (Electrochemical impedance spectroscopic) investigation has proven that β-substituted Zn<sup>II</sup>-porphyrinates, appears to be ascribed to a superior passivation of the TiO<sub>2</sub> surface against the charge recombination which involves I<sub>3</sub><sup>-</sup> species of the electrolyte. This superior screening effect can be related to the higher steric hindrance of the tetraarylporphyrinic architecture of such macrocyclic systems. Furthermore, pyrrolic functionalization of the porphyrinic core appears to be beneficial in tuning the properties of these dyes. In fact, they are strongly influenced by the introduction of π-delocalized systems which exert strong steric and electronic effects on the porphyrinic ring resulting in a dramatic alteration of their optical, electrochemical and spectroelectrochemical properties. Increasing the elongation of the π-chain in β-position, by adding thienyl units, the electronic absorption spectra of Zn<sup>II</sup>-porphyrinates cover a wide range of wavelengths producing a panchromatic effect in their IPCE spectra. The information extracted from our studies are helpful focusing on the development and synthesis of novel and more efficient β-substituted porphyrinic dyes which appear to be remarkable, viable and efficient alternatives to the more synthetically demanding porphyrinic dyes which exhibit the push-pull meso geometry.

### TAILORING ASSEMBLY OF REDUCED GRAPHENE PLATELETS TO CONTROL PROPERTIES OF RUBBER NANOCOMPOSITES

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**Concept:** Self-assembling of reduced graphene oxide (RGO) platelets (‘segregated’ arrangement), as a tailored interconnected network within natural rubber and butyl rubber matrices, is proposed as a mean for obtaining nanocomposites with significantly enhanced functional properties as compared to unloaded rubber, i.e. gas barrier properties and electric conductivity, even at very low filler contents. Interestingly, the prescribed spatial arrangement of the nanoparticles results to be much more effective in improving properties than homogeneous dispersion (‘not segregated’ arrangement) of platelets, even at low loadings. The ‘segregated’ structure originates from the confinement of platelets within the interstices of the coagulated latex particles, which act as a template for the network formation. The platelets are assembled on the latex particles giving rise to spheres with a core-shell structure, with a partial or complete covering depending on graphene amount. Conversely, the ‘not-segregated’ structure is obtained by destroying this interconnected network by further processing the RGO nanocomposite masterbatch via twin-roll mixing, thus determining a uniform orientation of exfoliated RGO platelets.

**Motivations and objectives:** The aim is exploiting self-assembling of RGO platelets to provide a cost-effective method to tailor the dispersion of nanoparticles inside the host matrix, allowing to significantly decrease the percolation threshold for electric conductivity and drastically change the dependence of gas barrier on nanofiller concentration.

**Results and discussion:** The presence of RGO nanoplatelets radically affect the dependence of gas barrier properties on nanofiller content. An example is provided in Figure 1 for the case of oxygen permeation in nanocomposites with natural rubber matrix where the ‘segregated structure (filled symbols) is compared with ‘not segregated’ one (empty symbols). Taking the real part of complex conductivity at the lowest investigated frequency, σ′<sub>0</sub>, as representative of the DC conductivity one can estimate the percolation threshold for electric conductivity in a nanocomposite. The optimized spatial distribution of the nanoplatelets attained in the case of ‘segregated’ structure, for the case of butyl rubber matrix, promotes an enhancement of σ′<sub>0</sub> of almost two orders of magnitude suggesting the building up of conductive paths of RGO throughout the rubber phase (see filled symbols in Figure 2). Conversely, the system having a ‘not-segregated’ morphology displays no evident changes as compared to neat matrix (see empty symbols in Figure 2). A value of critical RGO concentration as low as Φ<sub>c</sub> = 0.4 vol.% has been estimated for the “segregated” system according to the percolation theory (inset of Figure 2).

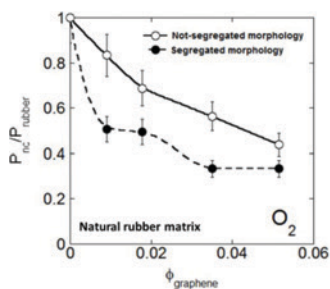


Fig. 1

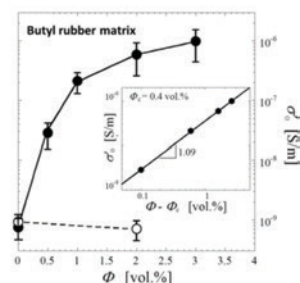


Fig. 2

### MULTILAYER POLYAMIDE/LAYERED SILICATE FILMS FOR FOOD PACKAGING APPLICATIONS

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**Concept:** Multilayer packaging structures, combining resins with different functional characteristics, represent a very attractive solution to simultaneously meet all the functions required in a packaging. In particular, multilayer films consisting of a core polyamide layer, having good oxygen barrier and mechanical performances, sandwiched between two polyolefin layers, characterized by low water vapor permeability and good sealability, are widely used for food contact applications. However, their effectiveness as barrier to gas can be not high enough for some food packaging applications, e.g. modified atmosphere packaging. The nanoclay incorporation into a polyamide resin significantly reduces its permeability to oxygen and enhances its mechanical resistance, making it superior to more expensive materials for food packaging, however the obtained performance improvement is strictly related to the adopted production technology and processing conditions. Despite the wide scientific literature devoted to the polyamide-based nanocomposites, few investigations were carried out to specifically assess these systems for flexible film packaging applications, even less in multilayer systems.

**Motivations and objectives:** The purpose of this work was to examine polyamide/clay nanocomposite films in a multilayer structure, produced by a lab-scale film blowing coextrusion pilot line, as a candidate to replace neat polyamide layers in multilayer packages for food applications. In this study, a copolyamide 6,66 (CS40LXW, Radici Groups) was used as polymer matrix and two organomodified layered silicates (Cloisite 30B and Dellite 43B) were selected as nanofillers. Nanocomposite systems at 4 wt% of silicate, produced by melt compounding in a twin-screw extruder, were then coupled by means of a tie-layer (Admer NF358E, Mitsui Chemicals) with an LDPE (Riblene FL30, Polimeri Europa) in three-layers coextruded structures with different layers thicknesses. The optical, mechanical, and barrier performances of the produced films were investigated and correlated to the different composition of the coextruded multilayer structures.

**Results and discussion:** The multilayer hybrid films, based on the copolyamide layer filled with Cloisite 30B, displayed the most significant oxygen and water vapor barrier improvements and the best mechanical properties, as shown in the following Table.

TABLE I

Layers (outer/inner)	Thickness [m]	P O <sub>2</sub> [cm <sup>3</sup> cm/m <sup>2</sup> d bar]	P (H <sub>2</sub> O) <sub>v</sub> [g cm/m <sup>2</sup> d]	E [MPa]	B [MPa]
PA/tie/PE		0,25	0,017	990150	22 2
PA+C30B/tie/PE	70	0,11	0,015	1260170	33 5
PA+D43B/tie/PE		0,17	0,016	1060110	29 3

Compared to the unfilled film, these nanocomposite multilayer structures could provide the same shelf-life, but with lower thicknesses, and/or increase the shelf-life of the packaged food. Moreover, such hybrid systems are characterized by an easy industrial applicability, since they are made with commercial materials and produced by conventional process technologies.

### THREE-LAYERED POROUS DEVICE IN PCL/PEG BLEND FOR INTERFACE TISSUE ENGINEERING

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**Concept:** Tissue interfaces, such as cartilage-to-bone, exhibit anisotropic structural properties, which gradually vary from one tissue to another. Consequently a regenerative scaffold designed for interface tissues should exhibit a gradient in composition, structure and mechanical features, mimicking those of the native zones. In particular, the architecture of pores plays a central role. Indeed, a biomedical implant should be designed with porosity

and pore size gradients simulating the structure of the two interface tissues. One of the most common techniques to prepare porous scaffolds is the particulate leaching method, which involves the selective leaching of a mineral or organic compound as porogen agents. The main advantage of particulate leaching methods is the effective control of porosity and pore size by variation of the amount and size of leachable particles.

**Motivations and objectives:** Aim of this work was to develop a method to prepare 3D porous scaffolds with a discrete pore size gradient. The scaffolds were prepared with polycaprolactone (PCL) with a partially miscible polymeric system: polyethylene glycol (PEG). PCL/PEG were melt blended with NaCl, in which the salt and PEG role as porogen agents. In particular the graded porous scaffolds were produced by a layer-by-layer compression molding method. Indeed, three layers, each containing salt with a different granulometry, were prepared individually by compression molding and then assembled together in order to form a three-layer scaffold. These samples were then leached in distilled water thus obtaining the graded porous scaffolds. The samples were mechanical characterized by compression tests and their morphology was evaluated by SEM.

**Results and discussion:** The SEM micrographs (Fig. 1) revealed that the samples exhibit a high degree of porosity with well interconnected pores having an average size that varies along the sample thickness. Moreover, although the layers are well distinguishable, the samples do not show any discontinuity at the interface between the different layers.

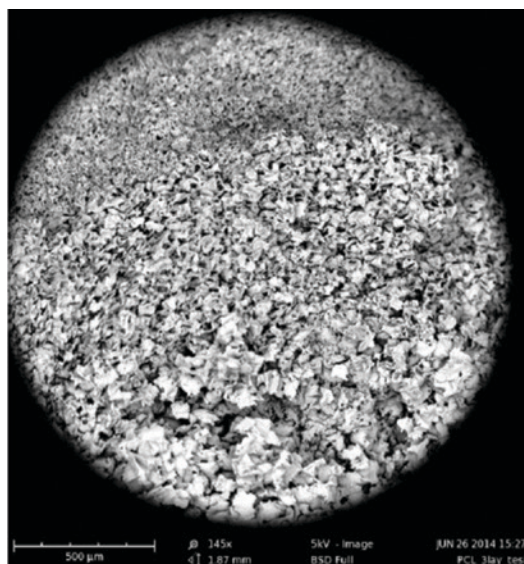


Fig. 1 - SEM micrographs of three-layer porous PCL/PEG scaffolds.

### COLORIMETRIC CHARACTERIZATIONS OF GONIO-APPARENT SURFACES FOR THE DEVELOPMENT OF MATERIALS WITH NEW VISUAL EFFECTS

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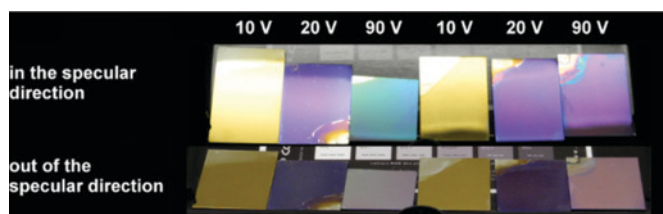
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**Concept:** Our aim is to develop materials with new visual effects, and to precisely control their colour variations with illumination and observation directions. We present colorimetric characterization of titanium anodized samples, that is, titanium samples on which titanium dioxide (TiO<sub>2</sub>) is grown at the surface of the sample by electrolysis. This material was shown to display promising features for generating particular visual effects, as it exhibits a wide gamut of structural gonio-apparent colours, with potential applications in architecture and design.

**Motivations and objectives:** Gonio-apparent surfaces are present in many industrial sectors such as automotive, cosmetics, plastics for consumer electronics, printing and security inks, architectural panels. They are characterized by large variations of their visual rendering, depending on illumination

and observation directions. Gonio-apparent colours first enter the market-place in the 1950s in the USA with the use of metal-flake pigments in automotive paints, to create "metallic paint" effect. However, neither standard geometries nor internationally accepted methods for assessing colour variations of gonio-apparent materials are available yet. Anodic TiO<sub>2</sub> films display promising features for generating particular visual effects, as it exhibits a wide gamut of structural gonio-apparent colours, with potential applications in architecture and design. Dense layers of TiO<sub>2</sub> on titanium-based substrates have various valuable physical properties that yield numerous potential industrial applications.

**Results and discussion:** Different surface preparations have been carried out on the samples, including mirror polishing and anodic oxidation at 10 V, 20 V and 90 V. At first sight, we observe that the colour of the samples, for the same anodizing potential, may vary with the surface finish, especially for the samples anodized at 90 V, which appear either pink or green in the same observation conditions. The chromatic paths of the samples are first investigated around the specular direction, for an incidence angle of 45°, with respect to the influence of the surface roughness: the most saturated colour are observed in the specular direction, which is consistent with the interferential origin of the colours. Moreover, 90 V sample was found to exhibit high gonio-apparent character.



**Fig. 1** - Digital colour pictures of the anodized samples. The incidence angle of the illuminant source is 45° and the observation angle is either 45° (specular direction) or 70° (out of the specular direction).

#### POLYMERISABLE BICONTINUOUS MICROEMULSIONS (PBM) AS COATING MATERIAL FOR WATER TREATMENT APPLICATIONS

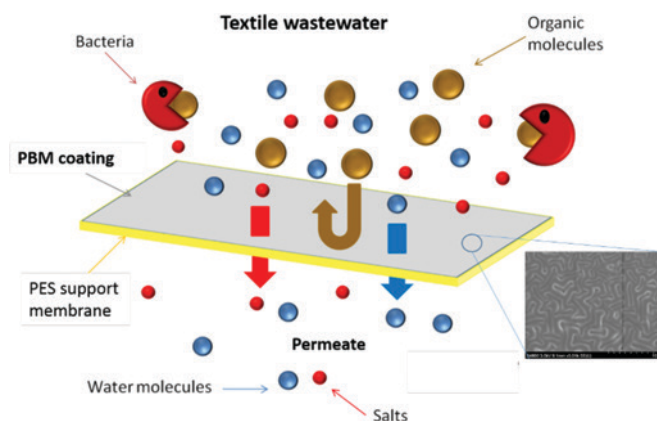
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**Concept:** The present work deals with the preparation, characterization and application of polymeric composite membranes obtained by the polymerization of a polymerisable bicontinuous microemulsion (PBM) and applied as coating material for commercial polyethersulfone (PES) membranes. In particular, the novel polymerisable surfactant acryloyloxyundecyltriethylammonium bromide (AUTEAB) was synthesised and used for the preparation of the bicontinuous microemulsion. The microemulsion range was found by the construction of a ternary phase diagram while the bicontinuous region was identified by conductivity measurements. Once prepared by the addition of a suitable monomer, water and cosurfactant, the microemulsion was then polymerised as coating material on the surface of a commercial polyethersulfone (PES) membrane. Among the main properties exhibited, PBM membranes presented an important antifouling property (evaluated by humic acid filtration tests) and antimicrobial activity (due to the presence of the synthesised surfactant) in comparison to uncoated PES membranes making them ideal candidates for membrane bioreactor (MBR) application.

**Motivations and objectives:** Water scarcity represents nowadays a more and more incumbent issue worldwide. Water resources are, in fact, not unlimited and the increasing water demand has a strong impact on water availability. For this reason different technologies have been applied so far in the optic of water reuse and water saving. Among them, membrane technologies find wide applications in the field of wastewater treatment and water reuse. The present study deals with the preparation of an innovative and efficient coating obtained by the polymerization of a bicontinuous microemulsion to be used for the preparation of membranes that can find application in water treatment processes such as MBR.

**Results and discussion:** Novel prepared PBM membranes prepared showed important properties in terms of antifouling and antimicrobial activity thanks to their relevant peculiar features, such as hydrophilic moiety, smoother surface and the typical polymerised bicontinuous structure. The combination of all these aspects made PBM coating an efficient technology for the modification of existing commercial membranes to be applied in the field of wastewater treatment in membrane bioreactor (MBR) technology. PBM membranes were then scaled up and used for the realization of an MBR module which was applied in model textile wastewater treatment. After six months of aerobic MBR tests, PBM membranes presented an improved antifouling activity, a longer lifecycle, a better rejections to organic compounds and a more constant water permeability in long term in comparison to uncoated PES membranes tested under the same conditions.

This work was supported by the European Union within the BioNexGen project (grant agreement no. CP-FP-246039-2) EU-FP7/project.



**Fig. 1** - PBM membranes separation mechanism in MBR technology.

#### ELECTROPOLYMERIZED NEAR-IR ELECTROCHROMIC AND HIGHLY PHOTOPOLYMERIZABLE THIN FILMS OF CYCLOMETALLATED COMPLEXES

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**Concept:** The complete characterization of novel electropolymerizable photoconductive and electrochromic organometallic complexes is presented. Cyclometallated complexes of general formula (PPy)M(O<sup>Δ</sup>N) (H(PPy) = 2-phenylpyridine, M = Pd(II) or Pt(II), H(O<sup>Δ</sup>N) = Schiff base), functionalized to be prone towards electropolymerization have been synthesized. Polymeric thin films of these complexes have been deposited by the electropolymerization process enabled by the presence of a triphenylamino group grafted onto the H(O<sup>Δ</sup>N) ancillary ligand. Noteworthy, the obtained films have shown high stability when tested in different organic solvents. Due to the robustness of the electrodeposited films, the redox behavior and the photoconductivity of both of the monomers (PPy)M(O<sup>Δ</sup>N) and the electropolymerized species have been investigated. The polymeric films of (PPy)M(O<sup>Δ</sup>N) have shown a very significant enhancement of photoconductivity when compared to their corresponding monomers in their amorphous melted state. Furthermore, the spectroelectrochemical characterization of the obtained thin films have evidenced the near-IR electrochromic absorption of the oxidized electrodeposited material.

**Motivations and objectives:** Organic-based optoelectronics have experienced in recent years impressive progress due to the development of novel organic photoconductors and electrochromics. Nonetheless, the introduction of metal centers in such active materials, leading to organometallic complexes has demonstrated to be an appealing strategy due to the enhancement of photo-generation efficiency, to the stability of the redox states, the readiness of visible region electronic transitions and the possibility to selectively tune either the metal and/or the ligands.

**Results and discussion:** Stable high quality thin films of organometallic complexes (PPy)M(O<sup>^</sup>N) (Fig. 1) have been deposited by electropolymerization on ITO substrates, showing improved photoconductive behavior with respect to their corresponding monomers and near IR electrochromism.

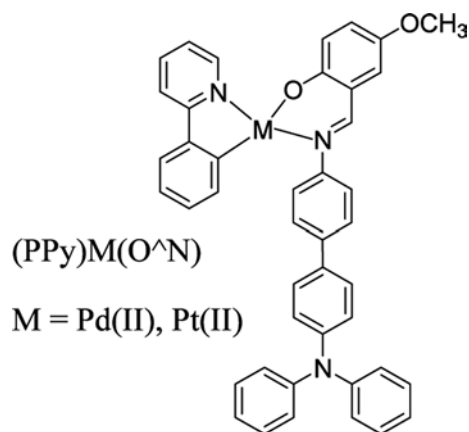


Fig. 1

#### REINFORCEMENT OF PERFLUOROPOLYETHERS COATINGS BY CERAMIC OXIDES SOL-GELS FOR FOULING MITIGATION ON METAL SURFACES

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**Concept:** In this research we developed a coating formulation containing  $\alpha$ ,  $\omega$ -substituted perfluoropolyethers (PFPE) and ceramic oxides sol-gels, for fouling mitigation on solid surfaces. Micrometer coatings were obtained on metal substrates by dip-coating procedure; they showed hydrophobic behavior (CA > 130°) and low CA hysteresis. The coatings resistance against shear stresses and chemicals increased thanks to the high mechanical properties of the ceramic oxides, compared to a simple PFPE coating. The ability of the coatings to mitigate particulate fouling was preliminary confirmed in presence of CaSO<sub>4</sub> in an appropriate test rig.

**Motivations and objectives:** One potential application of hydrophobic coatings concerns fouling mitigation. It has been demonstrated that low energy surfaces are able to influence the mechanism of deposition and removal of fouling particles on heat transfer surfaces, increasing the fouling induction period of the heat exchangers. This research aims to develop a hydrophobic organic-inorganic coating, combining a PFPE with a sol-gel network obtained from the hydrolysis of tetraethylorthosilicate (OTES) or Zr-*n*-propoxide, in order to improve the mechanical properties of the final coatings. The investigation focuses the attention on the important coatings parameters for a possible application on heat transfer surfaces, i.e., thickness, thermal resistance, surface roughness and chemical and physical resistance. Fouling mitigation ability of the coatings is assessed in particulate fouling conditions, in a specific test rig.

**Results and discussion:** Hydrophobic coatings were obtained by formulating in iso-propanol a commercial PFPE (Fluorolink®S10) with SiO<sub>2</sub> or ZrO<sub>2</sub> sol-gels, at different weight proportion (80/20, 1/05 and 1/1 respectively). The coatings resistance was investigated against erosion induced by liquid environments and shear stresses induced by a water flow. Compared to a simple PFPE coating, the resistance against shear stresses and aggressive environments increased of the 90% (Fig. 1). Fouling mitigation ability of coatings deposited on the internal surfaces of a stainless steel tube, was assessed in presence of a CaSO<sub>4</sub> solution (4 g/L), flowed inside a coated tube (temperature = 40°C, flowrate = 1.5 m/s). Thanks to the hydrophobic coating, the foulants deposition is 95% lower in respect to an uncoated surface.

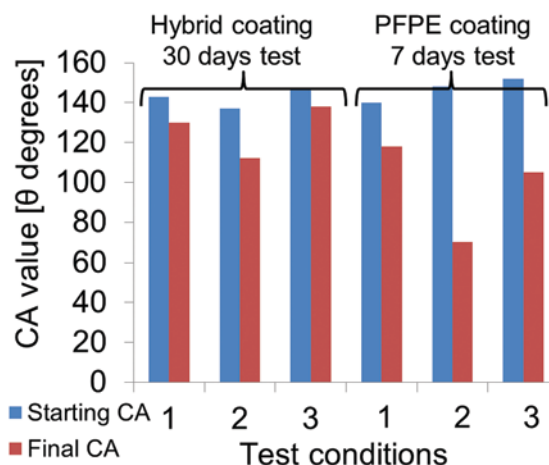


Fig. 1 - Resistance tests results. Legend: 1 = shear stress (T = 40°C, 2 m/s); 2 = HCl (pH = 2, T = 50°C); 3 = Seawater (pH = 8, T = 50°C).

#### CO<sub>2</sub> CAPTURE WITH METAL-ORGANIC FRAMEWORKS: AN AB INITIO MODELING STUDY

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**Concept:** Removal of carbon dioxide from environment is very important to reduce its concentration in the atmosphere. In this respect, porous materials have been identified as effective adsorbent to capture CO<sub>2</sub>. Among them, Metal-Organic Frameworks (MOFs) have recently attracted a lot of attention for their high porosity due to the crystalline structure with different topologies (cages, channels, ...) and chemical versatility that allows one to easily modify their surface properties. Adsorption capacity can then be tailored to enhance their performance in CO<sub>2</sub> separation and storage. In this respect, ab initio modeling offers a useful tool to shed some light on the interaction between carbon dioxide and MOFs. Here, the adsorption of CO<sub>2</sub> in different metal-organic frameworks with either open metal sites or amino functionalized ligands, has been investigated theoretically through fully periodic quantum mechanical calculations. All calculations have been carried out with the B3LYP-D2 method by using the periodic ab-initio code CRYSTAL.

**Motivations and objectives:** MOFs consist of inorganic nodes (e.g. metals or clusters) connected through organic linkers to form a porous three-dimensional framework. The combination of different nodes and linkers makes MOFs very versatile materials with promising applications in many fields. In particular, they have been investigated for the ability of capture carbon dioxide, which is one of the hottest topics in MOFs research. Different strategies have been employed for MOFs to increase adsorption capacity. Among them, we investigate (i) the presence of coordinatively unsaturated metal sites that can act as specific adsorption sites and (ii) amino-functionalized linkers. Our goal is to better understand at an atomistic level the interaction of carbon dioxide with the framework and guide the synthesis of MOFs with improved adsorption capacity.

**Results and discussion:** Results will be reported for small-to-medium MOFs (i.e. MOF-74) and giant MOFs, as MIL-100, for which isorecticular families with different metal atoms have been studied, namely: Mg, Ni, Zn for MOF-74 and Al, Sc, Cr and Fe for MIL-100. The electrostatic potential mapped on top of a charge density isosurface is used to highlight adsorption sites in the framework and rationalize interaction energies. For MOF-74(M) (M = Mg, Ni, Zn) computed results favorably compare with available experimental data. Predicted interaction energies increase correctly along the series: Zn < Ni < Mg. For instance, for MOF-74(Mg) a  $\Delta H^\circ$  (298K) of -41.4 kJ/mol is predicted, in very good agreement with the average experimental value of 42.7 kJ/mol. Instead, for MIL-100(M) (M = Al, Sc, Cr and Fe) computed interaction energies are definitely underestimated with respect to experimental values. A possible role of defects is expected. Work in progress to explore this hypothesis. Both hydroxylated and dehydroxylated forms of the amino-functionalized UiO-66, a Zr(IV)-based MOF, were investigated. Overall, the interaction with -NH<sub>2</sub> is rather small: less than 20 kJ/mol. A combined effect

of OH and NH<sub>2</sub> groups is observed, instead, that leads to an estimate  $\Delta H^0$  (298K) = -29.1 kJ/mol which nicely compares with the adsorption enthalpy of 27 kJ/mol.

We acknowledge PRACE initiative for computing resources (Grant: Project 2013081680).

#### FLUORINATED TRANSPARENT COATING IN THE PHOTOCATALYTIC OXIDATION OF HYDROSOLUBLE POLLUTANTS IN TURBID SUSPENSIONS

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**Concept:** The photodegradative activity of titanium dioxide immobilized into a multilayered transparent fluoropolymeric matrix has been studied. The multilayered coating photocatalytic activity towards hydrosoluble organic pollutants was evaluated in clear as well as in highly turbid conditions obtained by dispersing barium sulfate microparticles in the polluted solution. Rhodamine B-base was chosen as reference organic pollutant.

**Motivations and objectives:** The use of photocatalytic TiO<sub>2</sub> in suspension or slurry type reactors is well reported. However, the industrial feasibility of such systems is limited due to the low quantum efficiency reported for slurry processes and because a post-treatment catalyst recovery stage is needed.

**Results and discussion:** To overcome the above drawbacks TiO<sub>2</sub> was immobilized into a multilayer ionomeric-perfluorinated matrix and the photocatalytic activity of the obtained Photoactive Coating (PC) was tested. The peculiar nature of the PC allowed the evaluation of the photocatalytic efficiency in both clear and turbid conditions. The fluorinated polymeric matrix used is characterized by high chemical resistance, high transparency towards UV light, good gas permeability to oxygen and good wettability in order to obtain a favorable interaction with the polluted aqueous solutions. The PC photoactivity was evaluated and compared with the abatement performances observed by dispersed TiO<sub>2</sub>. All photodegradation tests were described through pseudo-first order kinetics. Results obtained showed that the TiO<sub>2</sub> containing coating had higher photocatalytic activity than dispersed titanium dioxide, particularly at low pollutant concentration. Further tests, conducted in presence of a solid suspension, proved the photoactive coating to be effective even in turbid solutions (Fig. 1). In addition, TiO<sub>2</sub> was not deactivated by slime interposition between the UV source and the pollutant. Indeed, TiO<sub>2</sub> activation and pollutant diffusion took place at the two opposite sides of the coating. Moreover, any costly separation of the catalyst from the purified water was avoided since the catalyst was immobilized in the fluorinated polymeric matrix.

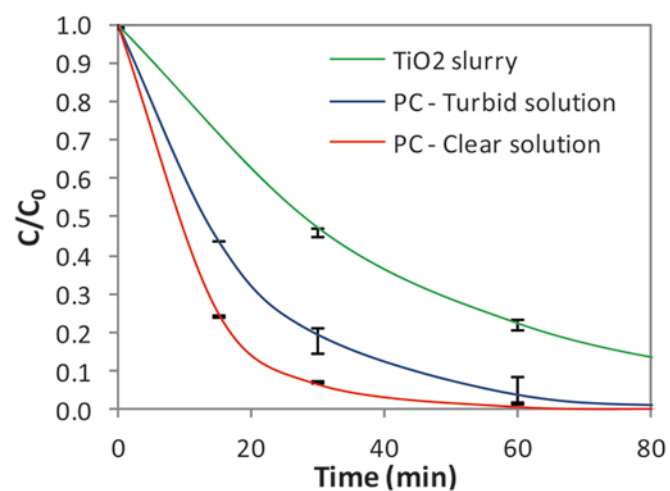


Fig. 1 - Photoactivity of PC, in both clear and turbid solutions, compared to the performances obtained by slurry TiO<sub>2</sub>.

#### CO<sub>2</sub> CAPTURE AND ACTIVATION IN MICROPOROUS MATERIALS

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**Concept:** Carbon dioxide is the most abundant human activity waste but it is also, a renewable non toxic sources of C1. CO<sub>2</sub> may become relevant as a chemical feedstock reintegrating it in the industrial processes. An additional problem to make feasible the use of CO<sub>2</sub> produced by post combustion plants, is its dilution.

**Motivations and objectives:** In order to overcome this problem, Carbon Capture can be considered a preliminary step for CO<sub>2</sub> Use (CCU). In this respect, the availability of microporous materials, such as Metal-Organic Frameworks (MOFs) or Poly-ionic liquids, characterized by high surface area, high adsorption capacity and selectivity towards CO<sub>2</sub>, can represent the first step to tailor new materials for CCU. The present work will present some research lines on going with the collaboration of other laboratories.

**Results and discussion:** Along the last five years at NIS laboratories, in collaboration with some major groups in Europe and overseas, an extensive research have been developed toward the understanding of CO<sub>2</sub> properties towards active surfaces. In this contribution the author will summarize major results obtained on a selection of materials that gave nice results in respect to selective adsorption and or activation towards CO<sub>2</sub>. In most cases the contribution of NIS was in relation to the characterization of the materials and their activities but, in the last two years, we started also some synthesis both in the area of MOFs and of poly-ionic liquids.

#### STEEL SCALE WASTE AS A NEW COMPONENT IN MORTARS PRODUCTION: THE IMPROVED EFFICIENCY OF HEATING FLOORS

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**Concept:** The use of industrial wastes in mortars production solves the problem of disposal and promotes the development of sustainable building materials. The scope of this study is the use of selected waste from steel industry as a partial replacement of aggregate in the production of mortars.

**Motivations and objectives:** The aim of this study is to evaluate if the addition of steel scale waste does not worsen the mortar's compression strength, with respect to a reference blank, waste free material. We also aim to demonstrate that the thermal conductivity of the new materials is improved as it should be their efficiency when used in the manufacturing of heating floors.

**Results and discussion:** In the present research are reported the results of some experiments obtained from the production, hydration and subsequent measurement of the mechanical properties and thermal conductivity of several mortars prepared using a commercial CEMII/B-LL cement, a steel scale waste, a commercial natural aggregate, a superplasticizer and water. Mortar pastes were made by replacing part of the natural aggregate with different proportions (5, 10, 20, 30 and 40% wt) of steel scale waste. Steel scale is formed on the surface of steel monoliths during the thermal treatments after casting; it is an oxide layer which mainly contains Fe oxides and minor fractions of other oxides; it is presently disposed of to landfill or, but only in few cases, used to prepare counterweights concretes.

#### PREPARATION AND CHARACTERIZATION OF Ce:YAG-PMMA AND Ce:YAG-PC COMPOSITES FOR WHITE LED

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**Concept:** Polymeric composites of lanthanide-doped materials were considered as potential candidates for the development of white LED. Ce:YAG-PMMA (YAG: yttrium aluminum garnet; PMMA: Polymethylmethacrylate)

and Ce:YAG-PC (PC: polycarbonate) composites were prepared by melt compounding. The characterization was performed using transmission electron microscopy, X-ray diffractometry, thermogravimetry and photoluminescence spectroscopy. The effect of filler quantity, in the range 0.1-5 wt.%, on the morphology, optical and thermal properties was investigated.

**Motivations and objectives:** Composites and luminescent polymers have been recently found to be potential candidates for the development of white LED, lasers and luminescent concentrators for solar cells. Due to its luminescence properties YAG doped with lanthanides ions is a good candidate as light emitting filler. However, since it has a low compatibility and affinity with polymers and compatibilizers, the preparation of composites is not easy. In a recent our work, the preparation of a polymeric nanocomposite containing Ce: YAG nanoparticles using in situ polymerization has been reported. A good dispersion of Ce:YAG nanoparticles has been obtained maintaining them luminescence properties. In addition, an increase of thermal stability and stiffness of PMMA was observed. Then, the preparation of Ce: YAG-PMMA composite has been performed by using the melt compounding method, which is not expensive, allows to obtain big quantitative of material, and limit the exposition to the carcinogenic monomer methyl-methacrylate used as starting precursor in the in situ polymerization. In this work the preparation of Ce:YAG-PC composites using the melt compounding method is reported. The study was performed as function of the filler quantity.

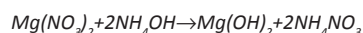
**Results and discussion:** Results showed that the particles of filler are homogeneously dispersed in each polymer and that the thermal stability of the polymer and the optical properties depend on the filler quantity.

#### CARBON BASED HYBRID MATERIALS FOR THERMOCHEMICAL STORAGE

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**Concept:** The MgO/H<sub>2</sub>O/Mg(OH)<sub>2</sub> Chemical Heat Pump (CHP), based on the reversible gas-solid chemical reaction  $Mg(OH)_2 \leftrightarrow MgO + H_2O$ , is a promising technology for the recovery of wasted heat that is inevitably produced by industrial processes. Novel hybrid materials made of magnesium hydroxide (Mg(OH)<sub>2</sub>) and a carbonaceous support (EG - exfoliated graphite or CNTs - carbon nanotubes) were synthesized via a Deposition-Precipitation (DP) method to improve the heat transfer properties of the storage medium:



The heat storage and output capacities of the obtained hybrid materials were evaluated by thermogravimetric analysis which simulates the CHP cycle and compared with that of pure Mg(OH)<sub>2</sub>. The developed hybrid materials showed higher storage capacity at lower reaction temperature and higher heat output rate with respect to pure Mg(OH)<sub>2</sub>.

**Motivations and objectives:** With respect to the common deposition procedure till now used, that consists in a physical mixing of preformed Mg(OH)<sub>2</sub> and carbonaceous material in ethanol, the idea is to directly grow Mg(OH)<sub>2</sub> crystals on graphite type materials in aqueous medium trading on the electrostatic interaction between the two materials due to their different point of zero charge (pH<sub>pzc</sub>) in solution. Thus, it is expected the improvement of the material stability under operating conditions.

**Results and discussion:** Both carbon based hybrid materials showed higher dehydration (heat storage mode) and hydration (heat output mode) conversions (Fig. 1). Hence, it can be argued that their storage and output capacities are improved due to the presence of the carbonaceous support which has the dual task (i) to enhanced the heat transfer property of the storage material and (ii) to avoid MgO sintering during dehydration reaction that has a negative impact not only on the thermodynamic equilibrium but also on reaction kinetic. Moreover, the CNTs based hybrid sample (CNTs-Mg(OH)<sub>2</sub>) exhibited the highest stored heat values and heat output rate: it can respond immediately in case of energy demand releasing most part of stored heat in ~10 minutes.

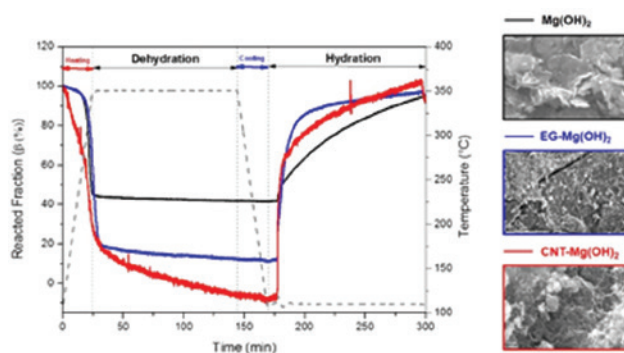


Fig. 1 - CHP cyclic experiment.

#### NANOSTRUCTURED MATERIALS FOR SENSING, ENERGY CONVERSION AND STORAGE

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**Concept:** It is well known that physical and surface properties of nanomaterials (e.g., confinement effects, high surface-to-volume ratio and short diffusion pathways for charge carriers) are promising to enhance efficiency of nanostructured devices for sensing, and for sustainable energy production, conversion, and storage. Many papers showing that nanostructured morphology (nanowires and/or nanotubes) is attractive to improve the performance of common electrode materials were published in recent years. However, the practical use of nanomaterials is often complicated by the lack of scalable and cost-efficient synthesis procedures and the challenge of integrating into devices 1D nanomaterials saving their structural features. Template electrodeposition allows scalable nanostructure production of different materials and their inclusion into device fabrication. In this work, examples of template electro-synthesis of different types of nanostructures will be given.

**Motivations and objectives:** In recent decades, nanostructured materials were extensively investigated for sensing, energy conversion and storage applications. Despite remarkable findings and achievements, performance of nanostructured devices needs further improvement in order to become profitable for commercialization. Electrochemical deposition is a facile method for fabricating either two- or one-dimensional nanostructured materials because it allows the tuning of the fundamental parameters controlling their final features. In addition, electrochemical processes are usually cheap and environmental friendly, so that they can be easily scaled-up from lab to industrial level. Here, the attention is focused on the synthesis of different type of materials for electrochemical sensing of H<sub>2</sub>O<sub>2</sub>, for innovative lead-acid and lithium-ion batteries, for photovoltaics, and for more efficient electrocatalysts. The aim was to obtain dimensionally stable nanostructured electrodes characterized by the presence of uniform array of nanowires and/or nanotubes with very high surface area and to show that the introduction of nanotechnology for fabricating electrodes is beneficial to improve device performances.

**Results and discussion:** In this work, the performance of different type of nanoelectrodes is discussed. In particular, the application of PbO<sub>2</sub> nanowires as positive electrode in lead acid batteries and of Ni-IrO<sub>2</sub> nanowires in alkaline electrolyzers are presented. Besides, preliminary results on the use of Cu and Pd nanostructures as sensors for detection of H<sub>2</sub>O<sub>2</sub> will be also shown.

#### EXPERIMENTAL CHARACTERIZATION OF ARTIFICIAL AGGREGATE/PCM COMPOSITES FOR THERMAL ENERGY STORAGE IN CONCRETES

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**Concept:** In this work, the technology to produce an innovative composite, characterized by low fabrication costs and high performance, is briefly described. The matrix is a porous aggregate for lightweight concretes, obtained from expanded clay, the dispersed phase is a recycled paraffinic wax with a high

storage capacity, which is the effective Phase Change Material (PCM) for Latent Heat Thermal Energy Storage (LHTES). The composite aggregate is obtained by an advanced incorporation technique, developed during the research activities of the present work. An adequate amount of PCM can be efficiently absorbed in the porous media, up to 30-40% w/w, depending on the porosity of selected support. This technique can be applied to different couples of porous media/PCM to obtain the desired thermal storage performance. In fact, by choosing different PCMs, on the basis of phase change temperature and latent heat value, the quantity of PCM absorbed can be defined during the design phase. The final results of the project will be the prototype of a Thermal Storage panel (TS panel), which can be used as wallboard for building applications.

**Motivations and objectives:** The energy storage composite proposed could be used as thick boards or panels into buildings, or as small component for heat recovery or heat buffering in machinery. In fact, by changing the type of dispersing phase, thermal properties can be tailored for different application. In particular LHTES with sustainable materials can be explored for mid-long term thermal storage. Currently, several eligible PCMs for high temperature range are under consideration. Fairly, the low temperature range up to room temperature, namely 20°C, is very difficult to manage because it requires the inglobation technique to be developed in a confined environment at very low temperature, for example in a refrigerator, and it is beyond the scope of this work.

**Results and discussion:** Several aggregate sizes have been tested in terms of inglobation potentials in water by simple immersion. Aggregate/PCM composites have been prepared and a vacuum impregnation procedure has been established. The effect of vacuum impregnation has been assessed by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform InfraRed (FT-IR), and Differential Scanning Calorimetry (DSC) techniques. Preliminary experimental results showed the incorporation and compatibility of porous solid support/PCM is high, resulting in a storage capacity suitable for thermal storage in buildings. The most relevant properties, obtained at the current state of development, are a thermal storage density of about 0.2 MJ/kg, a thermal storage temperature range between 40-55 °C and a supercooling of 6-7°C.

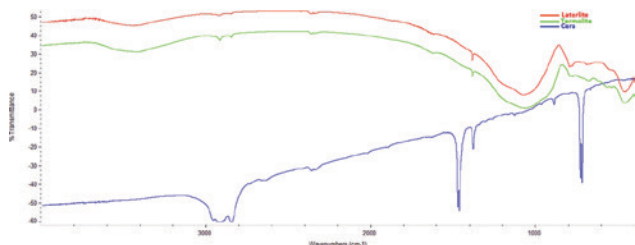


Fig. 1

#### PATTERNING AT MICRON AND SUB-MICRON SCALE BY GAS FOAMING

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**Concept:** The gas foaming technology has been utilized as a tool for imprinting, at a micron and submicron scale, a desired pattern on polymeric film and particles. Carbon dioxide and nitrogen up to pressures of 14 MPa were used as blowing agents for polystyrene films and spheres with thickness or diameter ranging from 200 nm to 50 μm. Focused Ion Beam-Scanning Electron Microscopy, Transmission Electron Microscopy and Confocal Microscopy were used to assess the occurrence of bubble within the film and the particles, and to assess the pattern, the shape, the dimension and the closed/open feature of the achieved porosity.

**Motivations and objectives:** Gaining a control over the morphology of small objects has becoming important in numerous fields of science and technology, e.g. in biomedicine, photonics, and pharmaceuticals. For instance, in drug delivery, hollow nanoparticles are used to transport and deliver in controlled manner delicate drugs within the body.

**Results and discussion:** A control over the morphology at micron and sub-micron scale can be achieved by using a “containing-barrier-deformation/stress transfer”-film approach, where a removable film embedding the particles served for the three functions of: i) containing the particles for ease

of handling, ii) avoiding the loss of the blowing agent as the gas is released and iii) allowing the non-isotropic deformation of the particles as well as of the hollow. In particular, hindering the loss of blowing agent by the film embedding the particles (so-called “barrier” function) has been demonstrated to be the key factor to successfully foam so-small particles and films, where, without the barrier film, the blowing agent would have diffused out of the polymer well before any bubble may have nucleated. The pictures below prove the efficacy of the proposed method in shaping thin film as well as small particles. On the left, a PS film where open cavities may be selectively imprinted; on the right, a kayak-shaped hollow PS particle.

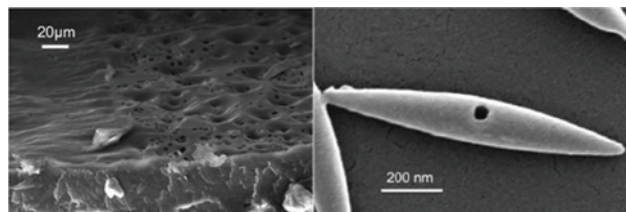


Fig. 1

#### THERMOPLASTIC COMPOSITES FOR NOVEL APPLICATIONS

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**Concept:** Thermoplastic composites in use today are mainly based on polymer matrices derived from petroleum and mineral based reinforcing agents. The present work is focused on a new concept for the development of truly thermoplastic based eco-composites made with constituents from renewable sources only.

**Motivations and objectives:** The use of green composites is attracting increasing interest in the composites field. Natural fiber reinforced composites are increasingly required in automotive and additive manufacturing. However, in most cases the matrices used are non-renewable. EU rules comply OEM to increase the use of materials from recycling and from renewable sources in automotive structures. Natural fiber reinforced composites partially satisfy the green requirements. The present research work aims to overcome the current limitation of natural reinforced thermoplastic composites by the use of fully renewable matrices. To obtain this final goal polymer blends based on polylactic acid (PLA) modified by the addition of lignin have been studied. The lignin based matrices have been reinforced with natural reinforcements and the obtained composites characterized in view of their use in automotive and fused deposition modelling applications.

**Results and discussion:** Polylactic acid PLA4032D by Natureworks was used as polymer matrix. Lignin specimens were obtained from GreenValue and Tecnaro. All the materials were used as received. At first the PLA/Lignin blends were mixed using astatic mixing chamber operating at 190°C. The choice of this processing temperature is due to low temperature stability of the lignin. Figure 1 reports the thermogravimetric analysis for the lignin. The influence of the poor thermal stability of lignin on the stability of the PLA/lignin blends was demonstrated by measuring the torque during mixing too. This finding highlighted that mixing lignin with PLA poses some limitations in terms of reworkability of the blends obtained. However, processing technology trials on PLA showed the feasibility to prepare filaments for Fused Filament Modelling with common consumer 3Dprinters.

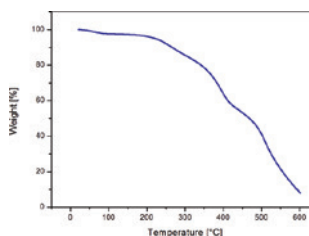


Fig. 1 - TGA on Lignin.

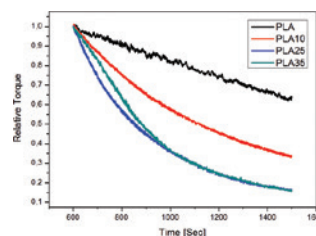


Fig. 2 - Relative torque for PLA/Lignin blends.

### MEMBRANES BASED ON POLYMERIC MATRICES AND GRAPHENE NANOPATELETS FOR CO<sub>2</sub> CAPTURE PROCESSES

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**Concept:** Composite membranes based on poly (1-trimethylsilyl-1-propyne) (PTMSP) and small amounts (<1 wt%) of Graphene (G) and Graphene Oxide (GO) nanoplatelets were obtained via physical dispersion in solution and evaporation and inspected for the application in CO<sub>2</sub> capture processes from gaseous streams. The idea behind the work is to optimize the permeability and selectivity of PTMSP by choosing the appropriate filler amount, size, solvent and preparation protocol. The effect of filler addition on the stability of PTMSP properties with time is also under investigation.

**Motivations and objectives:** CO<sub>2</sub> capture from flue gas or syngas is one of the essential strategies to reduce the increasing levels of CO<sub>2</sub> in the atmosphere and consequent global warming. One of the most promising and environmentally sustainable strategies to achieve such goal is the membrane separation process, which is less hazardous and expensive than physical absorption with amines. The development of a promising separation process requires the synthesis of a robust, stable, selective membrane material with high productivity. In this work we examine the potentiality of composite membranes based on PTMSP and Graphene, Graphene Oxide nanoplatelets. Indeed, PTMSP membranes per se, which are initially characterized by good separation performance, are prone to ageing and loss of transport properties with time, which can be reduced with the addition of inorganic fillers as done in this work.

**Results and discussion:** The permeability of various gases (He, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>) at 30°C was investigated, indicating that the addition of GO enhances permeability of all gases, while the graphene fillers lower the membrane permeability. The ideal selectivity of PTMSP, on the other hand, is almost always enhanced by addition of fillers. It was tested directly that such effects are due to a modification of the gas diffusivity, rather than of the solubility, of the polymer. Moreover, it was shown that some graphene-based fillers reduce the physical ageing of membrane performance. Such result indicates that those fillers hinder the polymer mobility and extend the polymer relaxation time, by inhibiting the macromolecular rearrangement.

### MULTI-FUNCTIONAL STABILIZERS-FUNCTIONALIZED CARBON NANOTUBES FOR ADVANCED ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE-BASED NANOCOMPOSITES

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**Concept:** Stabilizing molecules, such as hindered phenols (both synthetic and naturally occurring), polyphenols and hindered amine light stabilizers, were covalently linked or physically absorbed onto outer surface of multi-walled carbon nanotubes (CNTs) and the obtained multi-functional fillers (Stab-f-CNTs) were dispersed in Ultra High Molecular Weight Polyethylene (UHMWPE) aiming at obtaining advanced nanocomposites with enhanced thermo- and/or photo-oxidative stability, electrical and mechanical properties. The chemical grafting or physical absorption of stabilizing molecules is confirmed by spectroscopic, spectrometric and thermo-gravimetric analyses, and the influence of the multi-functional nanoparticles on the morphology, mechanical, electrical and rheological behaviour and thermo-/photo-oxidative stability of the nanocomposites are investigated. UHMWPE/Stab-f-CNTs nanocomposites show improved electrical and mechanical properties compared with those of bare CNTs based nanocomposites and, due to the multi-functional nature of used nanoparticles, shows enhanced thermo-/photo-oxidative stability caused by a synergic action between the immobilized stabilizing molecules and the radical scavenging activity of CNTs.

**Motivations and objectives:** Usually, anti-oxidants and radical scavengers stabilizers have been used to protect polymeric materials against thermo- and photo-degradation. However, the use of low molecular weight stabilizing systems is often restricted because of their possible physical loss by volatilization, migration, and water extraction. One of the possible strategies to overcome these drawbacks is the immobilization of the stabilizing molecules, through grafting or physical entrapment, onto the outer surface of different nanoparticles. In this way, CNTs act as efficient nano-carriers for the stabilizing molecules, improving also the dispersion of the latter in the host matrix in spite of their poor solubility.

**Results and discussion:** The Stab-f-CNTs containing nanocomposites show a surprisingly high thermo-/photo-oxidation resistance, with a five/ten-fold increase of the induction time of the degradation phenomena. Rather than to the inherent stabilizing action of the stabilizing molecules, such a notable result is believed to be due to their specific chemical interactions with the CNTs, which could exhibit a considerable radical scavenging activity due to the formation of structural defects on their outer surface. The latter represent acceptor-like localised states, which radically improve the thermo-/photo-oxidative resistance of the nanocomposites. Moreover, in Stab-f-CNTs-based polymer nanocomposites, the stabilizing activity is maximized because of the stabilizing molecules are localized and available at the interfacial area between polymeric phase and the inert nanofillers that is the critical area for the beginning of photo degradation process. Overall, our results demonstrate that immobilizing stabilizing molecules on nanoparticles, and using the latter as multifunctional filler for nanocomposites, is a viable route towards to produce high-performance polymeric materials.

This work is financially supported by the Italian Ministry of University and Research (MIUR) under the program FIRB 2010 – Futuro in Ricerca (Project cod: RBFR10DCS7).

### RECYCLABLE BIOBASED THERMOSET MATRIX FOR ADVANCED NATURAL FIBER REINFORCED COMPOSITES PROCESSED BY HIGH PRESSURE RESIN TRANSFER MOLDING

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**Concept:** Thermoset resins are encountering increasing restrictions in the automotive field due to their environmental limits and difficulties to be achieved very fast production speed (less than 5 min). The present paper investigates a novel concept of thermoset composites which is fully recyclable and easy to process in high volume production.

**Motivations and objectives:** The use of green thermosets is attracting increasing interest in the composites field. However, only the use of cleavable hardeners offers the possibility for a truly green approach with minimal environmental impact. The objectives of the present paper are: to assess an high production method suitable for automotive part production; to measure the environmental impact of green composites based on cleavable amines.

**Results and discussion:** The typical processing time for the composites studied was of 5 min at 120°C with average injection times of 20 sec. Omega shaped panels were obtained in a 1000ton press (Fig. 1) and, from

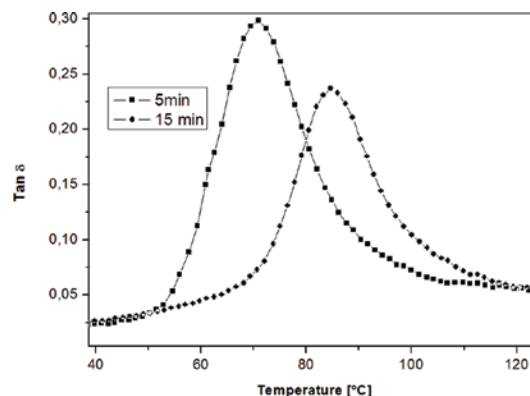


Fig. 1 - DMA analysis for laminates cured for 5 and 15 min.



these panels, samples for thermomechanical characterization were cut. Glass transition temperatures of  $\sim 70^\circ\text{C}$  were obtained with the 5 min cure schedule. Increasing curing time from 5 to 8 or 15 min the  $T_g$  increased to  $76^\circ\text{C}$  and  $85^\circ\text{C}$ . The  $T_g$  results depended also on the natural reinforcement type. Post curing at  $120^\circ\text{C}$  for 1 hr was applied to fully convert the thermoset reaching the best properties for the composites. The recycling of the composites was successful following the Connora Technology recycling scheme. This approach foresees the dissolution of the thermoset matrix in a water/acetic acid solution at  $80^\circ\text{C}$ . Following this approach the thermoset was transformed in a thermoplastic material which was further analyzed and the natural fibers were recovered with minimal influence on their structure.

#### UPCONVERSION EMISSION OF $\text{Tm}^{3+}/\text{Yb}^{3+}$ DOPED $\text{SrF}_2$ NANOPARTICLES: APPLICATION TO LIGHT RESPONSIVE NANOSTRUCTURED SYSTEMS

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**Concept:** The upconversion (UC) emission in the ultraviolet region of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  codoped nanoparticles (NPs) can be used for activating photoswitchable molecules, such as spiropyran. Water dispersible  $\text{SrF}_2:\text{Tm}^{3+}, \text{Yb}^{3+}$  NPs (10 nm average size) can be efficiently synthesized with an environmental friendly technique. The present investigation describes the ultraviolet emission properties of  $\text{Tm}^{3+}/\text{Yb}^{3+}$  codoped  $\text{SrF}_2$  NPs upon irradiation with a radiation in the near infrared region (980 nm), focusing on the effect of the environment on the light emission. Moreover, the use of this ultraviolet emission for the activation of spiropyran encapsulated in a nanostructured system has been investigated by using spectroscopic techniques and DLS measurements.

**Motivations and objectives:** Photoactivated nanostructured systems under irradiation of infrared radiation are interesting for drug delivery in biomedical application, in particular for the in-vivo use. In fact, to this aim, the wavelength of the excitation radiation should be in the biological window (700-1000 nm).

**Results and discussion:** High intensity ultraviolet bands at 350 nm and 360 nm are observed upon excitation at 980 nm for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  colloidal dispersions of the UC NPs, corresponding to transitions from  $^1\text{I}_6$  and  $^1\text{D}_2$  energy levels of  $\text{Tm}^{3+}$  ions. The UC intensities are strongly dependent on the temperature and on the  $\text{H}_2\text{O}/\text{D}_2\text{O}$  molar ratio in the media, due to the variation of multiphonon relaxation rates. Nanostructured systems encapsulating spiropyran have been prepared and characterized by DLS measurements. Investigation on the obtained UC NPs indicates that the UC ultraviolet radiation can efficiently activate the spiropyran molecule and a change of the hydrodynamic size of the nanostructured system is observed.

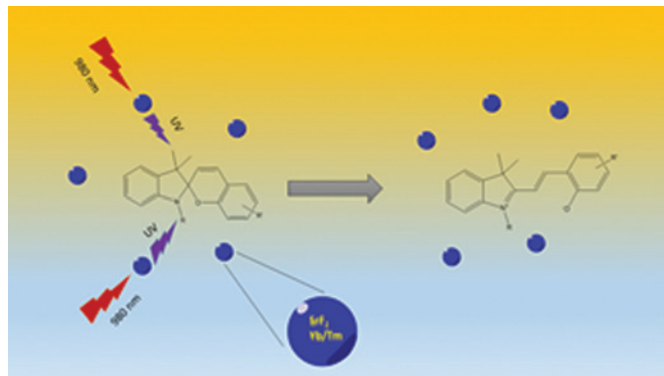


Fig. 1

#### STRUCTURAL AND MAGNETIC CHARACTERIZATION OF NANOMAGNETITE-EPOXY RESIN HYBRID SYSTEM BY MEANS OF *IN SITU* SYNTHETIC TECHNIQUES

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**Concept:** Stable suspensions of magnetite nanoparticles (MNPs) were prepared by non-hydrolytic sol-gel (NHSG) process using iron(III)-Acetylacetonate  $[\text{Fe}(\text{AcAc})_3]$  as metallic precursor and 2-ethyl-1,3-exanediol (ex-diol) as reactive solvent. The obtained magnetite suspensions were mixed directly with an aliphatic epoxy resin (bisphenol A diglycidyl ether, DGEBA) and the formulations were thermal cured to achieve composite materials with magnetic properties, by means of the *in situ* polymerization.

**Motivations and objectives:** The field of organic-inorganic hybrid materials has witnessed an increase of attention in the last decay. The possibility to combine inorganic nanoparticles and organic polymeric matrices allows to obtain new advanced materials showing peculiar properties. Among the different synthetic procedures, the sol-gel chemistry represents one of the preferred ways for the preparation of organic-inorganic hybrids thank to its mild conditions. The NHSG approach can be successfully used to obtain very pure and crystalline metal oxides. Polymeric nanocomposites containing MNPs were prepared by the *in situ* polymerization of DGEBA monomers directly into the MNPs suspension without any other additional step. The cationic polymerization produced a three-dimensional network in which the suspending medium ex-diol was covalently linked to the epoxy network according to the 'activated monomer' mechanism during the propagation step in the ring-opening polymerization.

**Results and discussion:** TEM images of dried powders show that the MNPs have spherical shape with diameters in the range 10-18 nm depending on the  $[\text{Fe}(\text{AcAc})_3]/[\text{ex-diol}]$  ratio (Fig. 1a). TEM images of NCs show that in all cases the nanoparticles are very well distributed but not evenly dispersed in the matrix and form an island-like structure of well-separated nanoparticle agglomerates (Fig. 1b). Magnetic measurements (inset Fig. 1b) of NCs indicate a highly correlated magnetic response and points to a ferromagnetic-like behavior of the embedded MNPs. However, the absence of contact interaction among adjacent nanoparticles in island-like agglomerates rules out the hypothesis of the presence of a standard ferromagnetic phase; the temperature dependence of both coercivity and low-field susceptibility indicate that the agglomerates can be considered as dipolar ferromagnets in the whole temperature range.

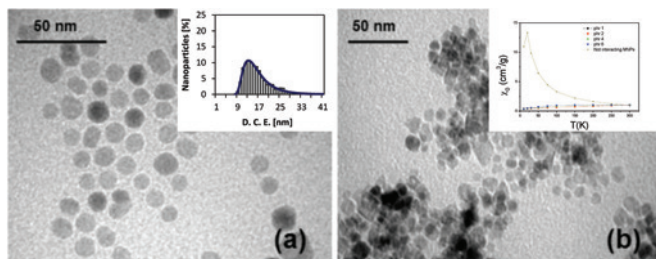


Fig. 1 - TEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles (a - in the inset MNPS distribution curve) and nanocomposites (b - in the inset magnetic susceptibility vs temp. plot of NCs).

#### ZWITTERIONIC MAGNETIC NANOPARTICLES AS A BACKBONE FOR BIOAPPLICATIONS

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**Concept:** Iron oxide nanocrystals coated with zwitterionic dopamine sulfonate (ZDS, see figure for structure) are magnetic nanoparticles (NPs) with

high colloidal stability in water. These ZDS-NPs can be a substantial improvement over PEG-coated NPs because the much smaller size of ZDS with respect to PEG (i) allows one to better control the NP surface chemistry and (ii) to obtain NPs that are excreted via the urinary system rather than captured by the MPS (liver, spleen) thus avoiding long-term permanence of the NPs in the body. As studied by DLS, ZDS-NPs did not adsorb proteins and were colloidal stable in a protein-rich medium, both pre-requisites for successful biomedical applications. Treatment of HepG2 cells with ZDS-NPs showed that the NPs (i) are non-cytotoxic, (ii) have a very low aspecific uptake, and (iii) are directed and accumulated in the cell lysosomes. ZDS-NPs are thus promising substrates for specific internalization studies and for anticancer therapy.

**Motivations and objectives:** Successful application of magnetic metal oxides NPs in the biomedical field requires NPs having not only good magnetic properties but also suitable stability and pharmacokinetic features. However, the synthesis of NPs with desired biodistribution and pharmacokinetics is still a major challenge. We focused our attention on zwitterionic coatings, in particular ZDS, which is able to strongly bind to iron ions. ZDS-coated NPs were shown to be very stable in water. At variance with polyelectrolyte coatings (e.g. polyacids, polylysine), ZDS should not adsorb proteins thanks to the absence of releasable counterions. We therefore prepared and characterized ZDS-coated iron oxide NPs and studied their interaction with proteins and how they are internalized by HepG2 cells.

**Results and discussion:** Monodisperse iron oxide nanocrystals were prepared by a solvothermal method and then coated with ZDS by two-step ligand exchange. ZDS-NPs in the cell culture medium (RPMI + 10% FBS) did not adsorb proteins and were colloidal stable for up to 24 h. Finally, we investigated the uptake of ZDS-NPs by hepatocarcinoma (HepG2) cells with increasing ZDS-NP dose (2.5-100  $\mu\text{gFe}/\text{ml}$ ). The treatment with ZDS-NPs did not affect cell viability and resulted in a very low, dose-dependent NP uptake, inferior than most reported data for the internalization of iron oxide NPs by HepG2 cells. Using fluorescently-tagged ZDS-NPs we could show that internalized NPs were sent to and accumulated in lysosomes.

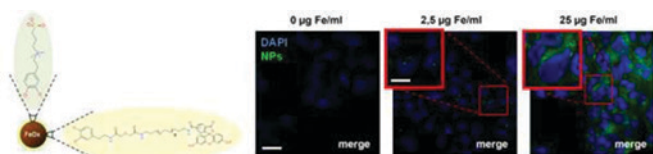


Fig. 1

#### INNOVATIVE SOL-GEL COATINGS FOR THIOL-MEDIATED CELL ADHESION

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**Concept:** Sol-gel technique has been widely used for different applications because it offers advantages such as the possibility of obtaining homogeneous hybrid materials under low temperature. Sol-gel followed by dip coating allow to deposit thin films (thickness <1  $\mu\text{m}$ ) on a wide variety of substrata, with a simple and inexpensive equipment. Sols were prepared by mixing TEOS, Ethanol, Water (H = 8) and HCl (pH2), with different amount of (3-Mercaptopropyl)trimethoxysilane (MSH), in order to obtain thiol-functionalized surfaces.

**Motivations and objectives:** Cell adhesion is a complex process that allows the binding of cells to a surface. Adhesion occurs from the interaction between some specific motifs of transmembrane proteins and the adsorbed protein layer on the surface. It is widely known that many transmembrane proteins do contain outward thiols located extracellularly, namely Exofacial Proteins Thiols (EPTs). Their ability to switch from an oxidized (-S-S-) to a reduced form (-SH) ensues from environmental conditions, is involved in many cell activation functions, and many studies have highlighted the role of EPTs for applications in different fields such as Magnetic Resonance Imaging (MRI) cell labeling, gene delivery and drug delivery. The aim of this study is to investigate the role of EPTs in cell adhesion on thiol-functionalized surfaces obtained by sol-gel dip coating technique.

**Results and discussion:** Glass surfaces coated through sol-gel dip coating process by using MSH, in combination with TEOS were characterized in terms of thickness, roughness, contact angle and density of functional

groups, and results were correlated to molar concentration of MSH. Cells behavior on thiolated surfaces demonstrated the possibility to exploit EPTs, naturally present on cell surface, as anchorage points for thiol-mediated cell adhesion. In particular the number of adherent cells increased by increasing the thiol density on the surfaces (Fig. 1). The role of EPTs as anchorage points for EPTs-mediated cell adhesion pave the way for the development of surfaces and devices for thiol-mediated cell selection on the basis of their EPTs content.

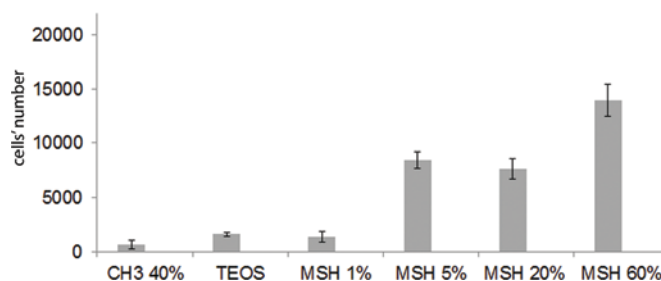


Fig. 1 - HeLa cell adhesion 30 minutes after seeding on different glass surfaces coated with MSH-based sols.

#### NANO-IMMUNO ASSAY DEVELOPMENT FOR THE DETECTION OF CANCER BIOMARKERS

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**Concept:** A promising strategy in clinical practice for cancer prevention is to perform an early non-invasive population screening. The detection and quantitative analysis of "new generation" cancer biomarkers, released and circulating in the bloodstream from tumor tissues, can be effectively exploited in primary and metastatic cancer diagnosis and prognosis and in therapeutic drug monitoring.

**Motivations and objectives:** The main goal of this work is to set-up a highly sensitive Atomic Force Microscopy (AFM)-based nano-immunoassay capable to perform the parallel analysis of different cancer biomarkers in a small sample volume and with a label-free technique. We focused here on the specific biomarker Human Epidermal Growth Factor Receptor 2 (Her2), relevant antigen found in breast, lung and gastric human cancers. For biorecognition we tested two monoclonal mouse Antibodies and a camelid Nanobody, specific for different epitopes of the extracellular domain of Her2 (ECD-Her2). Other techniques, such as standard ELISA, Fluorescence and Surface Plasmon Resonance assays, were performed for the profiling and characterization of the binders.

**Results and discussion:** We used Nanografting, a tip assisted Atomic Force Microscopy (AFM) nanolithography technique, to fabricate DNA nanoarrays. DNA nanospots created by nanografting were exploited in order to immobilize DNA-antibody conjugates that recognize specific proteins of interest. The determination of the antigen content of a biological sample was obtained from the analysis of AFM topographic profiles of the nanopatches before and after the sample incubation. This method has been previously set up to develop a nano-immunosensor for the successful detection of the malignant glioma biomarker GFAP in cell lysates. By measuring spot height variation we detected ECD-Her2 biomarker with high sensitivity (up to picomolar range); we were also able to optimize the device sensitivity by correlating the density of the DNA-antibody conjugates on the surface and their capability to bind the target. In order to characterize the binders suitable for the Nanoarray we also performed Fluorescence, ELISA and Surface Plasmon Resonance assays. As future perspectives we are exploiting DNA barcoding of our protein binders to move towards the multiplexing detection of different biomarkers, simultaneously on the same nanoarray, to increase the prognostic value of the test. In parallel we will explore the feasibility of other biomolecules (high-affinity Nanobodies, aptamers, bispecific Antibodies) to increase the sensitivity of the Nanoarray.

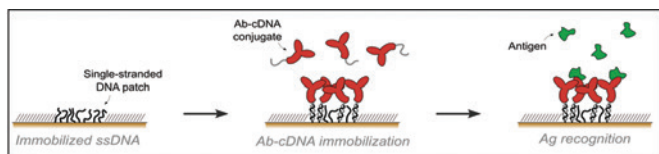


Fig. 1

### GOLD NANOPARTICLES OVER ZrO<sub>2</sub> AND CeO<sub>2</sub> SUBSTRATES TO ENHANCE THE CATALYTIC PERFORMANCE IN THE OXIDATIVE FURFURAL ESTERIFICATION PROCESS

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**Concept:** This work reports an effective and sustainable approach to produce methyl 2-furoate (2-MF) from furfural by selective oxidative esterification with methanol using size-controlled Au nanoparticles (NPs) based catalysts. Cerium dioxide (CeO<sub>2</sub>) and zirconium dioxide (ZrO<sub>2</sub>) were used as metal oxide supports; they were synthesized via a chemical precipitation method, while Au NPs were deposited onto their surface by two different techniques: i) deposition-precipitation (DP) and ii) photo-deposition. All the catalysts with Au deposited by precipitation were finally treated in air at 200 or 400°C. The main purpose was to optimize the methodology of synthesis identifying a method capable to modulate size and dispersion of the Au NPs, which represent the actual active sites controlling the catalytic performances. Results showed that Au/ZrO<sub>2</sub> catalyst (with Au deposited by DP) was the best catalyst tested in terms of high conversion and 2-MF selectivity, due to the small size of Au particles (<5 nm), opening new perspectives in the selective oxidative production of fine chemicals.

**Motivations and objectives:** In the last years, the climate changes, the negative effects of the oil prices on the global economy and the depletion of the oil resources, have focused the attention to the development of new methodologies for biomass conversion into compounds with higher added value. In this context, upgrading and valorization of C5 carbohydrates fraction coming from lignocellulosic wastes for the synthesis of valuable platform molecules, is of key relevance to diminish the dependence on fossil fuel sources. By the oxidative esterification reaction of furfural, it is possible to produce 2-MF, a compound that may widely be used in the field of flavourings and fragrances. The exceptional catalytic properties of Au NPs dispersed on metal-oxide based supports, has allowed finding a new and eco-friendly synthetic route for the oxidative esterification.

**Results and discussion:** Results were summarized in the Table below, showing the conversion and 2-MF selectivity values after 6 h of reaction for the most representative tested Au-NPs-based catalysts and as HRTEM of the most relevant Au/ZrO<sub>2</sub> sample treated at 400°C. The reaction mechanism for the furfural oxidative esterification with methanol passes through the formation of a hemiacetal intermediate. Subsequently, the hemiacetal can be oxidized directly into 2-MF, or can be converted into the corresponding 2-furaldehyde-dimethyl-acetal and then to 2-MF. Morphological characterization data of the most active catalysts suggest that having small and well dispersed Au NPs onto the metal oxide support is the key to enhance the catalytic performances, favouring the oxidation of the hemiacetal into ester, rather than the reoxidation of the acetal into the ester.

Sample	T (°C)	Conversion (%)	2-MF selectivity (%)
Au/CeO <sub>2</sub> <sup>a</sup>	200	88	8
Au/CeO <sub>2</sub> <sup>b</sup>	400	81	10
Au/CeO <sub>2</sub> <sup>c</sup>	-	84	82
Au/ZrO <sub>2</sub> <sup>a</sup>	200	63	10
Au/ZrO <sub>2</sub> <sup>b</sup>	400	99	100
Au/ZrO <sub>2</sub> <sup>c</sup>	-	57	90

<sup>a</sup> Au loading by deposition-precipitation  
<sup>b</sup> Au loading by photo-deposition

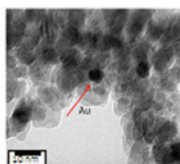


Fig. 1

### CALCAREOUS STONES IN CULTURAL HERITAGE. A FRACTAL MODEL FOR PREDICTING THERMAL CONDUCTIVITY

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**Concept:** In these days building recovery of cultural heritage is an important issue. In order to recreate thermo-hygrometric comfort, a deep study must be carried out. In these cases experimental tests, which need a great number of samples, cannot be carried out. For these reasons modeling procedure based on the reproduction of microstructure of the materials are growing into materials science branches. Recently, an intermingled fractal units (IFU) model aimed at reproducing pore size distribution of materials has been proposed. It is able to predict several properties like permeability as well as sorptivity. In this paper IFU model has been considered for predicting thermal conductivity (keff) values of calcareous stones used in cultural heritage. IFU model is based on mixing of fractal units base (Sierpinski carpets). In order to increase the simulating power of this model, during iteration process it is possible not involve all of filled square, so every iteration could have different configuration based on iterated square and solid forever square. Moreover, for settling pore volume fraction, a filled surface could be inserted. After mixing, IFU has porous microstructure very similar close to experimental one. So, IFU model must be converted in electrical pattern in which resistance are connected in series and parallel (ks thermal conductivity of solid phase; kf thermal conductivity of fluid phase). Solving the pattern it is possible to obtain thermal conductivity (keff) and to compare it with experimental value.

**Motivations and objectives:** Thermal insulation is an issue of remarkable novelty not only for modern construction, but also for cultural heritage. In Europe, the 40% of energy consumption is used for building stock. Indeed, heating and air conditioning of settings is one of the principle reasons of electrical energy usage. Moreover, it represents 36% of global CO<sub>2</sub> emissions. Europe 2020 strategy aims at reducing energy consumption of 20%. So, it is necessary to improve insulating properties of building components (especially older). The first step for recovering buildings is to know the real properties of materials. Experimental tests in lab, cannot carried out for materials from cultural heritage. Indeed, the number of samples they could be take away are very small. Modeling procedure in this moment is a very important source.

**Results and discussion:** The interpretation of the diffractogram through JCPDS database highlighted the presence of calcite as predominant phase. Other carbonate minerals were represented by ankerite and dolomite while detrital phases were proved by the presence of quartz and muscovite. For this reason ks = 3.5 W/(m·K), while kf = 0.026 W/(m·K) are considered. So, the keff average value calculated by IFU procedure is 1.27 W/(m·K) while experimental value kexp is 1.21 ± 0.06 W/(m·K). It is possible to see that calculated and experimental data are very close.

### Fe(III) 1,3,5-BENZENE TRICARBOXYLATE METAL ORGANIC FRAMEWORK

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**Concept:** The last decade has seen growing attention in the synthesis and characterization of crystalline porous metal organic frameworks (MOFs) compounds in virtue of their potential applications in gas storage, separation and catalysis. Among the different MOFs, the iron(III) 1,3,5-benzene tricarboxylate (Fe-BTC), well known as MIL-100(Fe), is one of most interesting 3D hybrid super-tetrahedral structure that displays a hierarchy of microporous (ca. 5.5 and 8.6 Å) and mesoporous (ca. 25 and 29 Å). The usually reported method for MOFs synthesis, including MIL-100(Fe), is the solvothermal one. Unfortunately, the solvothermal method imposes, already at the laboratory scale, hard reaction conditions, i.e. high temperature and pressure, use of large solvent amounts, and long synthesis times. Such reaction conditions would represent a serious drawback in the scale-up of the synthesis.

**Motivations and objectives:** In this study we propose the Liquid-Assisted Grinding (LAG) mehanosynthesis approach as an alternative route to synthesize a non-fluorinated Fe(BTC) sample with MIL-100(Fe) structure.

Through this technique, high yields can be obtained in short reaction times working under mild conditions (room temperature, ambient pressure) using small solvent amounts mounts. The  $\text{MFe}_{\text{LAG}}$  material, rapidly obtained by LAG, was characterized by XRDP, FTIR, SEM, TGA,  $\text{N}_2$  physisorption and adsorption microcalorimetry of  $\text{NH}_3$ . For comparison, the features of a commercial Fe-BTC sample (Basolite F300) were investigated as well. The adsorption performance of the obtained  $\text{MFe}_{\text{LAG}}$  sample for the removal of 4,6-dimethyldibenzothiophene (4,6-DMDBT) from 4,6DMDBT/n-heptane solutions simulating a diesel fuel was also investigated. The stringent regulations on the sulfur content of fuels make adsorption technology an interesting, environmentally-friendly alternative to the conventional catalytic hydrodesulfurization processes.

**Results and discussion:** Liquid-assisted grinding is an effective strategy for the synthesis with quantitative yields of high quality iron(III) 1,3,5-benzene tricarboxylate (Fe-BTC) MOF of predominant crystalline cubic phase with good thermal stability, high surface area and pore volume. In comparison, the structural and textural features of commercial Basolite F300 appear rather poor. Both  $\text{MFe}_{\text{LAG}}$  and the commercial sample have a quite high concentration of acid sites, as determined by ammonia adsorption calorimetry, with more pronounced heterogeneity of the sites in the case of Basolite F300. The  $\text{MFe}_{\text{LAG}}$  sample performs much better than the commercial one in the ambient temperature adsorption of 4,6-DMDBT from a simulated low-sulfur diesel fuel.

#### CATALYTIC BIOACTIVE GLASSES: CATALASE MIMETIC ACTIVITY, AN EXAMPLE

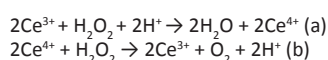
Malavasi G<sup>1,4</sup>, Nicolini V<sup>1</sup>, Gambuzzi E<sup>1,4</sup>, Menabue L<sup>1,4</sup>, Menziani MC<sup>1,4</sup>, Lusvardi G<sup>1,4</sup>, Pedone A<sup>1,4</sup>, Benedetti F<sup>2,4</sup>, Luches P<sup>3</sup>, D'Addato S<sup>2</sup>, Valeri S<sup>2,3</sup>

<sup>1</sup>Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy; <sup>2</sup>Department of Physical, Information and Mathematical Sciences, University of Modena and Reggio Emilia, Modena, Italy; <sup>3</sup>Neuroscience Institute (IN), CNR, Modena, Italy; <sup>4</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

**Concept:** The ability of a Ce-containing bioactive glasses to inhibit oxidative stress in terms of reduction of  $\text{H}_2\text{O}_2$ , by mimicking the catalase enzyme activity is demonstrated for the first time. The antioxidant properties of bioactive glasses containing  $\text{CeO}_2$  have been evaluated by following the degradation of hydrogen peroxide with time after immersion in  $\text{H}_2\text{O}_2$  aqueous solutions with different concentration. XPS, UV-Vis and magnetic measurements allowed us to determine the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio (bulk and surface) and to correlate it with the ability of the samples to show catalase mimetic activity. We have found that the bioactive glass (23.2Na<sub>2</sub>O-25.7CaO-43.4SiO<sub>2</sub>-2.4P<sub>2</sub>O<sub>5</sub>-5.3CeO<sub>2</sub>) immersed in 0.1M  $\text{H}_2\text{O}_2$  aqueous solution is able to degrade 90% of it in one week.

**Motivations and objectives:** In the field of biomaterial implantation, the so-called surgical stress response is a well-defined physiological mechanism that involves, during and after surgical procedures, the activation of inflammatory, endocrine, metabolic and immunologic mediators. Surgical stress includes the occurrence of oxidative stress, with production of reactive oxygen species ( $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ) that may overwhelm the defense systems of the organism. It has been demonstrated that the administration of antioxidants results in improved organ function, shortened convalescence, reduced morbidity occurring in the surgical stress response. In this context, biomaterials that can contrast the effects of oxidative stress and inhibit excessive reactive oxygen species generation may be a useful tool for therapies that target these medical problems. Bioactive glasses able to prevent oxidative stress after implantation would shorten the convalescence and reduce the amount of anti-inflammatory medications administered to patients. It has been shown that nanoparticles of  $\text{CeO}_2$ , are able to catalyze the decomposition of hydrogen peroxide into water and oxygen mimicking the catalase enzyme action. In this scenario we investigate the possibility to imprint catalase mimetic activity to Ce-doped bioactive glasses.

**Results and discussion:** The characterization carried out confirms that cerium is present in the two common oxidation states  $\text{Ce}^{3+}/\text{Ce}^{4+}$ , both in the bulk and on the surface. XPS analysis determined a  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio in the range 1.6-3.1. We found that all glasses are able to reduce the  $\text{H}_2\text{O}_2$  concentration. In particular, the BG\_Ce5.3 is able to degrade 31.7  $\mu\text{mol}$  of  $\text{H}_2\text{O}_2$  per min. The ability of the glasses to act as catalysts is also highlighted by the trend of  $\text{Ce}^{3+}/\text{Ce}^{4+}$  after the soaking in  $\text{H}_2\text{O}_2$  solution: the ratio shows a great variation at short time and it becomes more or less constant at longer time, suggesting a similar velocity of the two proposed reactions a) and b):



Thus, the employment of  $\text{CeO}_2$ -doped bioactive glasses could become a valid alternative to the addition of ceria nanoparticles to biomaterials.

#### GRAPHENE OXIDE AS NANOMATERIAL AND CATALYST

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**Concept:** The fine control of the structural order and of chemical functionalities in exfoliated and intercalated graphene oxide (GO), allows not only to achieve nanomaterials but also highly efficient and eco-friendly catalysts. In particular, intercalated GO can be relevant for control of antimicrobial release while exfoliated and functionalized GO can be relevant as fillers of polymers and as catalysts of many different (even diastereoselective) reactions.

**Motivations and objectives:** Particularly relevant is the dual role of exfoliated GO in thermosets, mainly in epoxide resins. In fact, the nanofiller not only improves physical properties but also catalyzes the crosslinking reaction, allowing completion of the curing reactions at largely lower temperatures.

**Results and discussion:** The first part of the contribution will describe preparation procedures and structural characterizations of graphite oxide, chemically reduced graphite oxide and exfoliated graphite oxide (often referred as graphene oxide, GO), which are the generally used as precursors for bulk production of graphene materials. The main emphasis will be given to the crystalline order along different crystal directions. Preparation and characterization of Graphite Oxide Intercalation Compounds (GOIC) will be also described. The catalytic activity of high-surface-area graphites and graphene oxide toward many organic reactions will be discussed. The second part of the contribution will be devoted to polymer composites: polymeric aerogels with large amount of graphene, (which can be used as masterbatches for polymer processing); the relevant influence of edge-carboxylation of graphite based materials on mechanical and electrical properties of polymer composites; the technologically relevant catalytic activity of graphene nanofillers on the curing (crosslinking) reactions of thermoset resins.

#### DEVELOPMENT AND MODELING OF HIGH PERFORMANCE ABLATIVE MATERIALS

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**Concept:** EPDM (Ethylene Propylene Diene Monomer) rubber reinforced with aramid fibers (or pulp) and nanosilica represents the state of the art of heat shielding material (EHSM) for the thermal protection of the structural case of Solid Rocket Motors (SRM), which serves as a pressure vessel for the combustion gases. SRMs must be protected against high temperature (in excess of 2800°C) and pressures (as high as 60 bar). An ablative liner made of EHSMs is placed between the SRM case made of metals or carbon/epoxy filament-wound composites and the solid fuel grain. New generation organic fibers can be used to replace aramid; then, in addition to the experimental testing, a numerical model of the degradation process of the produced EHSMs can be used to describe the ablation phenomena.

**Motivations and objectives:** In this work, Kynol fibers, i.e. a phenolic based reinforcement, were evaluated as reinforcement for EPDM in order to obtain a new class of ablatives and a comparison with aramid counterpart was carried out in terms of thermal properties. Moreover the modelling of the ablation process has also been considered thus to introduce a simple approach to validate the oxy-acetylene torch test results and to account for the in depth temperature profiles which are of extreme importance to size the thickness of insulation liners.

**Results and discussion:** Oxy-acetylene torch tests (heat flux of 500 W/cm<sup>2</sup> for 40 s in presence of a neutral hyperthermal environment) evidenced that EPDM/Kynol materials produced a flat char with the smaller dimensional change and the higher adhesion with the virgin material. On the other hand, the state of the art formulation i.e., aramid pulp, produced a char with a higher degree of expansion than Kynol and some macro fractures

were present on the burnt surface; however, EPDM/aramid exhibited the higher insulation properties. A 1D model was developed in order to describe the insulation capability of these materials taking into account two phenomena: 1) the reversible and irreversible thermal expansion of the virgin and charred material; 2) the coking process (char densification) due to the percolation of pyrolysis gases through porous carbonaceous skin followed by carbon deposition. The numerical results evidenced how the combination of the two processes – reversible and irreversible thermal expansion of the virgin and charred material coupled with the char densification – allowed the proper description of the in-depth temperature profiles and of the char densities.

#### PRELIMINARY STUDY ON DISSIMILAR Al/STEEL FRICTION STIR WELDING LAP JOINTS FOR AUTOMOTIVE APPLICATIONS

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**Concept:** The weldability by FSW of DC05 steel and AA6016 aluminum sheets have been evaluated. The tests were carried out with either constant tool displacement or vertical force and with varying tool rotation and feed rate. This preliminary study shows that DC05 steel and AA6016 aluminum sheets can be welded together if proper process parameters are used during the joining process. Particularly, maintaining constant the vertical force during the FSW appears a better solution than maintaining constant the tool displacement in obtaining sound FSW joints. In fact, a larger weldability of the DC05 steel and AA6016 aluminum sheets occur, and hence more variable process parameters can be used. Large defects can occur within the FSW joints due to an incomplete stirring with the two metals due to insufficient heat input and material mixing in the stirring area.

**Motivations and objectives:** Transportation industries, especially the automotive industry, continuously push for technical solutions that allow to reduce vehicle weight through the use of light metal alloys, as aluminum alloys. However, steels are still the main alloys used in a vehicle, due to their good properties of crash resistance, high formability, and weldability. A widespread usage of aluminum alloys in automotive industry is conditioned by the welding assembling of this metal with steel grades. Fusion welding of dissimilar steel to aluminum joints results in complex weld pool shapes, segregation, inclusions and porosities. Additionally, the low solubility of Fe in Al results in the formation of extremely brittle intermetallic layers. For these reasons, Friction Stir Welding could represent an attractive solution to limit the occurrence of these defects. A feasibility study for of FSW was carried out by evaluating the joints integrity evaluation of macroscopic defects, incomplete welding penetration, cracks. Vickers microhardness measurements were also performed on the FSW joints.

**Results and discussion:** Three different conditions can be obtained from the experimental tests: i) incomplete welding; ii) complete welding penetration with internal defects; iii) complete welding penetration without defects. In the first case, the welding conditions were not properly set to obtain a sound joint and the stirring of steel and aluminum was insufficient due to the poor softening induced by the welding tool.



Fig. 1 - Incomplete welding penetration (1750 rpm, 400 mm/min) and sound joint (2500 rpm, 200 mm/min).

#### THE FIRE ASSAY METHOD: GOLD NANO 3D SCAFFOLD FROM ANCIENT TIMES

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**Concept:** The fire assay process has been well known since ancient times as a method for measuring the gold content of precious alloys. However,

very little information is available about the microstructural evolution of the specimen undergoing the different steps of the process. FIB, TEM and SAED analyses well describe the evolution of the micro and nanostructure that generate the shape and color changing of the specimen, allowing for a better comprehension of the procedure.

**Motivations and objectives:** The fire assay process is still the most accurate and precise method for measuring the gold content in gold alloys. Nevertheless, limited knowledge is available about the microstructural evolution of the specimen undergoing the different steps of the process. Focused Ion Beam and Scanning/Transmission Electron microscopy have been applied to observe the change in microstructure of the samples undergoing the fire assay process. The performed observations reveal that the microstructure of the specimen is more complex than expected. Before the parting stage, the specimen is not a perfect gold-silver binary alloy but contains also copper-silver oxides and other residual compounds. The parting stage appears to be a dealloying process leading to a nanoporous gold nanostructure. What observed after partition explains the evolution of the shape and colour of the specimen and may allow for a better comprehension of the procedure and an improvement in the method.

**Results and discussion:** What reported in this work clarifies why all the stages of the procedure must be performed in order to obtain good results. Particularly, the action of lead as a scavenger of base metals and the logic of adding silver in precise amounts during the cupellation stage in order to have the nanoporous gold are understood. Finally, the microstructural analyses reveal the reason why it is necessary to make use of all the well-known working methods in the various phases of the procedure. The cupellation process appears to be a dealloying process which can be improved thanks to the knowledge of the mechanisms of nanoporosity evolution and nanoporous gold generation, in particular, in order to avoid the cracks inside the cornet which may be responsible for loosing small pieces of material and producing

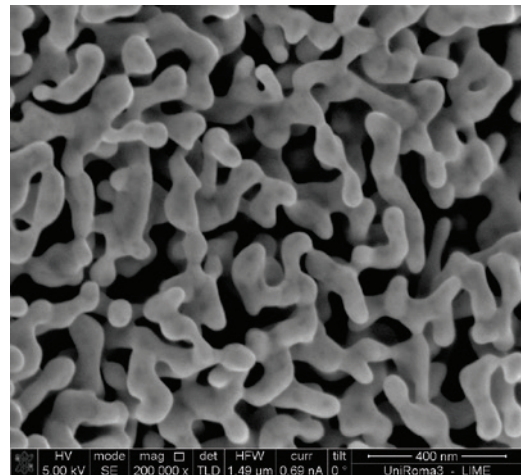


Fig. 1 - Detail of the cornet microstructure after the partition process. A nanoporous morphology characterizes the whole specimen.

errors in the gold content measurement. Therefore, the analysts who perform the fire assay test daily can better understand what they usually do and improve the procedure further.

#### INDUCTION WELDING OF THERMOPLASTIC MATRIX COMPOSITES AND HYBRID WELDING OF THERMOSETTING MATRIX COMPOSITES

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**Concept:** In this work, modeling and implementation of continuous induction welding devoted to join Poly(p-phenylene sulfide) (PPS) and Poly(ether-ether-ketone) (PEEK) carbon composites was carried out. The experimental

activities were extended to the welding of carbon reinforced epoxy matrix composites, cured using as a last ply a thermoplastic film. The resulting hybrid joint was characterized by properties depending both on the adhesion between the last thermoplastic ply at joint interface to the epoxy matrix and on the welding processing conditions. A finite element (FE) model coupling electromagnetic and temperature equations was also applied to the prediction of temperature distribution and the optimization of processing parameters.

**Motivations and objectives:** Thermoplastic matrix composites are characterized by several advantages that make them a potential substitute of thermosetting matrix composites in aeronautic applications. Among other advantages, joining by welding provides a faster assembly route for complex parts in comparison with adhesion bonding, commonly used with thermosetting composites. Among welding technologies developed at the laboratory level in the last twenty years, induction welding is finding a renewed interest since it can provide adequate mechanical properties, such as high shear, fatigue and peeling strength of joints, and several processing advantages, such as high efficiency and repeatability together with an elevated Technological Readiness Level (TRL) close to industrial.

**Results and discussion:** The finite element analysis of the process has been able to optimize the process parameters such as electrical power applied to the coil, velocity of the welding head and cooling conditions at the upper surface of the joints. The FE model has been validated comparing the experimental temperature, measured at the joint interface during a welding process, with the model. In Figure 1 a comparison of the numerical and experimental temperatures during a dynamic welding experiment at the joint interface of two PEEK/carbon laminates is reported. A good agreement is observed until a faster cooling is caused by the contact of the joining part with a cooling cylinder, not considered in the model.

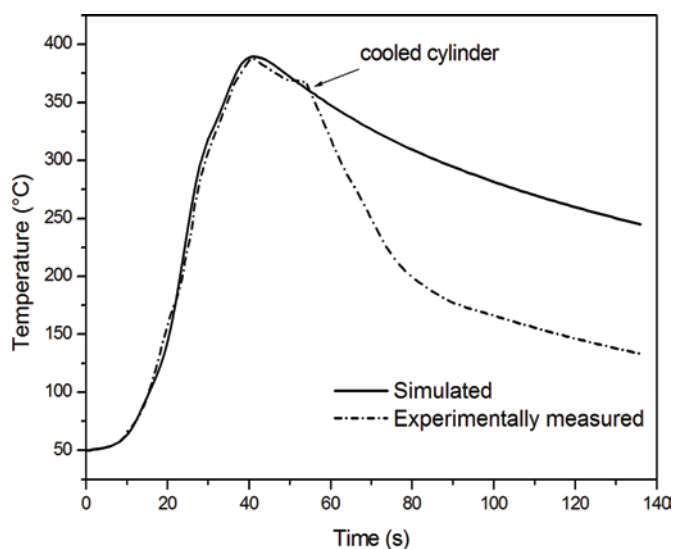


Fig. 1 - Comparison of the numerical and experimental temperatures during a dynamic welding experiment at the joint interface of two PEEK/carbon laminates.

#### HIGH SURFACE AREA CNTs BY CCVD ON CoMoMg CATALYSTS

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**Concept:** High surface area Carbon Nanotubes (CNTs) are obtained by Catalytic Chemical Vapor Deposition (CCVD) of methane on Cobalt-Molybdenum-Magnesium (CoMoMg) catalysts. Three kinds of catalyst preparation methods are investigated (Sol gel, Wet Impregnation and Wetness impregnation) to compare produced CNTs in terms of yield and morphology. In Sol Gel method

metallic precursors ( $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ ) are mixed with deionized water and citric acid and the solution is foamed at 120°C. In Wet Impregnation, MgO support is soaked with a  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$  solution and then dried at 120°C. In Wetness impregnation, MgO support is impregnated dropwise with  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ -solution, and after drying, with a further  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ -solution. The weight of the components is determined in order to have molar ratios  $\text{Mo}/\text{Co} = 30$ ,  $\text{Mo}/\text{Mg} = 3$ . All the catalysts are calcinated in air at 750°C for 5 hours. CNT synthesis is carried out using  $\text{CH}_4$  ( $\Phi_{\text{CH}_4} = 550$  sccm) as carbon source for 30 min, after a heating in He atmosphere ( $\Phi_{\text{He}} = 500$  sccm). Catalyst structure and CNT morphology, varying catalyst preparation method, are investigated by means of X-Ray analysis, Scanning Electron Microscopy, BET, Thermogravimetric analysis and Raman spectroscopy.

**Motivations and objectives:** CNTs raise considerable interest in research world because their possible applications in many fields such as hydrogen storage, electromechanical actuators and field emission display. For these applications, CNTs are required to possess a high surface area (SA). Until today, most of the CNTs reported in literature generally have a SA in the range of 100-300  $\text{m}^2/\text{g}$ . In order to improve the properties of CNTs, post-reaction treatments are usually applied. Among the used methods, modification via KOH activation appears to be the favorite route to improve the CNTs' surface area. In this work, high surface area CNTs are obtained directly by synthesis, without resorting to subsequent treatments after reaction.

**Results and discussion:** Using different catalyst preparation, obtained CNTs (SG-CNTs, W-CNTs, WN-CNTs: CNTs synthesized respectively on Sol Gel, Wet and Wetness impregnation catalysts) show a sponge-like structure (Fig. 1), in which CNT bundles are tightly interconnected by means of catalyst's particles that represent the nodes of a highly porous structure. The surface area of the three samples is higher than the ones reported in literature (Tab. I), especially CNTs obtained on catalyst prepared by sol gel method report, in addition to a good crystallinity ( $I_G/I_D = 0.86$ ), the highest surface area of 650  $\text{m}^2/\text{g}$ . These results make the obtained products interesting for different applications.

TABLE I - Surface area (SA) of obtained CNTs

Sample	SA ( $\text{m}^2/\text{g}$ )
SG-CNTs	650
W-CNTs	460
WN-CNTs	400

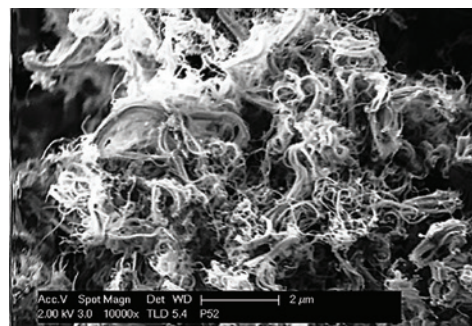


Fig. 1 - Sponge-like structure of obtained CNTs.

#### CHITOSAN NANOPARTICLES FOR THE CONTROLLED DELIVERY OF ANTIMICROBIAL PEPTIDES (AMPs): A VERSATILE TOOL FOR THE DEVELOPMENT OF NEW THERAPEUTICS AGAINST MICROBIAL INFECTIONS

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**Concept:** With the dramatic rise in antibiotic resistance, novel antimicrobials are urgently needed. Antimicrobial peptides (AMPs), an important compo-

ment of the innate immune defense secreted by numerous living organisms, represent a novel class of antibiotics against a range of infectious bacteria, including multi-resistant isolates. Despite impressive antimicrobial activity, the therapeutic potential of these peptides is currently limited, due to their poor stability in biological fluids and their potential toxicity. A solution for an efficient and safe use of AMPs as therapeutic agents is to develop drug delivery systems for their controlled and targeted release.

**Motivations and objectives:** Polymeric nanoparticles (NPs) offer various perspectives for the administration of conventional and nonconventional drugs (e.g. peptides): they allow specific and controlled release of therapeutic agents, tuned pharmacokinetics profiles and greatly preserve the drug from early degradation under physiological conditions. In the present study, the development of new therapeutics against microbial infections was addressed by the formulation of chitosan-based nanoparticles loaded with AMPs, with the aim to improve their stability, reduce their systemic toxicity and enhance their therapeutic effects. The strategy undertaken will be presented and discussed with particular reference to a) the choice of Chitosan as of polymer matrix, b) the development of NPs loaded with model peptide Renin substrate I, sharing physical-chemical features with selected AMPs and c) the preparation and characterization of chitosan based NPs loaded with the antimicrobial peptide Temporin 1-b.

**Results and discussion:** Chitosan-based nanoparticles prepared by ionotropic gelation in presence of cationic peptides (Renin substrate I or Temporin 1-b) allowed for the obtainment of "core-shell" NPs with tuneable linear release rates, which resulted to be mainly affected by the NPs radius and peptide concentration. The intrinsic antimicrobial activity of Chitosan ensured a "burst" effect, which is maintained by the gradual release of the Temporin (T-b1). The developed nanoparticles evidenced a sustained action against *S. epidermidis* for at least 4 days, with almost 4-log reduction of the number of viable bacteria compared to plain chitosan nanoparticles and 6-log reduction compared to plain T-1b. Furthermore, the NPs showed full in vitro cytocompatibility toward murine fibroblasts, highlighting its role in reducing the toxicity of the peptide towards mammalian cells. The obtained results support the suitability of the prepared nanosystems for the administration of several AMPs of therapeutic interest and other synthetic AMPs with analogous physical characteristics.

#### ADVANCED SYNCHROTRON RADIATION AND NEUTRON SCATTERING TECHNIQUES FOR MICROSTRUCTURAL CHARACTERIZATION IN INDUSTRIAL RESEARCH

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**Concept:** The rapid development of new materials and their application in an extremely wide variety of research and technological fields has led to the request of increasingly sophisticated characterization methods. In particular residual stress measurements by X-ray synchrotron radiation and neutron diffraction, small angle scattering of these two types of radiation and 3D imaging techniques with spatial resolution at the micron or even sub-micron scale, like micro- and nano-computerized tomography, have gained a great relevance in recent years. Experimental beamlines are available to this end in several European countries. We mention only the Italian one, namely Elettra in Trieste and the most powerful one, ESRF in Grenoble (France).

**Motivations and objectives:** Residual stresses are autobalancing stresses existing in a free body not submitted to any external surface force. Several manufacturing processes and thermal and mechanical treatments leave residual stresses within the components. In alternative to more conventional methods to determine residual stresses, the Bragg diffraction of X-rays and neutrons can be used to determine in non-destructive way the residual elastic strains, and by knowing the elastic constants of the material and by using the elasticity equations, it is possible to obtain the elastic residual stresses. Small Angle Scattering of neutrons or X-rays allow the determination of structural features, such as the volume fraction, specific surface and size distribution of inhomogeneities imbedded in a matrix, in a huge variety of materials of industrial interest. These non-destructive techniques are complementary to Transmission Electron Microscopy. The X-ray or neutron microtomography is similar to conventional Computed Tomography employed in Medicine, but with much higher spatial resolution reaching values below the micron. These techniques allow to obtain a 3D imaging of the investigated samples.

**Results and discussion:** At first some results are presented concerning the determination of residual stresses in a material for the first wall of a fusion reactor submitted to thermal fatigue, which result in good agreement with theoretical predictions. Then results are presented of residual stresses determined in components consisting of metal matrix composites, of interest either for the aeronautical or for the automotive industry, and in a welded plate of an Al alloy delivered by ESA and used in space research. Results of applications of Small Angle Scattering are presented related to the microstructure investigation of precipitation in Al-Li and Mg-Y-Nd alloys and of the creep damage in AISI 304 stainless steel. Finally the results of imaging are presented, obtained by microtomography, in the study of fracture of Metal Matrix Composites, in sintering of metallic powders and 3D structure of graded Al foams for multifunctional aerospace applications. All the presented results are discussed and very often compared to theoretical predictions.

#### RANDOM LASING FROM DYE-DOPED POLYMER FILMS FILLED WITH DIATOM FRUSTULES

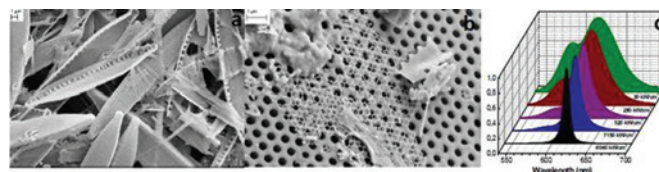
Lamastra FR<sup>1,7</sup>, De Angelis R<sup>1,2</sup>, Antonucci A<sup>3,4</sup>, Salvatori D<sup>2</sup>, Proposito P<sup>1,2</sup>, Casalboni M<sup>1,2</sup>, Congesti R<sup>4</sup>, Melino S<sup>5</sup>, Nanni F<sup>1,6</sup>

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**Concept:** Random lasers consisting of rhodamine B (RhB)-doped polymethylmethacrylate (PMMA) films filled with diatom silica shells (frustules) were prepared by solvent casting. Two different kinds of frustules were used, the first represented by diatomite (DE), fossil material composed by a mixture of frustules from different diatom species; the second was composed by diatom frustules from freshwater biofilm, a more homogeneous biosilica, dominated by one frustule type (Fig. 1a, b). Chemical properties, morphology and photoluminescence (PL) of both types of frustules were investigated by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Spectral Analysis (SA) using Confocal Laser Scanning Microscopy (CLSM), respectively. Random laser experiments were carried out on dye-doped polymer films loaded with DE or frustules from biofilms.

**Motivations and objectives:** Diatoms are photosynthetic microorganisms colonising every aquatic environment. Diatom frustules exhibit unique micro- and nano-porous architectures, which contribute to high surface area. Frustules display efficient photoluminescence within the visible spectrum, light harvesting abilities and they act as photonic crystals. Moreover, their composition can be chemically modified or biologically functionalized with antibodies. Given these properties, frustules have been explored for application in devices such as optical gas sensor platforms, photoanodes for dye sensitised solar cells and biosensors. Given the ability of frustules of multiple scattering and localization of light, we explored their use as scatterers in random lasers. A random laser is a system formed by a random assembly of elastic scatterers dispersed into an optical gain medium. The multiple scattering of photons replaces the standard optical cavity of traditional lasers.

**Results and discussion:** PL of frustules from biofilm was higher with respect to DE due to superficial silanol groups, that were not detected in DE. An incoherent random lasing from RhB-doped PMMA films filled with DE or biofilm frustules was observed (Fig. 1c). The laser threshold depends on the kind of frustule and diminishes at increasing frustule content.



**Fig. 1** - SEM micrographs showing the porous architecture of biofilm frustules (a) and DE (b). Normalised PL spectrum at different excitation power density of RhB-doped PMMA film filled with 20 wt% of DE (c).

### SMART COATING FOR CULTURAL HERITAGE: PHOTOCATALYTIC SELF-CLEANING BY TiO<sub>2</sub> BASIC SOLS

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**Concept:** The basic nanocrystalline TiO<sub>2</sub> by sol-gel processes is an easy way to obtain photocatalytic de-soiling coatings is promising for applications in the field of Cultural Heritage. A basic sol was proposed for carbonatic stones that should not be treated with acidic coatings. Different types of limestone used in historic buildings were used as substrates. The compatibility of the coatings was examined according to the UNI-Normal protocols by measuring the water absorption by capillarity and colorimetric parameters. Photocatalytic oxidation of methyl orange (MeO) and methylene blue (MB) was taken as indicator of the activity of nano-TiO<sub>2</sub> sols and coatings.

**Motivations and objectives:** The main forms of deterioration on the stone facades are related to the accumulation of pollutants and to soiling processes, with the development of black crusts and other decay forms. Photocatalysis is an oxidation process that can be used for the decomposition of various environmental pollutants in both gaseous and liquid phases. Titanium dioxide is the most widely studied and the photoactive nanocrystalline titania obtained by sol-gel process is a promising de-soiling coating material. The objective is the optimization of a new self-cleaning coating based on TiO<sub>2</sub> nanoparticles obtained by sol-gel in a basic environment, to be used for carbonatic stones.

**Results and discussion:** XRD and Raman measurements confirm the crystalline nature of titania in anatase form with negligible brookite. The Raman peak positions and FWHM suggest anatase nanocrystals with 5-10 nm size. SEM-EDS shows a penetration depth of a few microns and surface distribution fairly homogeneous. A fast photocatalytic activity was measured for both TiO<sub>2</sub> sol and coatings. The self-cleaning TiO<sub>2</sub>-based basic treatment does not introduce colorimetric changes compared to the untreated limestone and does not alter the properties of the stone as determined by measurements of the water capillarity absorption.

Support from MAECI (project "NANO4HER, Nanotechnology at the service of cultural heritage preservation", Italy-Israel Scientific and Technological Cooperation) is gratefully acknowledged.

### MECHANISM AND KINETICS OF ELECTROCHEMICAL PROCESSES BASED ON ELECTROCATALYSIS

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**Concept:** This work deals with the study of the electrochemical process of water oxidation catalyzed by IrO<sub>x</sub>. The main results are associated to the understanding of the changes of charge state, local geometric and electronic environment, which lead to a better comprehension of the mechanistic and kinetic aspects of the entire process. Combination of electrochemistry and X ray Absorption Spectroscopy (XAS) allowed performing in situ and in operando measurements different electrochemical conditions. XAS spectra were collected at the European Synchrotron radiation Facility (ESRF, Grenoble, France) at the Ir- L<sub>III</sub> edge. XANES (X ray Absorption Near Edge Spectroscopy) evidenced that Ir assumes at least three oxidation states during the process, thus it was possible to draw important conclusions linked to the catalytic cycle. Dispersive-XAS technique allowed to study the kinetics of the process which showed a diffusion control. Furthermore, EXAFS (Extended X-ray Absorption Fine Structure) analysis proved the flexibility of the material in accommodating different oxidation states. Finally, in a recent experiment we investigated photo-anodes, made of a semiconductor domain (Fe<sub>2</sub>O<sub>3</sub>) and an electrocatalytic domain (IrO<sub>x</sub>) in order to study the role of the electrocatalyst when coupled to a semiconductor for light-driven electrochemical processes.

**Motivations and objectives:** The water splitting process, which plays a key role in the energy and environment fields, is catalyzed by materials consisting of iridium oxide IrO<sub>x</sub>. The catalytic mechanism through which they act has not yet been clarified. The purpose of this work is to shed light on the mechanisms and kinetics that govern this electrochemical phenomenon in order to understand the best conditions for the occurring process.

**Results and discussion:** This work demonstrated that during the reaction Ir is present both in the Ir(III) and Ir(V) oxidation states. This represent the first experimental evidence concerning the turnover mechanism in which IrO<sub>2</sub> acts as an electrocatalyst for the water splitting reaction. The figure shows a model for Ir oxidation states in the considered potential window up to the water oxidation conditions as derived by XANES spectra fittings.

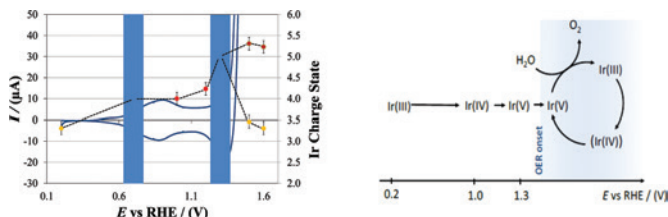


Fig. 1

### ENTIRE PHOTOCATALYTIC TILES (60 × 60 CM) EVALUATION IN NO<sub>x</sub> DEGRADATION IN A CONTINUOUS BENCH-SCALE REACTOR

Stucchi M<sup>1,2</sup>, Bianchi CL<sup>1,2</sup>, Pirola C<sup>1,2</sup>, Vitali S<sup>1</sup>, Capucci V<sup>3</sup>

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**Concept:** Pigmentary and micrometric commercial TiO<sub>2</sub> was successfully deposited on porcelain grès tiles, which were tested on the NO<sub>x</sub> photodegradation, showing a very good photocatalytic activity; the reactor structure allows to test tiles of size 60 × 60 cm directly, simulating in a very realistic way their ability to make better air quality. In particular, we show a reproducible way to test material in industrial scale and not just in laboratory scale. The TiO<sub>2</sub> powders are commercial and micrometric, regardless of which there are no papers in literature. As well as to demonstrate that micrometric TiO<sub>2</sub> can be used in photocatalysis, it is important to underline that it is less dangerous for health than the nanopowders, it is easier to handle and, not less important, it is absolutely cheaper.

**Motivations and objectives:** Nowadays it is so important to find new strategies to clean the environment and the possibility to reduce the greenhouse gases emissions is increasingly in demand; NO<sub>x</sub> in particular are strictly monitored all over the world. TiO<sub>2</sub> photocatalysis is a promising technique to break down pollutants and it is possible to directly use it on building materials: however, find a serious and reproducible way to test them and confirm their photo-efficiency would be significant. Although a lot of different reactors have already been developed, they work with small samples and the conditions are often very far from the reality. In this work a reactor able to test photocatalytic building materials in large size is presented, working both under artificial and solar light: the porcelain grès tiles was provided by GranitiFiandre, and they are industrially prepared making use of a particular commercial micro-sized TiO<sub>2</sub>, according with the fact that TiO<sub>2</sub> nanoparticles can cause negative health effects.

**Results and discussion:** First the photo-activity of these building materials has been demonstrated, showing off their real power to degrade nitrogen oxides. No less important, however, is the creation of a system in which is possible to work with samples of tiles with a size of 3600 cm<sup>2</sup>, coming very close to reality. In particular, we made a comparison of different source of light, working both under UV and solar, and we performed degradation kinetics of different duration, from a few hours to days. Therefore a complete picture of data is proposed, with an accurate description of the phenomenon.

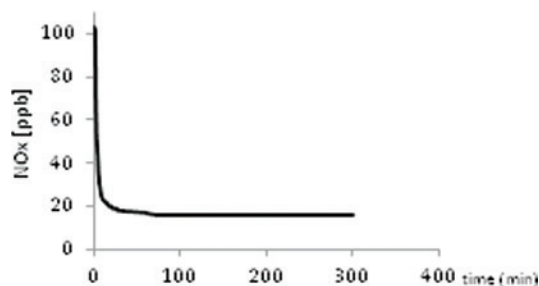


Fig. 1



### PHOTODEGRADATION OF PHENOL WITH COMMERCIAL TiO<sub>2</sub> IN POWDER OR COATED ON PORCELAIN GRÈS TILES

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**Concept:** Titanium dioxide (TiO<sub>2</sub>) catalyst is often used as nano-sized particles exhibit the best photoactivity. The main target of this work is the possible substitution of nano-TiO<sub>2</sub> with a micro-sized system active in the photodegradation of the phenol in water phase; moreover, micro-TiO<sub>2</sub> has been tested in both powder form and coated on commercially available porcelain grès tile. Conversion and mineralization degree have been checked for six hours by analytical analysis to investigate both the reaction pathway and the nature of intermediates and end-products. The nano-sized powder (P25) exhibits the best results mainly in the first reaction time, but interesting results have been achieved by the micro-sized sample both in powder form and as coating material, allowing an easier separation between the depolluted water and the semiconductor at the end of the reaction.

**Motivations and objectives:** Phenol is extremely toxic for both humans and environment, therefore its removal from wastewater represents a serious problem. It has been extensively investigated, considering its high chemical stability and toxicity at low concentrations too. Almost all recent literature is focused on the use of nano-sized photocatalytic powders to obtain high mineralization values, even if some recent studies have underlined the dangerous effects on human health correlated with the use of nano-sized materials. Therefore, the main target of the present work is the comparison of the performances of two commercial TiO<sub>2</sub> powdered catalysts: a nano-sized powder (Evonik P25) and a micro-sized powder (Kronos 1077). This latter was also industrially coated on the surface of a ceramic tile and its photoefficiency was investigated as well. The nature of intermediates and/or end-products has been also carried out employing FTIR spectroscopy.

**Results and discussion:** Kinetic studies were performed using two different reactor set-up as described in and three different phenol concentrations. A strong influence of the pollutant concentration on the final conversions is evident in all cases, besides a good performance of the micro-sized sample. FTIR data indicate the break-up of the phenyl ring leading to aliphatic short chain end-products. Interesting results were also achieved by the photocatalytic tiles obtaining a 50% of phenol degradation with an initial concentration of 15 ppm thus opening the way to possible industrial use of these material in water decontamination.

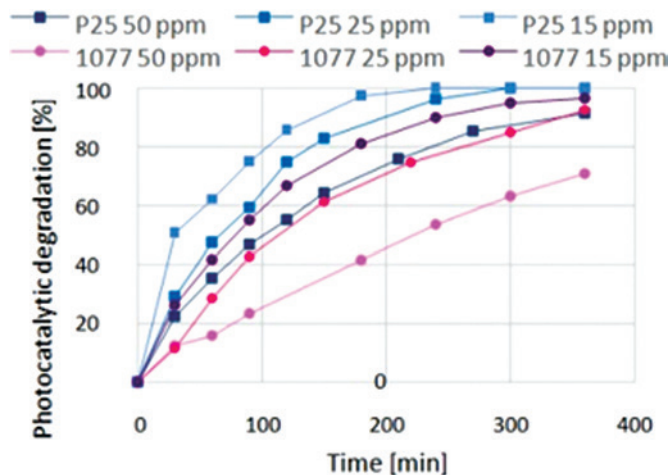


Fig. 1

### SUPRAMOLECULAR CHAIN-LIKE ASSEMBLIES OF Fe<sub>4</sub> SINGLE-MOLECULE MAGNETS AND Ru<sub>2</sub> PADDLEWHEELS

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**Concept:** The deliberate organization of Single-Molecule Magnets (SMMs) into supramolecular structures can enhance their functionality, and the introduction of redox-responsive linkers further suggests the possibility to use electron transfer to tune intermolecular interaction in arrays of SMMs.

**Motivations and objectives:** SMMs provide nanoscale, chemically-tunable units displaying magnetic hysteresis and quantum magnetism at the molecular level. For this reason they have been proposed as components of molecular spintronic devices or as qubits for quantum computation. Weak coupling between two or more SMMs can be used to enhance their functionality: on one side, each SMM can act as a bias on its neighbour(s), generating a better memory effect; on the other side, entanglement between quantum states is an important resource for quantum information processing.

**Results and discussion:** The fully-controlled assembly of the tetrairon(III) SMM [Fe<sub>4</sub>(pPy)<sub>2</sub>(dpm)<sub>6</sub>] (1) with an S = 5 ground state (H<sub>3</sub>pPy = tripodal ligand bearing a 4-pyridyl substituent and Hdpm = dipivaloylmethane), into one-dimensional supramolecular structures held together by coordination bonds has been achieved. 1 acts as a ditopic synthon and reacts with the paddlewheel dimers [Ru<sub>2</sub>(OAc)<sub>4</sub>(MeOH)<sub>2</sub>] and [Ru<sub>2</sub>(OAc)<sub>4</sub>(THF)<sub>2</sub>(BF<sub>4</sub>)<sub>x</sub>] to give the supramolecular chains [Fe<sub>4</sub>(pPy)<sub>2</sub>(dpm)<sub>6</sub>]<sub>n</sub>[Ru<sub>2</sub>(OAc)<sub>4</sub>]<sub>m</sub>(BF<sub>4</sub>)<sub>x</sub> with x = 0 (2a) or 1 (2b), respectively. Crystal structures of 1-2EtOH and 2b (Fig. 1), together with preliminary data of 2a, have been obtained. Polymers 2a and 2b differ in the electron count on the diruthenium bridges, which are both paramagnetic with s = 1 and 3/2, respectively. However, at low temperature, the diruthenium(II,II) paddlewheels in 2a behave as effective s<sub>eff</sub> = 0 spins and act as magnetic insulators. By contrast, the mixed-valent (II,III) bridges (s<sub>eff</sub> = 1/2) in 2b introduce weak intrachain exchange bias with concomitant enhancement of the remnant magnetization.

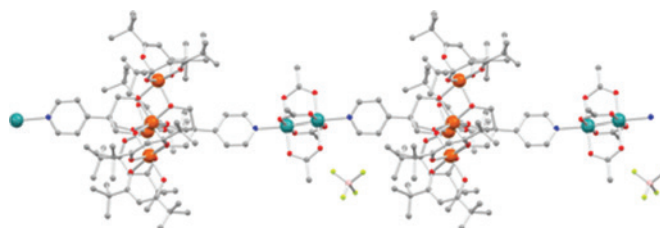


Fig. 1 - Molecular structure of 2b viewed along **b** showing two repeating units running along the **c** axis; colour code: Ru = sky blue, Fe = orange, F = yellow, O = red, N = blue, C = grey, B = pink, H omitted.

### CNTs ASSISTED SYNTHESIS OF NANOSIZED SAPO-34

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**Concept:** We propose a new approach for the synthesis of an engineered hybrid material, made of SAPO-34 and carbon nanotubes (CNTs), which act as nanoreactors where nanozeolites grow. Carbon nanotubes (CNTs) were synthesized and then oxidized to ensure the presence of appropriate functional groups. Bohem titration was carried out in order to estimate the concentration of acid sites on CNTs after functionalization with HNO<sub>3</sub> vapours, and then to dosing the exact amount of templating agent (TEAOH) that needs to be adsorbed on their surface for the synthesis of the hybrid. Therefore, a stoichiometric amount of TEOH is adsorbed, so that TEA<sup>+</sup> ions

are not free in solution, as well as occurs in the traditional hydrothermal synthesis of SAPO-34, but well anchored on the surface of CNTs, in a fan-shaped configuration. SAPO-34/CNTs hybrid was prepared by hydrothermal synthesis from a solution of precursors. All the samples synthesized were systematically characterized by means of X-Ray Diffractometry (XRD), TGA and SEM.

**Motivations and objectives:** In recent years, the interest of many researchers focused on the reduction of the zeolite crystals size and on its emerging applications both in catalysis than in separation processes. The literature data report several methods for the synthesis of SAPO-34. Some of them show a considerable heterogeneity of the particle size, while in others there is a considerable loss in the crystallinity of the final product. The aim of this work is to develop a novel method for the synthesis of nano-sized SAPO-34 based on the direct grow of zeolite on CNTs, which will act as nanoreactors. Due to the particular configuration assumed by the templating agent upon interaction with the CNTs, the available space where the formation reaction of zeolites can take place is very small, and molecules of nanometric dimensions can be obtained.

**Results and discussion:** Electron microscopy investigations showed the formation of SAPO-34 nanocrystals embedded in a network of carbon nanotubes (Fig. 1). XRD analysis confirmed the purity of the zeolite. Optimizations of reaction time and TGA adsorption conditions are under evaluation.

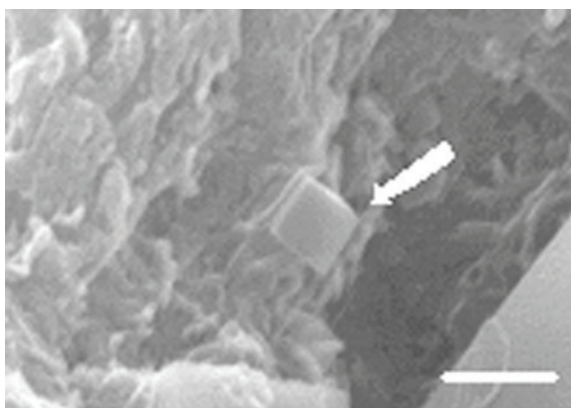


Fig. 1 - SEM image of the synthesized sample.

#### MAGNETIC HYPERThERMIa IN GOLD-IRON OXIDE DIMERIC NANOSTRUCTURES

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**Concept:** Gold-Iron oxides heterodimers and hollow iron oxides nanoparticles were successfully synthesized with two different synthetic techniques and their morphology and magnetic properties were characterized using TEM and AGFM (alternating gradient force magnetometer). Hyperthermia measurements were performed and SAR (Specific Absorption Rate) values were determined.

**Motivations and objectives:** Both magnetic and gold nanoparticles have found great interest in the applied research in the last decades, especially in the biomedical field. Gold - Iron oxides nanocomposites allow the combination of the properties of these materials (e.g. magnetic and plasmonic). Even if some studies on these structures are already present in literature a thorough investigation of their hyperthermic properties is still lacking. The aim of the work is to obtain, in a reproducible way, Au-Iron oxide heterodimers, with tunable magnetic domain, and hollow magnetic nanostructures by Au etching, and comparatively study their hyperthermic behaviour.

**Results and discussion:** Gold-Iron oxide heterodimers were obtained with a high temperature thermal decomposition of an iron precursor in the presence of gold seed (Au nanoparticles with  $d = 8$  nm). Varying the Au/Fe ratio

is possible to tune the dimension of the magnetic component. The etching of gold is achieved by a treatment with Iodine at room temperature. All the investigated materials show good hyperthermic properties and SAR (up to 225 W/g) was found to be dependent not only on the magnetic component size, but also on the presence of gold.

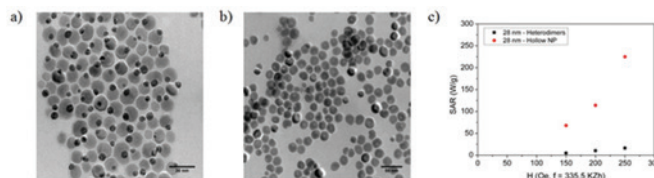


Fig. 1 - TEM micrographs of: a) Au-Fe<sub>3</sub>O<sub>4</sub> heterodimers and b) hollow magnetic nanoparticles. c) SAR vs H in 28 nm heterodimeric and hollow nanoparticles.

#### ADVANCED CEMENT-BASED COMPOSITES CONTAINING CARBON FIBERS AND CARBON NANOTUBES

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**Concept:** In this work advanced cement-based nanocomposites were prepared by adding carbon nanotubes and carbon fibers to a grade G oil cement, with the goal of improving the scarce piezoresistive properties of pure cement, aiming at an application in the real-time monitoring of stresses, in particular for oil&gas applications. The main concerns are the high dry resistivity of pure cement, and the fact that the water content and the local variations in water content inside the cement matrix heavily influence both electrical conductivity and piezoresistivity. The presence of highly conducting phases in the cement should guarantee better and more stable properties, that are needed for the application of these materials in real applications. To improve dispersion of carbon nanotubes and fibers in water and their adhesion to cement, either a dispersing agent or a chemical functionalization was used, allowing for a dramatic decrease both in the electrical resistivity of the composite cement, and in the dry-to-wet resistivity ratio. Moreover, the oxidative chemical functionalization of the carbon phases allowed for an improvement in compression strength.

**Motivations and objectives:** Cement is known as a piezo-resistive material, i.e. a material capable of varying the electrical resistivity as a function of applied stress. This would allow a real-time control on the stress applied to the cement, but for the fact that the piezoresistive effect is not strong, the electrical resistivity of dry cement is very high, and the content of water dramatically modifies the electrical conductivity of cement. With the goal of improving the electrical and piezoresistive properties of the cement, in this work the preparation of a cement-based composite material containing very low amounts of carbon nanotubes and carbon fibers is described. Oxidative functionalization was used to improve the dispersion of the phases in water and compatibility between matrix and carbon-based second phases.

**Results and discussion:** The functionalization of the carbon fibers results in a better dispersion and better adhesion with the cement, allowing a reduction of resistivity, dry-to-wet resistivity ratio and an improvement of mechanical strength. In the case of carbon nanotubes the results are less evident, due to the short length of nanotubes that increases the number of electrical contacts inside the electrical-conducting network. However the simultaneous use of carbon fibers and nanotubes seems to guarantee very good properties, both from the electrical and mechanical point of view. A simple model is used to give an explanation for the behavior of the composites, and piezoresistivity of both cement and cement-based composites is measured by measuring the electrical resistivity of the material under applied stress.

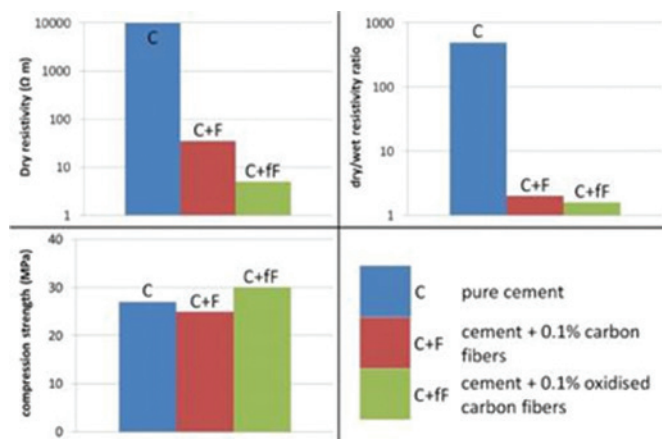


Fig. 1

### LANTHANUM FERRITES FOR NEW SOURCES OF ENERGY

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**Concept:** Perovskite-type  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  (LSFCu2020) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  (LSFCu4020) oxides were synthesized and deeply investigated as a novel "cobalt-free" cathode for doped lanthanum gallate (LSGM) electrolyte material. The chemical stability with LSGM electrolyte was studied by XRD, EDX and ToF-SIMS techniques. The electrochemical properties of LSFCu pellets were investigated in the temperature range 600-750°C by electrochemical impedance spectroscopy (EIS). Area Specific Resistance values of LSFCu/LSGM/LSFCu and LSFCu-GDC/LSGM/LSFCu-GDC symmetrical cells were evaluated. Fuel cells were prepared using LSFCu as cathode material on LSGM pellet and electrochemical tests were performed and compared to similar fuel cells prepared by using commercial  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  (LSFCo). The maximum current density and power density recorded for LSFCu and LSFCo were comparable demonstrating that Cu can be used as substitutes Co.

**Motivations and objectives:** Cobalt-doped lanthanum ferrites have been investigated for application as cathode in Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC) using  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  (LSGM) electrolyte material. Particularly at 700-500 °C they show mixed ionic-electronic conductivity, with electronic conductivity as high as 100  $\text{S cm}^{-1}$ , and good catalytic activity for oxygen reduction reaction (ORR). Because of their flexible redox behavior however, most of these materials lack proper chemical stability. Match with the electrolyte and easy evaporation are among other issues preventing the use of cobalt containing oxides for practical long-term applications.

**Results and discussion:** Interdiffusion between LSFCu and LSGM with the formation of solid solution was observed above 1100 °C. In IT range (550-750°C) the conductivity was larger than 150  $\text{S cm}^{-1}$  demonstrating that LSFCu has suitable electrical property for cathode application. The electrochemical performances measured in symmetrical and single cells using LSFCu2020 were comparable with that of more widely investigated LSFCo. The highest electrochemical performance was achieved with LSFCu4020-GDC electrodes in hydrogen fuels. Finally, LSFCu results a potential candidate for application in LSGM based IT-SOFCs.

The financial support of INSTM and of the Lombardy Region (Project "Ferriti di lantanio per nuove Fonti di Energia", Ferriti-NFE) is acknowledged.

### SUPPORTED GOLD NANOPARTICLES FOR THE OXIDATIVE CLEAVAGE OF VICINAL DIOLS

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**Concept:** This paper reports about the results of a study aimed at the development of a more sustainable catalytic process for adipic acid (AA) synthesis,

by means of a two-step transformation starting from cyclohexene; the latter is first transformed into *trans*-1,2-cyclohexanediol (CHD) with hydrogen peroxide, and then the glycol is oxidized with oxygen. In regard to the second step, we studied the reactivity of different catalysts in water: alumina-supported  $\text{Ru}(\text{OH})_3$ , homogeneous Keggin-type P/Mo/V heteropolycompounds, and Au nanoparticles supported on  $\text{TiO}_2$  and  $\text{MgO}$ . Catalysts based on Au nanoparticles (NPs) turned out to be much more selective than alumina-supported  $\text{Ru}(\text{OH})_3$  because of the ability of Au nanoparticles to coordinate only one hydroxyl group thus avoiding the concomitant oxidation of both C-OH groups in CHD.

**Motivations and objectives:** In recent years, many studies showed that Au NPs are active catalysts for the liquid phase oxidation of alcohols in basic aqueous solutions; in particular, they are able to oxidize 1,2-diols and cleave selectively the C-C bond. For instance, Au NPs can oxidize the primary OH group of 1,2-propandiol to lactic acid or oxidize both OH groups in sequence to yield pyruvic acid. Supported Au NPs are also active for the oxidative cleavage of 9,10-dihydroxystearic acid with molecular oxygen to produce azelaic acid and pelargonic acid. We decided to study the reactivity of Au in the oxidative cleavage of CHD by supporting NPs on two different materials: titania and magnesia. In fact, a different reactivity is expected because of the different characteristics of the supports.

**Results and discussion:** We tested the reactivity of Au/ $\text{TiO}_2$  and Au/ $\text{MgO}$  (in both cases containing 1,5 % wt Au) at different pH values; with both catalysts a basic pH was necessary in order to allow CHD oxidation; therefore, the basicity of  $\text{MgO}$  was not strong enough to activate the reactant. However, we obtained better AA yield with respect to Ru-based catalysts, while working with a less basic pH: yields were 24% with Au/ $\text{TiO}_2$ , 22% with Au/ $\text{MgO}$  and only 3% with  $\text{Ru}(\text{OH})_3/\text{Al}_2\text{O}_3$  after 5 h of reaction. Au/ $\text{MgO}$  also showed a better selectivity to AA, because of the limited formation of dicarboxylic acids other than AA. This was due to various factors: (a) Au-based catalysts required less basic conditions than Ru-based systems, while strongly basic conditions favored the oxidehydrogenation of CHD into 1,2-cyclohexanedione, which was transformed into several undesired by-products. (b) the first intermediate in CHD oxidation with Au-based systems was 2-hydroxycyclohexanone, which underwent a very selective transformation into AA. The Au-based catalysts underwent deactivation phenomena, primarily due to the formation of carbonaceous residua, as highlighted by means of TEM. This phenomenon was more evident with the Au/ $\text{MgO}$  catalysts.

### HOT CORROSION RESISTANCE OF CERAMIC-METALLIC THERMAL SPRAYED COATINGS

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**Concept:** In this work, five different ceramic-metallic composite coatings were produced and characterized: four commercial compositions ( $\text{Cr}_3\text{C}_2$ -NiCr,  $\text{Cr}_3\text{C}_2$ -self fusing alloy,  $\text{Cr}_3\text{C}_2$ -NiCrAlY,  $\text{Cr}_3\text{C}_2$ -CoNiCrAlY) were deposited by thermal spray techniques (HVOF and APS), optimizing the deposition parameters by DOE technique. A new composite powder, composed by ceramic fillers, silica nanoparticles and a NiCr matrix, was developed and the related coating deposited. Characterization of coatings was carried out in terms of microstructural features (porosity, composition, phases distribution, micro-hardness) and resistance in hot corrosion tests: samples were exposed to a mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$  salts at 750°C in air.

**Motivations and objectives:** Fuel used in diesel engines for naval propulsion has a high content of impurities, like vanadium and sulfates. Such impurities form aggressive compounds, responsible for hot corrosion phenomena that can lead to severe degradation of the engine's components, especially of exhaust valves. Thus, a protective coating is needed in order to prevent the valves from degrading because of the corrosive environment.

**Results and discussion:** XRD, SEM and EDS analyses show the formation of nickel vanadate, chromium oxide and nickel oxide on the surface exposed to the salt mixture. The corrosion/oxidation kinetics seems to be strongly dependent to the amount of metallic phases in the coatings and to the porosity of deposited layer. The innovative nanostructured coating exhibits a good hot corrosion resistance even if characterized by a high metallic phases content.

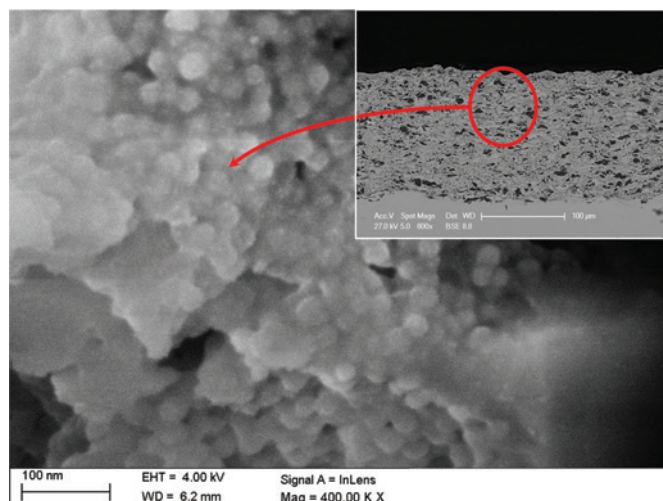


Fig. 1 - Nanostructured coating.

#### EVALUATION OF SIBS COPOLYMERS SUITABILITY FOR BIOMEDICAL APPLICATIONS

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**Concept:** Biostable elastomers are highly desirable in biomedical applications where the risk of failure due to oxidation, hydrolysis, mechanical stresses and enzymatic or bacterial attack has to be avoided. Styrene-block-Isobutylene-block-Styrene (SIBS) copolymers are biostable thermoplastic elastomers developed at the beginning of the XXI century, with properties overlapping both the silicone rubbers and polyurethanes. In this work we compared different not biomedical-grade SIBS copolymers with a biomedical-grade one. Solvent-cast films were prepared and characterized for morphology (SEM), laser profilometry, ATR-FT IR, uniaxial tensile properties, tensile and creep/recovery tests with a Dynamic Mechanical Analyzer. Cytotoxicity and cyto-compatibility were investigated in vitro with murine fibroblasts of the cell line L929.

**Motivations and objectives:** Up to now, only one SIBS is a *biomedical-grade* material produced by Innovia LCC. Our interest was to evaluate the suitability for a biomedical use of other SIBS elastomers presently used for different applications, such as pipes, caps, adhesives and components for dampers of noise and vibration (SIBSTAR<sup>®</sup>, Kaneka).

**Results and discussion:** Tensile mechanical tests (Fig. 1a) confirmed an elastomeric behavior, evidencing variable stiffness values correlated to a different soft/hard segment aggregation in the copolymers. In addition, creep/recovery behavior (Fig. 1b) highlighted a different viscous contribution. The in vitro cytotoxicity test proved no release of low molecular weight products. In cytocompatibility tests, cells exhibited the physiological elongated shape, and good proliferation, forming, at 7 days, cell sheets that completely covered the SIBS surface. These results confirmed the suitability of the Innovia SIBS for applications in contact with cells, but also demonstrated that SIBstar<sup>®</sup> SIBS could be used in biomedical applications.

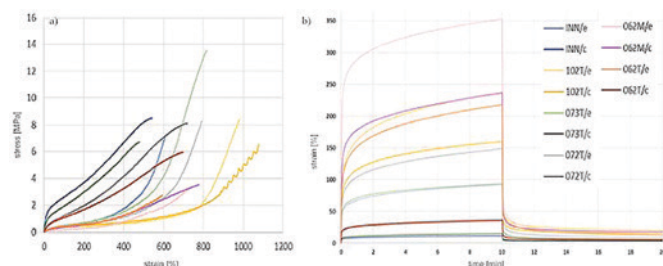


Fig 1 - SIBS copolymers: (a) uniaxial tensile properties; (b) creep/recovery tests.

#### THE NATURE OF THE ACTIVE PHASE IN FeVO<sub>4</sub> CATALYST FOR THE IN-SITU ACTIVATION OF METHANOL IN THE GAS-PHASE METHYLATION OF PHENOL

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**Concept:** Alkylphenols are important chemicals and intermediates used in a wide range of applications, produced by catalytic methylation of phenol with methanol in a gas-phase reactor. This reaction is strongly affected by the catalyst type used, that must be optimized in order to minimize methanol decomposition, maximise the selectivity toward the desired alkylated phenol and finally prevent catalyst deactivation. In previous papers, we found that indeed the reaction mechanism includes the in-situ dehydrogenation of methanol to formaldehyde, which acts as the true electrophilic reagent for the activated phenolate; this reaction is the rate-limiting step of the overall process. Therefore we selected Fe/V/O-based systems as catalysts; in fact, FeVO<sub>4</sub> has been reported to be active and selective in the dehydrogenation of methanol to formaldehyde. We carried out the investigation of the chemical-physical characteristics of this catalytic system by means of reactivity tests, XRD, SEM, TEM, FT-IR and Raman spectroscopy.

**Motivations and objectives:** We performed a comparison between traditional basic catalysts reported in the literature (MgO-based system, conventionally used for the gas-phase methylation of phenolics) and iron vanadate. Indeed methanol is reported to react over MgO. However, on basic catalysts phenol is easily activated but, on the other hand, drawbacks of this system are (i) the occurrence of methanol decomposition due to other undesired reaction; (ii) methanol dehydrogenation to formaldehyde only occurs at high temperature, and (iii) the strong interaction of phenolics with the basic sites finally is responsible for catalyst deactivation. In order to try to cope with these problems and optimize the process performance, we studied FeVO<sub>4</sub> as catalyst for phenol methylation. In particular we focused our attention on the understanding of the nature of the active phase.

**Results and discussion:** The Fe/V/O catalyst turned out to be very active, with complete conversion of phenol at 320°C already, also showing no deactivation and very high selectivity to the desired ortho-dimethylated product (2,6-xyleneol). We also found that the catalyst underwent structural modifications during the first hour of reaction, showing a progressive reduction until the formation of a stable, partially reduced Fe/V mixed oxide, which finally was the active, selective and stable catalyst. Moreover this phase could be easily reoxidized with generation of the starting FeVO<sub>4</sub> material. By means of FT-IR spectroscopy, we also found that the catalyst is able to generate the phenolate species, but it gives weaker interaction with the molecule than MgO does, thus favoring the quick desorption of the reaction products. Furthermore the energetically preferred mode of adsorption leads to an almost orthogonal orientation of the aromatic ring with respect to the catalyst surface, a characteristic finally leading to high regio-selectivity for methylation in the ortho position.

#### CONTINUOUS MULTILAYERED COMPOSITE HYDROGEL AS OSTEOCHONDRAL SUBSTITUTE

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**Concept:** Cartilage is a highly organized avascular soft tissue that assembles from nano-to macro-scale to produce a complex structural network. To mimic high complex cartilage tissue, we developed a stable three layers composite polyvinyl alcohol (PVA) based hydrogel, characterized by a tailored gradient of mechanical properties as a consequence of different degrees of crosslinking and enrichment with nano-hydroxyapatite (HA). The optimized synthesis method implies chemical crosslinking of each layer directly onto the previous one to ensure a drastic reduction of the material discontinuities and brittleness. The multilayered composite was physically, chemically and mechanically characterized by infrared spectroscopy, differential scanning calorimetry, thermogravimetry, scanning electron microscopy and rheometry in order to compare its physico-chemical characteristics

with those of cartilage tissue. Experimental measurements show that the rheological behavior of the multilayered composite (MSC) was very similar to that of the tibial plateau of human cartilage. The water content of each MSC layer is similar to that of articular cartilage, producing the same gradient of interstitial fluid and the mesoporous structure strictly resembles that of articular cartilage, allowing similar transport of both nutrients and metabolic waste to and from the cells. Finally, the cytocompatibility tests show that the composite material has no toxic effects towards osteoblasts or chondrocytes and doesn't hinder cells proliferation. Thus, the developed multilayered composite hydrogel can be considered a promising potential substitute for damaged cartilage tissue.

**Motivations and objectives:** Hydrogels are excellent biomimetic materials and their structural, morphological and mechanical properties can be modulated on the basis of the required application. However, to simulate a high organized material like articular cartilage only one material could be insufficient. For this purpose the use of composite materials is recommended, but they usually present material discontinuities and brittleness. In this work we describe a chemical procedure that enables to control the crosslinking degree gradient along the whole material thickness, allowing to drastically reduce the material discontinuities and brittleness and providing a stable chemical multilayered composite material. Furthermore, the choice of PVA/calcium phosphate composites allows to obtain a total biocompatible hydrogel for cartilage tissue replacement.

**Results and discussion:** The composite hydrogel showed a water content comparable to that of the deepest and the highest cartilage layers, respectively. Furthermore, the multi-layered material displayed rheological properties strictly comparable with those of cartilage in terms of both complex modulus and recovery.

TABLE I

Compound	Hydrogel WC (%)	Cartilage Ref.	Hydrogel G* (Mpa)	Cartilage Ref.	Hydrogel Recovery 1s (%)	Cartilage Ref.
Deepest Layer	63 ± 3	≈60	/	/	/	/
Highest Layer	83 ± 3	≈85	/	/	/	/
Multilayer (MSC)	/	/	0.032 ± 0.003	0.030 ± 0.003	70	70

#### EFFECT OF GRAPHENE OXIDE ON THE PROPERTIES OF A PLA/PEG BLEND

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**Concept:** PLA was melt-blended with a not miscible PEG ( $M_w = 20,000$ ) and two home-synthesized GO samples with different chemical compositions. Two processing methods were implemented and the effect of type of GO, technique adopted and processing conditions on the interphase and ultimate performance of the nanocomposites were fully analyzed from a spectroscopic, morphological, dynamic-mechanical point of view.

**Motivations and objectives:** PLA/PEG blends attracted significant interest in tissue engineering due to their cytocompatibility and biodegradability. Nevertheless, PLA/PEG miscibility was found to be metastable, thus resulting in not adequate mechanical performance. Amphiphilic GO could be suitable to enhance the mechanical properties without affecting cytocompatibility and biodegradability. We report the effect of two different types of GO on the degradation and stability of PLA/PEG blends.

**Results and discussion:** PLA-PEG are partially miscible. The addition of GO-1 and GO-2 (a highly oxidized GO with C/O = 1.5) via a two-step procedure results in a strong enhancement of interphase region, as evidenced by SEM and loss factor fitted curves, not reported. Moreover, based on the type of processing, two-step procedure (w+m) led to a stronger improvement of mechanical properties with respect to melt mixing, due the prevention of lamellae re-stacking. The chemistry of GO-2 promoted a fast degradation of PLA, monitored by rheological tests (Fig. 1a) where it is well-evident that the behavior of complex viscosity of GO-2 containing samples become similar to that of pure PEG. This issue

is ascribed to the hydrolytic scission of PLA macromolecules in acidic medium (Fig. 1b), due to the high content (>10%) of reactive -COOH moieties of GO-2. Indeed, ATR measurements (Fig. 1c) put into evidence the strong increase of the signal centered at around 3400  $\text{cm}^{-1}$  attributed to -OH terminal groups of the degradation products. The less oxidized GO-1 provided an increased stiffness and toughness and a better thermo-mechanical performance. The study of the loss factor plots, collected by DMA tests, suggests that the observed improvements could be likely ascribed to the strong interfacial adhesion.

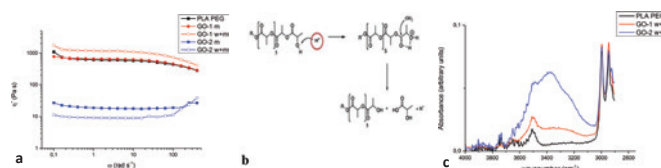


Fig. 1 - Rheology of PLA-PEG-GO systems (a), mechanism of hydrolytic scission in acidic medium (b), ATR spectra (c).

#### FRACTURE TOUGHNESS AND HARDNESS OPTIMIZATION IN CERAMIC COATINGS

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**Concept:** Fracture toughness is one of the foremost mechanical parameters in ceramic materials, even more in ceramic coating for mechanical applications. In bulk materials, one has traditionally to choose between high ductility and low hardness of metals and high hardness and brittleness of ceramics. Its value in application design and dimensioning is however contrasted with the difficulty to measure it in materials in films form, instead of bulk. In this work a new toughness assessment methodology is proposed, complementary to the previously developed ones, and highly useful for coatings optimization. A first of its kind toughness-driven process parameters-performance optimization is presented, showing the results on a well-known coating, the CrN.

**Motivations and objectives:** State of the art toughness assessment of thin (less than 10 μm thick typically) coatings is to do very low load indentation with sharp tips and measuring the resulting cracks lengths, or measuring bending forces needed to crack notched micro fabricated cantilevers. Various problems with this tests resulted in the development of a novel indentation technique, the nanoindentation on FIB-made pillars. Complementary to this nanoscale technology, a macro scale complementary test has been devised and implemented. The new test methods allow an optimization of the coating toughness. The Cr-N system has been chosen as the coating to optimize due both to the literature available and the number of possible compounds obtainable in a reactive magnetron sputtering system like the one owned by RomaTRE University. The process variables chosen were sputtering gas composition, pressure, bias, power on target and pressure-distance ratio to explore as much as possible the Thornton diagram.

**Results and discussion:** Samples of Cr<sub>x</sub>N<sub>y</sub> on Stainless steel were successfully produced and characterized both with the new toughness assessment techniques and the standard hardness, scratch testing and XRD measurement technologies. Great differences in toughness were measured changing gas mix composition proving the possibility of toughness tuning to the application.

#### METHANATION OF CO<sub>2</sub> OVER γ-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>-CeO<sub>2</sub> COMPOSITE OXIDE SUPPORTED Ni-BASED CATALYSTS

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**Concept:** Composite oxide supported Ni-based catalysts were prepared by wet impregnation technique and applied for the methanation of carbon dioxide. The composite oxide supports were prepared by impregnation-precipitation method using a commercial γ-Al<sub>2</sub>O<sub>3</sub> powder as a host with variation of the percentage (5-15%) of loading ZrO<sub>2</sub>, TiO<sub>2</sub> and CeO<sub>2</sub> promoters from their respective salt precursors. NH<sub>4</sub>OH was used as precipitating agent. The

as prepared catalysts were characterized by AAS, XRD, BET and H<sub>2</sub>-TPR. Catalytic activities of the newly synthesized catalysts (10 mg) were investigated towards hydrogenation of CO<sub>2</sub> at atmospheric pressure using a fixed bed reactor. Experimental results revealed that the composite oxide supported Ni-based catalysts showed a better conversion and stability than the γ-Al<sub>2</sub>O<sub>3</sub> only supported Ni-based catalyst.

**Motivations and objectives:** Increasing emissions of CO<sub>2</sub> arising from the widespread production of energy from fossil fuels is a critical matter regarding the global warming. The hydrogenation of CO<sub>2</sub> into oxygenates and/or hydrocarbons have been the most investigated reactions to obtain fuels. Among several hydrogenation reactions, methanation of CO<sub>2</sub> following the Sabatier reaction is the most advantageous one regarding thermodynamics. Nickel based catalysts are the most studied materials for the latter reaction, because of their high activity and low price, but metal sintering at reaction conditions diminishes their industrial viability. The type of support used for heterogeneous catalysts is an important factor to consider on solving such problems. In this work, we focused our attention on the selection of supports for Ni-based catalysts with low Ni content.

**Results and discussion:** From H<sub>2</sub>-TPR profiles, β- and γ-peaks (weak and strong interaction of NiO species with support) shifts downwards for the composite oxide supported Ni-based catalysts, suggesting a weaker interaction between NiO and the support. These results to have more β-type NiO species which are active in the catalytic reaction. Among the catalysts investigated the Ni/C<sub>1</sub> catalyst which has 15% of each loading oxide shows better activity (62.24% conversion of CO<sub>2</sub> to CH<sub>4</sub> at 350°C).

The authors would like to thank The HELMETH EU project "Integrated High-Temperature Electrolysis and Methanation for Effective Power to Gas Conversion" and SINCHEM grant i.e. a Joint Doctorate program selected under the Erasmus Mundus Action 1 Program (FPA 2013-0037).

#### HYDROPHOBIC BEHAVIOR OF SELF-CLEANING AND AR SOL-GEL TITANIA COATINGS FOR PV GLASS SURFACE

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**Concept:** Antireflection (AR) titania coatings having self-cleaning capabilities suitable for photovoltaic (PV) glass surface applications were developed by two different post-synthesis treatments which determine the reduction of surface energy, the key factor for obtaining hydrophobic surfaces. Two methodologies were used: a stearic acid treatment and a silanization process with methyltrichlorosilane performed in different solvent. Both treatments favor the air trapping below the rainwater, characteristic of a hydrophobic surface. By comparing the methods, it was observed that the stearic acid treatment produces an average contact angle (60°) similar to that obtained with the silanization (75-78°) well-known for its good results, encouraging so the use of the bio-compatible chemical.

**Motivations and objectives:** We are moving toward a decentralized and more sustainable production of energy in which the installed PV capacity is fast increasing. In PV devices, the periodic maintenance required to remove fouling formation, responsible of efficiency losses, can be eliminated by covering the front glass with a photoactive self-cleaning TiO<sub>2</sub> thin film. The focus of this work is to modify the hydrophilic nature of the TiO<sub>2</sub> film into a hydrophobic one, without affecting its transparency and anti-reflection properties, improving so the self-cleaning behavior.

**Results and discussion:** Transparent AR titania coatings, fabricated by a sol-gel method followed by dip-coating deposition described elsewhere, were used as starting material for hydrophobic treatments. Figure 1 illustrates the wettability maps which highlight the hydrophobic behavior of the surface after each treatment. Using stearic acid (Fig. 1b) constant wettability values and homogeneously distributed on the surface are observed, whereas with the silanization the surface is less uniform even if the contact angle is higher (Figs. 1c and d). These results provide useful insights in order to improve the surface properties and the quality of the functional TiO<sub>2</sub> coatings.

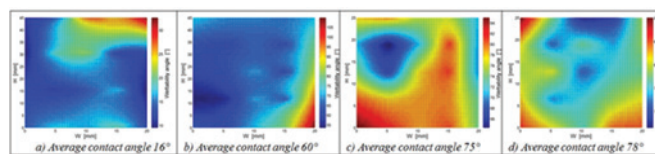


Fig. 1 - Wettability maps and corresponding average contact angle of: a) TiO<sub>2</sub> film; b) TiO<sub>2</sub> film treated with stearic acid; c) TiO<sub>2</sub> film silanized in toluene solution; d) TiO<sub>2</sub> film silanized in ethanol solution.

#### WAVELENGTH DISPERSION OF THE LOCAL FIELD INTENSITY IN SILVER-GOLD NANOCAGES

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**Concept:** This study provides a combined theoretical and experimental analysis of the far-field (extinction) and of the near-field (SERS enhancement) spectral distribution in silver-gold nanocages (NCs). Chitosan protected NCs have been synthesized by galvanic replacement and characterized by TEM, STEM and ICP. Finite Element Method (FEM) simulations have been used to predict the optical properties of a single NC and also of NC dimers with a variable gap distance. The spectral distribution of the local field in a dispersion of NCs has been experimentally measured by Wavelength Scanned SERS (WS-SERS).

**Motivations and objectives:** A lot of effort has been spent in recent years to figure out the interplay between the optical far- and the near-field response of metal nanostructures. The basic problem to address is whether the excitation wavelength dependence of the Raman enhancement is predictable on the basis of the extinction/absorption features of the sample, and therefore if a guideline exists indicating the spectral region with the maximum SERS activity. We have investigate this issue, for the first time, in the case of NCs in solution. We think that our study can also have practical implications in fields where NCs, or hollow NPs in general, are exploited as carriers, e.g., in drug delivery applications, while monitoring the transport process by surface enhanced spectroscopies.

**Results and discussion:** The experimental WS-SERS data showed that the near-field is distributed in the same spectral region as the extinction and that the absolute value of the enhancement factor remains very low throughout the spectral region explored (568-800 nm). This behavior differs from what observed in the literature for filled NPs, where the local field enhancement lies strongly red-shifted with respect to the extinction due to the unavoidable presence of aggregates. FEM simulations evidence that in NC dimers, reducing the gap, both near- and far- field spectra shift to the red with respect to the isolated NC, in analogy to what happens with filled NP dimers. However, while the field enhancement in a filled NP dimer is remarkably larger compared to the single NP, the enhancement in a NC dimer is instead only slightly larger with respect to the isolated NC. We propose that the experimental correlation observed between the SERS profile and the extinction is accidental and originates from the limited increase in amplification provided by NC aggregates with respect to isolated NCs. In the Figure below: field intensity distribution around a NC at λ = 754 nm on the NC surface (left) and at 1.3 nm from the metallic surface (middle); experimental extinction and WS-SERS data (right).

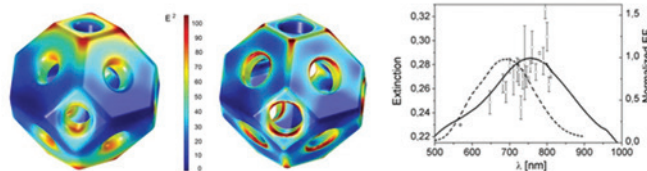


Fig. 1

### EXPERIMENTAL AND THEORETICAL STUDIES OF Cr(II)/SiO<sub>2</sub> BASED PHILLIPS CATALYST FOR ETHYLENE POLYMERIZATION

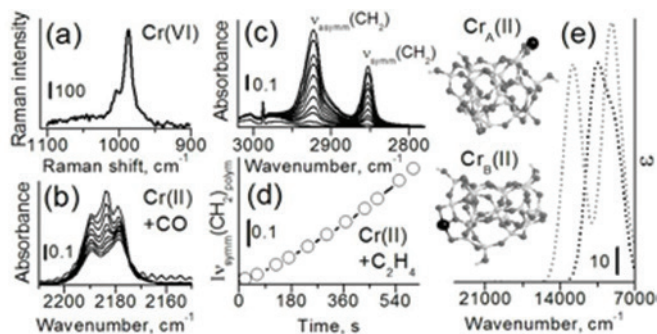
Damin A<sup>1,3</sup>, Budnyk A<sup>2</sup>, Groppo E<sup>1,3</sup>, Zecchina A<sup>1,3</sup>, Bordiga S<sup>1,3</sup>

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**Concept:** The Phillips catalyst is a highly versatile Cr/SiO<sub>2</sub> system accounting for the production of several types of poly-ethylene. It is still the subject of an intense industrial and academic research, both from an experimental and theoretical point of view. The determination of the structure and the oxidation state of the active sites (obtained after reduction of Cr(VI) species by ethylene itself) of the real catalysts remains however difficult, as such as the deep understanding of the mechanism which brings to the formation of poly-ethylene from ethylene molecules interacting with Cr species: for this, the study of Cr(II)/SiO<sub>2</sub> (obtained after reduction of Cr(VI) by CO and able to polymerize ethylene at room temperature) constitutes a good model for the real catalyst and it could give further insights in the comprehension on how real catalyst should work.

**Motivations and objectives:** The sol-gel methods allows to obtain optically transparent monoliths displaying high surface area. Both properties facilitate the spectroscopic investigation of the structure and the catalytic activity of metal centres (present in very low concentration) in transmittance geometry. In the present work, we report an experimental study of catalytic activity of the Cr(II)/SiO<sub>2</sub> model systems at different hydroxylation degree of the silica support. The experimental results were then used for validating theoretical models of the Cr(II)/SiO<sub>2</sub> catalyst, based on embedded cluster approach and at DFT level of theory: such models will be adopted for exploring the reactivity of Cr(II) towards the ethylene molecule.

**Results and discussion:** Figure 1 presents some experimental results (a-d) together with clusters of Cr<sub>A</sub>(II) and Cr<sub>B</sub>(II) sites adopted to model Cr(II)/SiO<sub>2</sub> systems in their highly dehydroxylated form (e). A systematic investigation of the hydroxylation state of the surface on the Cr(II)/SiO<sub>2</sub> sample as a function of the activation temperature in the 550-750°C interval was performed in terms of distribution of fully isolated and weakly interacting hydroxyl groups. Experimental observations allowed for development of cluster models of Cr<sub>A</sub> and Cr<sub>B</sub> sites, which satisfactory reproduce the main experimental data.



**Fig. 1** - Experimental results on Cr 0.1 wt% activated at 650°C: (a) Raman spectrum (325 nm laser line) in air, (b) CO 100 mbar adsorption on Cr(II)/SiO<sub>2</sub> at RT, (c) FTIR of polymerization of 100 mbar C<sub>2</sub>H<sub>4</sub> at RT, (d) the kinetics of polymerization followed at 2853 cm<sup>-1</sup>, and graphical representation of Cr<sub>A</sub>(II) and Cr<sub>B</sub>(II) clusters and computed UV-Vis spectra for both models (e).

### COLLOIDAL TiO<sub>2</sub> NANORODS FOR PHOTOCATALYSIS: A FEMTOSECOND TRANSIENT ABSORPTION STUDY

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**Concept:** The excitation-dependent relaxation dynamics of charge carriers in anatase TiO<sub>2</sub> nanorods (NRs) was investigated by femtosecond transient

absorption spectroscopy. This technique is a widely known effective tool with unique capabilities for elucidating the electron-hole (e<sup>-</sup>h<sup>+</sup>) recombination dynamics of nanocrystals. Colloidal dispersions of such anisotropic nanocrystals were excited in the UV-vis range using three different pump wavelengths, *i.e.* above, close to, and below the direct band gap of anatase. We show that the ultrafast dynamics strongly depends on the excitation wavelength, and influences most of the processes contributing to the relaxation dynamics.

**Motivations and objectives:** TiO<sub>2</sub> nanocrystals are successfully exploited in applications related to energy conversion, such as photocatalysis and photovoltaics, thanks to their ability to generate e<sup>-</sup>h<sup>+</sup> pairs under proper lighting. In addition, the rod-like nanocrystal shape magnifies this effect, due to a larger surface/volume ratio and a higher number of active sites of interaction with the environment. The conversion efficiency is correlated to the lifetimes of e<sup>-</sup> and h<sup>+</sup> before their recombination, which in turn are influenced by several factors. Excitation energy plays a major role, as it defines the initial potential of the carriers. An excitation-dependent investigation of the charge carrier dynamics is thus expected to provide major information crucial for understanding their reactivity and for further rationalizing their behavior in photocatalytic applications.

**Results and discussion:** TiO<sub>2</sub> NRs were synthesized by a colloidal chemistry route and dispersed in an organic solvent, thanks to oleate ions coordinating the nanocrystal surfaces. We performed pump-probe experiments in a weak-excitation regime by pumping at 300, 350, and 430 nm and probing in a broadband spectral range extending from 450 to 750 nm. The temporal evolution of photoinduced absorption changes was found to be strongly dependent on the excitation conditions, both at short and long time delays. Nonetheless, the initial charge carriers trapping in surface defect states occurs very rapidly after the photogeneration in all investigated cases. The two distinct TA bands at 500 and 700 nm, typically attributed to trapped h<sup>+</sup> and e<sup>-</sup> in anatase, are accessible only when TiO<sub>2</sub> nanorods are photoexcited well above the band gap, while there is no evidence of such bands when excitation occurs close to or below the band gap. In such cases the observed dynamics are attributed to excitonic states. This evidence is also supported by the persistence of a long-lasting TA contribution ascribable to such bound states.

### THERMAL AND MECHANICAL EVALUATION OF PLLA MEMBRANES TO APPLICATION IN TISSUE ENGINEERING

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**Concept:** The growing interest in materials for applications in the human body led to a new area of research, concerning the development of biomaterials, which assume an important role in the tissue engineering. Phase separation techniques have become an important procedure to obtain porous structures, especially in the field of polymer membranes. Polymeric membranes prepared via DIPS (Diffusion Induced Phase Separation) are widely studied and utilized as scaffolds to regeneration of tissue. A three-dimensional membrane to favour the growth of 16 HBE (Human Bronchial Epithelium) must be thin, porous, mechanically stable, permeable to nutrients and must support the cell adhesion process. The surface morphological characteristics of a PLLA membrane play a crucial role in the interaction between cells and scaffold. Cell adhesion is features important to evaluate the cell-biomaterial interaction for the prediction of possible in vivo reactions when these polymers are used to substitute body parts or to stimulate the regeneration of damaged tissues.

**Motivations and objectives:** Poly (L)-lactide membrane with different surface morphologies were prepared through a Diffusion Induced Phase Separation (DIPS) protocol starting from a ternary solution made of polymer, dioxane (solvent) and water (non-solvent). Aim of this study is the thermal and mechanical evaluation of PLLA membranes, with different pore diameters, to stimulate cell adhesion and growth in vitro. The film morphology, mechanical and thermal characteristics were investigated by using scanning electron microscopy (SEM), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC).

**Results and discussion:** PLLA Membranes for 16 HBE culture have been produced via DIPS which have morphology, thermal and mechanical properties different. The cell adhesion and growth can be elevated drastically changing

pore size of scaffold, which provides more porous topology among the foams and might facilitate the cell attachment, stiffness and crystallinity.

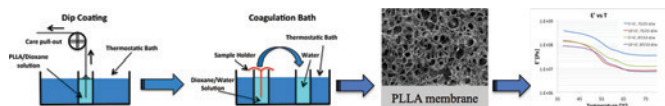


Fig. 1

### MOLECULAR DYNAMIC SIMULATION ON POLYAMIDE 6/GRAPHENE NANO-LAYERS NANOCOMPOSITES

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**Concept:** In this work results obtained from Molecular Dynamic Simulation (MDS) on Polyamide 6 (PA6) chains in graphene containing nanocomposites are presented. Through detailed MDS, the interface of complex nanocomposites systems can be fully characterized, furthermore different physical properties, such as density, end-to-end distance  $\langle R_{ee} \rangle$ , and average radius of gyration  $\langle R_g \rangle$  of polymers chains can be predicted. This issue is useful for the design of highly value-added nanocomposites and the optimization of their production process, by defining transformation steps and status variables (temperature, time and pressure), that can also help the industrial production.

**Motivations and objectives:** The work investigates the change of PA6 physical properties due to the adding of graphene nano-layers. Specifically, the MDS conducted on a representative volume of polymer chains positioned between two nano-layers, considering each polymer chain contains a fixed number of monomers. Really, a complete study could consider a Gaussian distribution of chain length and an investigation about how the distance between each group of chains is related with density, density distribution,  $\langle R_{ee} \rangle$  and  $\langle R_g \rangle$ . These parameters are relevant because the final properties and performance of polymer-based nanocomposites are related to the entanglements between chains, and the absorption of monomer to the graphene layer. MDS is run by using *Gromacs* software, the molecular structure adopted is a polymeric chain of PA6, simulation are conducted adopting 3 systems. Each investigated system is constituted by 50 chains of respectively 4, 8 and 12 periodic units of  $-(CH_2)_5-(C=O)-NH_2-$ , terminated with a methyl group. Force field adopted for the simulation is the Optimized Potentials for Liquid Simulations - All Atom (OPLS/AA), the simulation is conducted in 2 steps. At the first step the polymer system is hold at 500°K and pressure of 1 atm, (NPT simulation) for 50ns, in order to obtain the initial constant density, after the simulation is conducted at constant volume (NVT), using a cooling rate of 2K/ns from 500°K to 293°K (environment temperature of 20°K) for 104ns.

**Results and discussion:** A correlation between bulk density and number of monomer, at constant layer distance, is estimated. It is also calculated the density distribution along the interlayer distance. It is possible to appreciate a peak of density close to each nano-layer; as minor is distance between nano-layers into polymeric melt, as well pronounced is the density peak. Viscosity properties are correlated with the values of  $\langle R_{ee} \rangle$  and  $\langle R_g \rangle$  of chains and the obtained correlation curves can be customize the fabrication in order to control the viscoelastic properties of polymer-based nanocomposites containing graphene nano-layers.

### 3D-PAPER: A NOVEL HIGHLY SUSTAINABLE MATERIAL FOR 3D PRINTING

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**Concept:** The growing success of 3d printing requires the development of materials with high environmental sustainability. Nowadays, printing materials are essentially based on ABS (having the same recycling and separate collection issues as the other non-biodegradable synthetic polymers) and on PLA, derived from corn starch, compostable, but not yet recyclable. New more sustainable materials are necessary.

**Motivation and objectives:** The joint research laboratory Politecnico di Milano-Ghelfi Ondulati has developed a new material, named 3d-paper, having high sustainability and characterised by:

- 30÷50% cellulose fiber content, obtained from recycled paperboard;
- water soluble polymeric matrix produced without subtraction of agricultural soil for human food production;
- recyclability with paper and paperboard.

**Results and discussion:** Filaments, 1.75 mm in diameter (Fig. 1a), were extruded on a co-rotating twin-screw extruder after mechanical mixing of the two main components (i.e cellulose and water soluble polymer). Printing tests were performed on a 3d-FDM (Fused Deposition Modelling) printer in comparison with ABS and PLA, used as reference materials (Fig. 1b). 3d printing tests of 3d-paper materials showed high printing speed and the possibility to obtain very low thicknesses. Uniaxial mechanical tensile characterisation was carried out on extruded filaments and dog-bone 3d printed specimens. Test results, summarized in Table I, showed low modulus and high elastic recovery of 3d-paper materials. Solubility tests showed solubilisation of the 3d-paper materials in water also at room temperature.

TABLE I - Tensile mechanical properties (E,  $\sigma_r$  and  $\epsilon_r$ ) of 3d printed materials

	1,75 mm extruded filaments			dog bone		
	E (MPa)	$\sigma_r$ (MPa)	$\epsilon_r$ (%)	E (MPa)	$\sigma_r$ (MPa)	$\epsilon_r$ (%)
ABS	1313 ± 142	32,7 ± 3,3	5,0 ± 0,2	868 ± 204	32.8 ± 3.3	5,0 ± 0.2
PLA	1472 ± 171	45,0 ± 2,1	46,9 ± 21,2	1413 ± 151	42.8 ± 4.3	4.5 ± 0.4
3d-paper <sub>30%</sub>	253 ± 35	20,8 ± 0,8	17,5 ± 2,9	40 ± 2	6.8 ± 0.1	53.6 ± 4.8
3d-paper <sub>50%</sub>	497 ± 59	23,3 ± 1,0	8,1 ± 1,2	98 ± 8	7.2 ± 0.6	17.2 ± 0.7

The experiments confirmed the very interesting properties of 3d paper materials: sustainability, water solubility, high printing speed, low modulus, high elastic recovery.

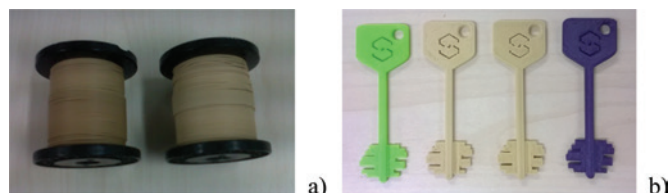


Fig. 1 - (a) Extruded filaments: 3d-paper<sub>30%</sub> and 3d-paper<sub>50%</sub> (b) 3d printed objects: PLA, 3d-paper<sub>30%</sub>, 3d-paper<sub>50%</sub>, ABS.

### WEAR RESISTANCE OF CF/UHMWPE BIOMATERIALS OBTAINED BY DIFFERENT MIXING METHODS

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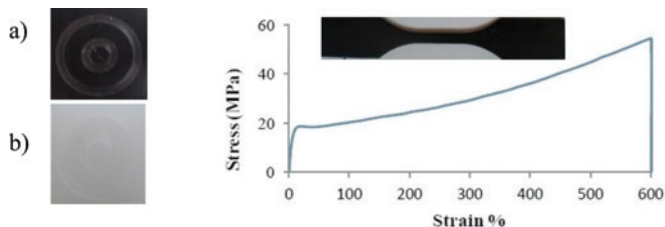
**Concept:** The aim of this work is to improve the wear resistance of UHMWPE through the addition of 1%wt. of carbon nanofiber (CF) and 2%wt. of paraffin oil retaining the typical ductility of pure material. Different preparation methods (hot plate and magnetic stir bar "MS", ultrasonic bath "US", ball milling "BM", twin-screw extrusion "EX") were employed in order to find the optimum dispersion method of filler into the polymeric matrix choosing the best conditions for synthesized UHMWPE nanocomposites.

**Motivations and objectives:** From the viewpoint of design, the prosthetic joint device has a service time indicated by the designer based on the weakest part of an existing device. The total joint replacements consists of two main parts are femoral prosthesis and cup. The femoral prosthesis is made of stainless steel and the cup made of UHMWPE, because of the combination of well lubricity, impact resistance and abrasion resistance. Nevertheless, the



cup is considered weaker part because it is made of polymer material. The design criteria in this case depend mainly on the wear due to permanent relative motion between two parts. So wear is the most important effective factor directly on the service time.

**Results and discussion:** The wear tests were conducted using a pin-on-disc wear tester at room temperature under dry sliding conditions (Fig. 1, left panel). The tests of flat samples against steel pin were carried out at a linear velocity of 1 m/s, normal load 30N. The results showed that the BM represents the best method to produce CNFT/UHMWPE with well dispersion and excellent wear resistance among the tested ones. The nanocomposites made by BM and EX showed a good mechanical ductile behavior (Fig. 1, right panel).



**Fig. 1** - Wear tracks for (a) CF/UHMWPE and (b) UHMWPE (left panel); CF/UHMWPE tensile curve (right panel).

#### SYNTHESIS AND CHARACTERIZATION OF PEGYLATED GRAPHENE OXIDE FOR SORAFENIB MODIFIED RELEASE

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**Concept:** Graphene, a single layer of sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb two-dimensional (2-D) crystal lattice, has evoked enormous interest throughout the scientific community since its first appearance in 2004. Due to its unique structure and geometry, graphene possesses remarkable physical-chemical properties (including large specific surface area and biocompatibility) that enable it to be an ideal material for several applications, ranging from quantum physics, nanoelectronics, energy research, catalysis and engineering of nanocomposites and biomaterials. In the area of nanomedicine, graphene and its derivatives can be exploited for a broad range of applications, including a new generation of biosensors, nanocarriers for drug delivery and probes for cell and biological imaging. In particular, graphene oxide (GO), synthesized by intensive oxidation of crystalline graphite and then turned into a monolayer material by sonication, consists of aromatic planes and polar functional groups which consequently provide it an excellent capability to adsorb aromatic compounds via  $\pi$ - $\pi$  stacking and hydrogen bonding. In order to improve its biocompatibility and physiological stability, some biocompatible polymer can be introduced onto GO. Among the commercially available polymers, poly(ethylene glycol) (PEG) is a very useful reagent in biology because of its minimal toxicity, biocompatibility, protein resistance, and good solubility in water or other common solvents.

**Motivations and objectives:** Sorafenib is a small molecule that acting as a multi-kinases inhibitor blocks tumor-cell proliferation and tumor angiogenesis. It increases the rate of apoptosis in a wide range of tumor models and is the first drug that is clinically approved for patients with advanced hepatocellular carcinoma (HCC). In the present study, we aimed to develop a GO-PEG based carrier for enhanced delivery and controlled release of sorafenib into specific cancer cells.

**Results and discussion:** Herein, we developed a GO-PEG nanocarrier for enhanced delivery and controlled release of sorafenib into specific cancer cells. GO-PEG was first synthesized dispersing GO in bi-distilled water followed by adding PEG<sub>2000</sub>-NH<sub>2</sub>. For the preparation of sorafenib loaded GO-PEG a solution of sorafenib in DMSO was added to an aqueous GO-PEG dispersion at pH 8.4, and the obtained solution was kept under magnetic stirring at room temperature overnight. The empty and drug-loaded GO-PEG were charac-

terized in terms of size, zeta potential, polydispersity, morphology and drug loading capacity. The release kinetic studies, carried out in an appropriate medium mimicking the physiological environment, confirmed that this system permits a controlled release of sorafenib.

#### RECYCLING OF YTTRIA-STABILIZED ZrO<sub>2</sub> (YSZ) FOR CERAMIC TILE GLAZES AND PIGMENTS

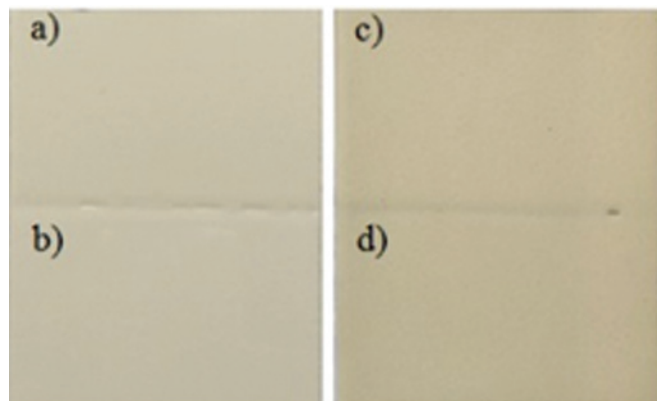
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**Concept:** Thermal spraying overspray of yttria stabilized ZrO<sub>2</sub> (YSZ) powders have been characterized by means of grain size laser technique, scanning electron microscopy, X-ray fluorescence, X-ray diffraction and colour measurement. Two different powders, APS5 and APS6, coming from two different thermal spray process has been analyzed. The results showed that only APS6 is strongly polluted with metallic element as Ni, Co and Cr. Both powders have been sieved, in order to separate the pollutant particles, and each fraction has been characterized, to verify the content of metallic pollutant particles. The sieved fraction with the lower grain size results suitable to substitute zirconium oxide into ceramic frits, glazes and pigments formulation. Frits, glazes and pigments produced with standard and recycled zirconium oxide have been analyzed by means of scanning electron microscopy, X-ray diffraction, chemical durability and colour measurement. The final results demonstrate that the less polluted thermal spraying overspray of yttrium stabilized zirconia powders can replace zirconium oxide for the production of frits and glaze to obtain super-white surfaces, whereas the most polluted powders can be used for the formulation of at least five pigments for ceramic body.

**Motivations and objectives:** Thermal spraying overspray powders are a relevant waste for the coating industry because of their great amount, up to 70-90% of the starting powder, and the presence of hazardous element as Ni, Co, Cr. The recycle of these powders is even more strategic considering the increasing costs of the raw materials, as in the case of zirconia. On the other hand the high cost of zirconia is a strong limit in the tile manufacturing industry. The aim of this study is to employ thermal spraying overspray powders into the formulation of ceramic frits, glazes and pigments, in order to avoid hazardous waste disposal and save high priced raw material. This study is a part of the activity done under the LIFE ReTSW-SINT project.

**Results and discussion:** The main results of this study, suggest that the colour of the waste yttrium stabilized zirconia is strictly related with the content of metallic pollutants. We found out also that the pollutant content is concentrated mainly at the fraction of the powders with the highest grain size. For this reason the fractions of waste powders with the lower grain size has been employed in super-white glaze whereas the others fractions for pigment formulations. APS5 waste powder is suitable to replace Zirconium Oxide in frits for white glazes formulation, in the amount of 100 wt%, whereas APS6 waste powder is suitable and more advisable than APS5 to replace a part of the pigment in the amount of 5wt% for five colours: green, grey, beige, yellow and brown, as shown in Figure 1.



**Fig. 1** - a) Standard white glaze; b) APS5 white glaze; c) Standard yellow pigment; d) APS6 yellow.

### $\gamma$ -TiAl ALLOYS PRODUCED BY ELECTRON BEAM MELTING FOR AEROSPACE AND AUTOMOTIVE APPLICATIONS

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**Concept:**  $\gamma$ -TiAl materials represent an important class of structural materials which, thanks to their excellent physical and mechanical properties, play an important role in the aerospace and automotive industries. In particular, they are considered an attractive alternative to nickel-based superalloys due to a lower density. In this work, realized within the European projects TIALCHARGER and E-BREAK and the Regional Project Great2020 Fasell, three kind of  $\gamma$ -TiAl alloys have been investigated: 48-2-2 alloy (aerospace, E-BREAK), TNM alloy (aerospace, E-Break, Great2020 Fasell) and RNT650 alloy (automotive, TIALCHARGER).

**Motivations and objectives:** The Electron Beam Melting (EBM) is an additive manufacturing technology that uses an electron beam to generate parts by selectively melting the powder layer by layer according to CAD data. This technology presents several advantages in terms of costs and energy saving compared to the conventional manufacturing processes. The aims of this work are the evaluation of the powder's recyclability and the optimization of the EBM process parameters using a DOE to obtain the desired microstructure for a specific application after the heat treatment on the well known 48-2-2 alloy, and contemporary the set up of EBM process and the heat treatments on new generation alloys: TNM for turbine blades and RNT650 alloy for turbocharger wheels.

**Results and discussion:** Regarding the recyclability, the analysis performed on powder recycled several times and used for several EBM cycles confirm that, for what concerns particle size distribution, flowability and apparent density, the recycling process adopted doesn't change the powder properties. Regarding the chemistry, it is evident that the recycling process generates only a very small amount of oxygen pick-up which will not affect the specimen production. For the TNM alloy, two heat treatment that give a near lamellar microstructure with the presence of some  $\beta$ -phase have been set. This kind of microstructure is considered the most promising, for the application of this alloy, in terms of tensile properties with sufficient creep properties. For the RNT650 alloy a heat treatment was set up to obtain a near lamellar microstructure both on samples bars and on hollow and full turbocharger wheels. In the image below an EBM turbine blade, a hollow and a normal turbocharger wheel are represented.

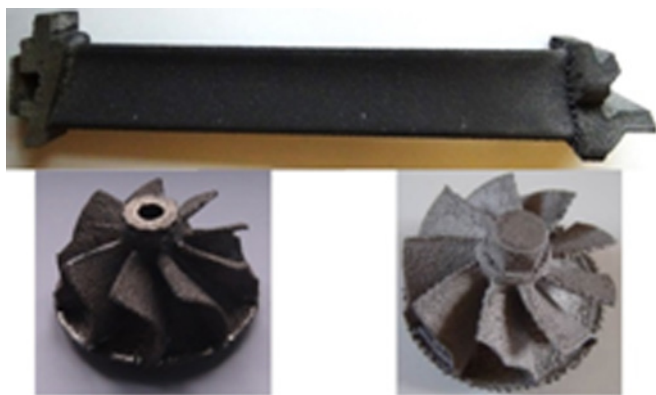


Fig. 1 - Low pressure turbine blade, hollow and normal turbocharger wheel.

### POROUS GLASSES BY USING SALT AS TEMPORARY SPACE HOLDER

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**Concept:** In the present work starting from a spray dry powder (containing at least 70% of cullet), salt was added in different percentages and grain size dis-

tributions in order to obtain porous materials. The prepared mixtures were pressed by uniaxial pressing, obtaining pellets with a diameter of 40 mm. The obtained green samples were dried at 110°C overnight, thereafter a heat treatment at 800-950°C in air for 10-45 minutes was applied. Finally, they were leached in hot distilled water for 4h. The study was planned using the Design of Experiments approach. Seven factors such as temperature, holding time, grain size of salt, thickness of the green body, heating rate, pressure and wt% of salt, were varied during the experimental work. The raw materials and the final porous products were characterized by means of X-Ray powder diffraction, hot stage microscope, optical microscopy, optical dilatometry, apparent density, porosity and particle size distribution. Furthermore, the apparent density values were analysed through statistical methods in order to evaluate all its possible correlation with the selected input factors (or experimental conditions).

**Motivations and objectives:** Nowadays, increased sensibility to environmental issues together with the orientation towards the reuse of waste materials opens to a wide range of new eco-compatible products. In the field of waste management is strengthened the concept of recovery and improvement of wastes arising from different production for their use in new industrial sectors. In this perspective, porous glass production represents an excellent opportunity to re-use large quantities of glass waste. In the present project, glass cullet as glass matrix and salt as pore forming agent were used for the production of porous materials for high-performance buildings in terms of weight and thermal insulation. The use of salt were taken into account considering the possible advantages in terms of adjustable porosity amount, pore shape, and pore size distribution and zero CO<sub>2</sub>-emission.

**Results and discussion:** Porous samples with density between 0.6-1.1g/cm<sup>3</sup> were developed. In Figure 1, the sample obtained using 70wt% of salt is shown as example. The data analysis demonstrated the strong effect of the amount of salt on the apparent density, as expected. Particularly, increasing the wt% of salt from 50 to 70%, the density decreases from 0.98 to 0.87 g/cm<sup>3</sup>, due to the presence of more pores.

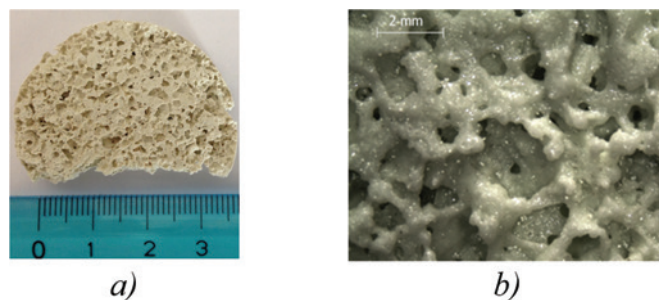


Fig. 1 - a) Porous product obtained with 70 wt% of salt (s70) b) s70 structure at 32x.

### PRELIMINARY SYSTEMATIC INVESTIGATION ON THE UPTAKE OF TITANIA NANOPARTICLES IN SOIL-PLANT SYSTEM

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**Concept:** This study shows the preliminary results on the uptake and effects of TiO<sub>2</sub>-NPs in crop species growing in agronomic soil with different OM (organic matter) content. Standard germination tests for cress (*Lepidium sativum*) were performed in soil matrixes containing different amount of pristine TiO<sub>2</sub>-NPs (*Sigma Aldrich*, average particle size 25 nm, anatase 99.7%, specific surface area 200-220 m<sup>2</sup>/g). Moreover, sorghum (*Sorghum vulgare*, var. Reggal) and pea (*Pisum sativum*, var. Utrillo) species grew for 30 days in controlled laboratory conditions in soils with and without organic fertilization and different amount of NPs added (0, 200, 400 and 800 mg/kg soil). The effect of NPs and OM added to soil was investigated in plants (Ti accumulation and translocation in plant tissues, biomass, macronutrients content) and soil (bioavailable P and Ti). ICP-OES and UV-Vis techniques were used to detect Ti and P, respectively.

**Motivations and objectives:** Nanomaterial products become waste and could be accumulated in the environment, being soil one of the final sink at the end of their life cycle. Soil is susceptible to the accumulation of nanosized-titania directly from fertilizer and/or plant protection products or indirectly from the use of wastewater sewage sludge as manure. Moreover, NPs uptake by agronomic cultures and their translocation to edible plants represent a direct transfer into food chain. Although several studies investigated the accumulation and effects of titania NPs on different plant species, few were conducted in real farm soil and studied in the soil-crop system. Soil OM present or added to the soil to improve fertility could be an important factor that influence the mobility and transfer of NPs into the food chain. It is known that both  $\text{TiO}_2$ -NPs and soil OM are ubiquitous, thus such systematic investigations are of great relevance for health and environment.

**Results and discussion:** Generally, the germination tests performed in cress did not show significant root inhibition. A slight inhibition effect was observed respect to the control soil for 800 mg/kg  $\text{TiO}_2$ -NPs added to the soil without organic fertilization. In soils loaded with OM content the presence of 200 or 400 mg/kg  $\text{TiO}_2$ -NPs also resulted in a slight root inhibition. Moreover, the roots of both sorghum and pea plantlets showed an increased Ti amount as a result of increased NPs concentration in soils. In the presence of increasing amount of  $\text{TiO}_2$ -NPs, a tendency of reduced bioavailable P was found in soil without OM fertilization after the growth of sorghum plants.

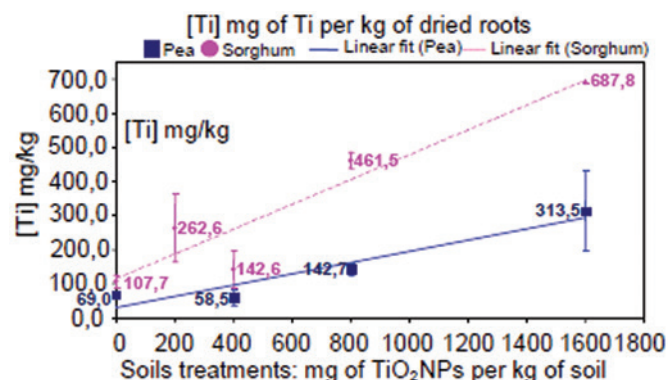


Fig. 1 - Titanium content of sorghum (●) and Pea (■) 30 days old plantlets grown on  $\text{TiO}_2$ -NPs spiked farm soil.

#### ARUNDO DONAX PARTICLES AS REINFORCEMENT FOR PLA BASED COMPOSITES

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**Concept:** Poly(lactic acid) (PLA) is a suitable alternative to conventional petroleum-based polymers in several common applications. Nevertheless, PLA is often modified in many ways to improve its properties, e.g. by the introduction of fillers or fibers, especially for structural applications. Combining PLA with lignocellulosic fibers results in decreased price and increased stiffness, while maintaining the environmental advantage, i.e. compostability. There is a wide range of different natural fibers that are used as fillers of polymeric composites: i.e., obtained from plants grown for their fibre content and from agricultural wastes or by-products. Nevertheless, there are some others that can be potentially used as reinforcements for thermoplastic matrices but not yet investigated, e.g. Arundo donax. A. donax is a perennial rhizomatous grass that grows plenty and naturally in all the temperate areas of Europe. This species shows very high growth rate, it is invasive and aggressive but with almost no economic value and, moreover, difficult to be disposed.

**Motivations and objectives:** Aim of this work was to use particles obtained by grinding the culms of Arundo Donax used as reinforcement for PLA based composites. The influence of the content (10 wt% and 20 wt%) and size (150-300 mm and 300-500 mm) of Arundo Donax filler (ADF) on the morphology and on the properties of PLA-ADF composites was evaluated. The composites were prepared by melt compounding the PLA with ADF using a co-rotating

modular twin screw extruder. For comparison, neat PLA was processed under the same conditions. Both the neat PLA and the composites were characterized by SEM, DSC, tensile and flexural measurements.

**Results and discussion:** The melt compounding of PLA and ADF with a co-rotating twin screw extruder allowed easily obtaining a biocomposite with a good level of filler dispersion, although the extrusion decreases the dimensions, and the l/d distribution of ADF. The addition of ADF significantly influenced all the investigated properties. In particular, by increasing the ADF content, both the tensile and flexural moduli greatly increased whereas the ADF size did not influence significantly the composite stiffness. On the contrary, both the tensile strength and the flexural strength of the filled materials decreased if compared with the neat PLA (Fig. 1).

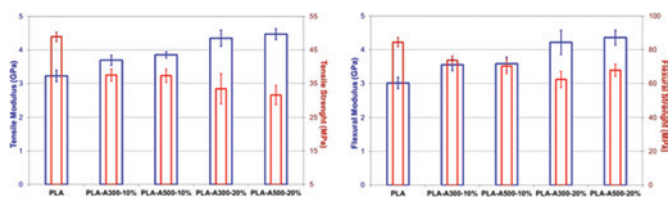


Fig. 1 - Tensile and flexural properties of neat PLA and ADF-reinforced PLA biocomposites.

#### CATIONIC SOLID LIPID NANOPARTICLES COMPLEXED WITH GENETIC MATERIAL FOR LIVER TUMOR TREATMENT

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**Concept:** Gene therapy is a growing field of medicine with great potential for the treatment of several diseases and it is based on the delivery of nucleic acids (DNA, RNA, etc.) to specific cells. To achieve their therapeutic effects, the nucleic acids need to cross several biological barriers and be protected from the degradation by nucleases, present in biological fluids and intracellular compartments, to successfully gain access to their intracellular targets. To overcome these hurdles, it is necessary to deliver the genetic material with biocompatible carriers able to facilitate its translocation across the cell membranes and protect it from being degraded while circulating in the bloodstream. At this purpose, viral and non-viral vectors have been used. Viral vectors usually have high transfection efficiencies, although there are several concerns about their use in human therapy such as an increased immune response, the possible recombination of oncogenes and the difficulty in scale-up. For these reasons, non-viral vectors have emerged as promising carriers due to their reduced immune response, low toxicity and their safety in comparison to viral vectors. Within this field, the use of solid lipid nanoparticles (SLN), made up of biocompatible and biodegradable lipids, solid at room and body temperatures, is of particular importance.

**Motivations and objectives:** In the present study, we aimed to develop cationic solid lipid nanoparticles able to efficiently bind, protect and deliver nucleic acids for the treatment of hepatocellular carcinoma. These nanosystems were designed in order to get features that made them suitable for parenteral administration (size, surface charge and hemocompatibility). We studied their potential as gene delivery systems carrying out biological assays (cytotoxicity, transfection, protection of the genetic material by DNase degradation) on human hepatocellular carcinoma Hep3B cells.

**Results and discussion:** Two different nanosystems were prepared, characterized in terms of size, polydispersity index and zeta potential, and complexed with siRNA and a DNA plasmid using different weight ratios. The physical binding between SLN and the nucleic acids was confirmed by Dynamic Light Scattering measurements and electrophoretic mobility studies. We also verified the acceptability of prepared formulations for parenteral administration performing hemocompatibility assays on human erythrocytes. Finally, in vitro biological characterization confirmed that these nanosystems are not toxic and able to protect and efficiently transfect genetic material to Hep3B cells.

**LIGHT RESPONSIVE NANOSTRUCTURED SYSTEMS FOR DRUG DELIVERY**Botturi A<sup>1,2</sup>, Pedroni M<sup>1,2</sup>, Speghini A<sup>1,2</sup><sup>1</sup>Department of Biotechnology, University of Verona, Verona, Italy; <sup>2</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

**Concept:** Spiroprans are interesting photoswitching systems that can be activated using light in the optical region<sup>1</sup>. The present investigation is focused on the preparation of spiropran encapsulated micelles based on a block copolymer. The characterization of the micelles under ultraviolet light irradiation has been investigated using DLS measurements and spectroscopic techniques. We exploit the upconversion (UC) emission in the ultraviolet region of Tm<sup>3+</sup>/Yb<sup>3+</sup> codoped SrF<sub>2</sub> nanoparticles (NPs) upon near infrared radiation (at around 980 nm), to activate the spiropran molecules.

**Motivations and objectives:** The use of radiation in the near infrared region (NIR) in the biological window (700-1000 nm) is useful for in-vivo applications where light penetration is an important issue. The target of the investigation is to use an NIR excitation radiation to activate nanostructured systems that can be used for drug delivery in-vivo.

**Results and discussion:** Nanostructured systems encapsulating spiropran molecules have been prepared by mixing the reagents with a high-speed disperser. The hydrodynamic radius of the obtained micelles incorporating the spiropran molecules has been found to be around 200 nm. The ultraviolet bands generated under excitation at 980 nm for water colloidal dispersions of Tm<sup>3+</sup>/Yb<sup>3+</sup> codoped SrF<sub>2</sub> NPs can efficiently activate the spiropran molecule by conversion in merocyanine. The hydrophilicity nature of the merocyanine form leads to change in the hydrodynamic size of the nanostructured system.

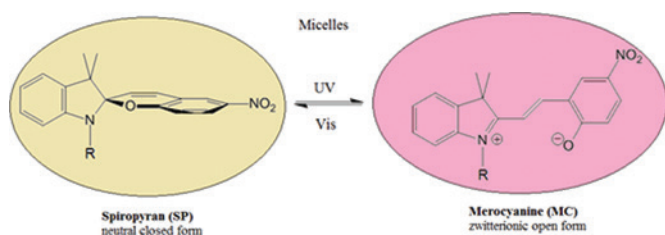


Fig. 1

**CORROSION OF CERAMIC PARTICLE REINFORCED METAL MATRIX COMPOSITES (MMC)**Bragaglia M<sup>1,3</sup>, Montesperelli G<sup>1,3</sup>, Montanari R<sup>2</sup><sup>1</sup>Department of Enterprise Engineering "Mario Lucertini", University of Rome "Tor Vergata", Rome, Italy; <sup>2</sup>Department of Industrial Engineering, University of Rome "Tor Vergata", Rome, Italy; <sup>3</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

**Concept:** The aim of the present work is to study the effect of corrosion on two different (AA6061, AA2618) Aluminum Matrix Composites (AMC<sub>p</sub>) with alumina (Al<sub>2</sub>O<sub>3</sub>) particles reinforcement. Corrosion tests were performed using electrochemical techniques, EIS (Electrochemical Impedance Spectroscopy) and potentiodynamic polarization test in 3,5% NaCl solution on both reinforced and unreinforced alloys.

**Motivations and objectives:** Metal matrix composites (MMC) are advanced materials, composed of a metal matrix and a reinforcement, characterized by high physical and mechanical properties. They have a wide number of application in particular in aeronautical and in automotive field, due to their low weight, high strength and stiffness. The weight reduction achieved by the use of MMC results in a reduction of fuel consumption, pollution emission and consequent cost savings. Generally, the matrix is a light alloy such as Aluminum, Magnesium and Titanium alloys and provides a suitable support for the reinforcement. The reinforcement is a ceramic material (SiC, Al<sub>2</sub>O<sub>3</sub>, TiC, TiN) in the form of particles, whiskers or long fibers. In the wide field of MMC, particles reinforced metal matrix composites (MMC<sub>p</sub>) find a prominent role due to the good compromise between their mechanical properties, such as low density, high Young modulus, good machinability, and their easy and economic production process. Typical applications are combustion engine components, disk brake, wheel rim, advanced sport gear and gas tur-

bine engine equipment. Although their high mechanical performances, it has not been clearly demonstrated if MMC<sub>p</sub> corrosion resistance is adequate and comparable to the unreinforced alloy. It is not completely clear if the presence of the reinforcement phase enhances or decreases the corrosion MMC<sub>p</sub> susceptibility, and if the particles reinforcement plays a role in the corrosion mechanism.

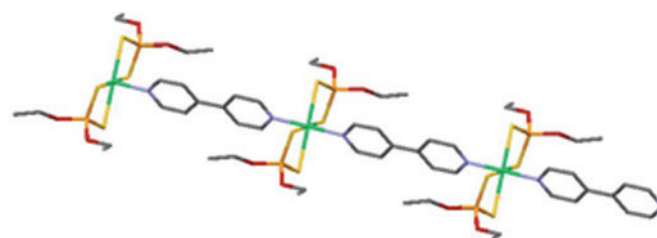
**Results and discussion:** The electrochemical characterization shows that Al<sub>2</sub>O<sub>3</sub> particles reinforced AMC can be used as substitute of the unreinforced alloy. In particular, the AA6061-Al<sub>2</sub>O<sub>3</sub> showed a better corrosion behavior than the AA2618-Al<sub>2</sub>O<sub>3</sub>. The optical microscopy (OM), the scanning electron microscopy (SEM-EDS) and the x-ray diffraction (XRD) analyses showed that the AMC corrosion resistance is influenced by the presence of alumina particles but in a greater way by the intermetallic phases presence which weakens the alumina protective film, exposing the aluminum matrix to the corrosive environment and thus inducing a pitting attack.

**MECHANOSYNTHESIS STUDY OF [Ni((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>·bipy] LAYERED COORDINATION POLYMER**Cabras V<sup>1,2</sup>, Pilloni M<sup>1,2</sup>, Scano S<sup>1</sup>, Lai R<sup>1</sup>, Ennas G<sup>1,2</sup>, Aragoni MC<sup>1,2</sup><sup>1</sup>Department of Chemical and Geological Science, University of Cagliari, Cagliari, Italy; <sup>2</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

**Concept:** Coordination polymers (CPs), in some cases also named Metal Organic Frameworks (MOFs), have attracted the attention for their potential applications in gas storage, gas/vapor separation, catalysis and drug delivery. Moreover, beyond their huge chemical versatility, they are particularly interesting for design strategies and for crystal engineering. These new hybrid organic-inorganic materials were synthesized by connecting metal ions with polytopic organic linkers giving rise to chains (1D), layers (2D) or frameworks (3D) ordered structures. One of the most rational synthesizing methods use the "pillaring" strategy which consists, under solvothermal conditions, in connecting well-defined 2D layers with appropriate pillars.

**Motivations and objectives:** We present here how pillaring can be achieved by a mechanochemical approach and we report on the reactivity study under grinding conditions between Ni(II) complexes and N-donor aromatic ligands such as pyridinyl and bipyridine derivatives to obtain 2D layered compounds.

**Results and discussion:** Synthesis of the coordination polymer [Ni((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>·bipy]<sub>∞</sub> (Fig. 1) was obtained by grinding *bis*-(*O*, *O'*-diethyldithiophosphato)nickel(II) [Ni((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>] (1) and 4,4'-bipyridine (bipy) (2) in a ball milling shaker apparatus (SPEX 8000) teflon jacketed with and without added solvent, giving rise to Liquid Assisted Grinding (LAG) and Solvent free methods respectively. Several grinding variables (milling time, balls size, ball impact frequency, full/empty volume ratio, powder/balls mass ratio and reaction stoichiometry) were investigated in order to promote reaction between (1) and (2). The synthesized ball milling sample has been compared to the corresponding sample prepared by solvothermal approach. Samples were characterized by X-ray Powder Diffraction (XRPD), Infrared Spectroscopy (IR), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The obtained results indicate that solvothermal and ball milling samples were isostructural with very similar thermal behavior.

Fig. 1 - [Ni((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>·bipy]<sub>∞</sub> coordination polymer (hydrogen atoms have been omitted for simplicity).

### INNOVATIVE COMPOSITES BASED ON COMPOSTABLE POLYMERS AND NATURAL FILLERS FOR FOOD PACKAGING

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**Concept:** Composite films and fibers based on compostable polymers (e.g. polylactide (PLA)) and natural fillers (e.g. diatomite, egg shell derived calcium carbonate, antioxidant and antimicrobial agents) were successfully produced by solvent casting and electrospinning technique, respectively. Appropriate antioxidant and antimicrobial molecules were stabilized by immobilization on particles surface via chemi/physi-sorption. The prepared functionalised particles were used as fillers, acting both as reinforcing fillers, thermal and gas barrier and carrier of antioxidant and antimicrobial molecules. The efficacy of the chemi/physi-sorption protocols was demonstrated by observation at scanning electron microscopy (SEM), X-ray diffraction and FT-IR spectroscopy measurements. Morphology and filler dispersion were analysed at SEM, the thermal properties by differential scanning calorimetry (DSC), the phase analysis by XRD, the mechanical properties by uniaxial tensile tests.

**Motivations and objectives:** In the food packaging field biopolymers have attracted a lot of interest as promising alternative to the non-biodegradable petrochemical-derived polymers, currently used in this sector. However, their industrial application is limited by their poor mechanical, thermal and barrier properties. In this framework, the development of multifunctional compostable systems with improved features needs to be urgently addressed. To achieve this aim, composite systems based on PLA and functional fillers were prepared and tested. Suitable fillers with immobilized antioxidant/antimicrobial agents were employed in order to provide a double gas barrier effect, by mechanical action of the used particles that generate a tortuous path, preventing the gas flux, and oxygen scavenger activity of the used antioxidants. This novel approach allows not only to confer an enhanced barrier to gases but also to directly interact with the environment, extending shelf life and food quality.

**Results and discussion:** The selected antioxidant and antimicrobial agents were successfully immobilized on the particle surface (Fig. 1a). Defect-free composite films and electrospun mats consisted of randomly oriented fibers were obtained. The fillers were well dispersed and showed good compatibility with the polymeric matrix. The addition of inorganic fillers allowed to improve the mechanical properties in terms of Young modulus and tensile strength, due to the good interface filler/matrix (Fig. 1b), whereas the natural antioxidants usually act as plasticizers.

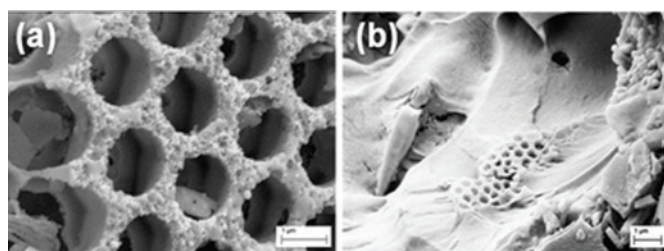


Fig. 1 - SEM micrographs of ascorbic acid physisorbed on diatomite (a) and of stress-strained surface of PLA loaded with diatomite (b).

### GOLD SILICA NANOPARTICLES: VERSATILE SYNTHESIS FOR A VERSATILE MATERIAL

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**Concept:** Nanoparticles (NPs) have gained a lot of interest due to their exceptional and fascinating properties, which have been accomplishing vital role in emerging science and technology according to their structures that permit multifunctional applications. In fact, NPs are versatile materials and adjust-

ing the reaction conditions, it is possible to synthesize them in different way (about size, shape) according to the field of application. Control of NPs size, shape and coating has been the focus of continuous efforts.

**Motivations and objectives:** In this light, our group is working on the preparation of nanostructured materials for applications in the field of metamaterials and treatment of neoplastic diseases. Both areas have required the preparation of gold NPs, but with different characteristics: in particular, the biomedical domain requires water soluble systems, while in the field of metamaterials is desirable to have nanoparticle systems compatible with a series of organic solvents for successive treatment in the preparation of dedicated devices. Our objective is to optimize synthetic protocol addressed to the final NPs use.

**Results and discussion:** On this basis, it was planned and realized the preparation and characterization of gold-core/silica-shell NPs entrapping transition metal complexes (TMCs) to test them as sensitizers in photodynamic therapy; the used synthetic strategy was the sol-gel method, in a quaternary water/oil microemulsion, and using HAuCl<sub>4</sub> source of gold, APTES and TEOS as silica source, NaBH<sub>4</sub> and a thiol as reducing and coating gold agents. The reaction occurs at room temperature and permits to produce homogeneous water soluble nanoparticles, with a gold core more or less of 5 nm. These NPs generate <sup>1</sup>O<sub>2</sub> and were administered to tumor cell culture. Alongside, NPs with larger size was obtained by single-phase aqueous reduction of HAuCl<sub>4</sub> by sodium citrate. The resulting particles are coated with negatively charged citrate ions and dispersed in water. This reaction is more sensible to temperature, concentration and pH, but allows an easy way to change citrate coating with polymeric one (e.g. PVP) compatible with organic solvents. Thanks to the intense plasmonic band, these NPs (Fig. 1) are suitable to be used in gain-assisted system for metamaterial application.

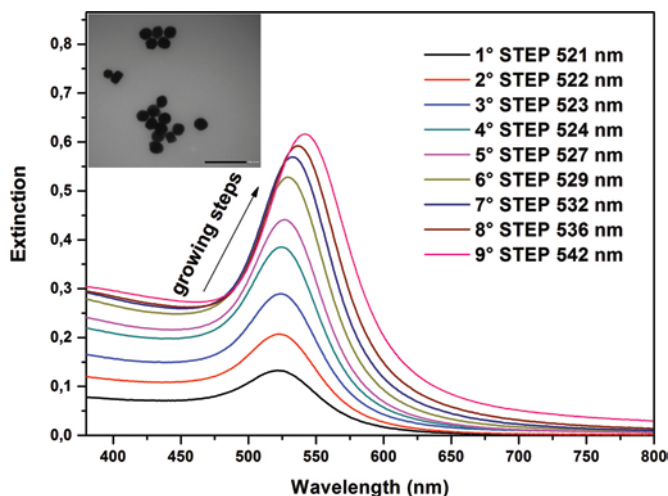


Fig. 1 - TEM images of the PVP-coated gold NP and plasmonic bands.

### PREPARATION AND PHYSICO-CHEMICAL CHARACTERIZATION OF BIOCOSMOSITES BASED ON CELLULOSE DERIVATIVES AND MCM-41

Saladino <sup>ML1,2</sup>, Bertolino <sup>V1,2</sup>, Colomba <sup>P1,2</sup>, Caponetti <sup>E1,2,3</sup>

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**Concept:** Biocompatible and biodegradable composites can be used in several fields such as medicine, alimentary industry, conservation of cultural heritage, and tissue engineering. Cellulose derivatives are applied as components of hydrogel formulations, used as drug-delivery system, in synthesis of new temperature-responsive hydrogel for functional finishing of cotton knitwear, in coating formulations to reduce oil uptake in deep-fat frying potato strips and dough discs. The incorporation of mesoporous silica in the cellulose open to new applications. The preparation of the composites was performed by solvent casting. The characterization was performed using X-ray diffractometry, transmission electron microscopy, thermogravimetry and NMR spectroscopy.

**Motivations and objectives:** The goal of this work was the preparation of composites based on the mesoporous silica MCM-41 as filler and three different cellulose derivatives, carboxymethylcellulose, hydroxypropylmethylcellulose and methylcellulose. The MCM-41 is nontoxic, biocompatible and has been used as adjuvant and excipient in medicine, in pharmacy, as adsorbent for pollution and for heavy metals in water. The use of MCM-41 as filler in a biocompatible composite can improve the thermal and mechanical properties of the polymer. In addition, the possibility to incorporate drugs and/or biocides in the MCM-41 pores could lead to the develop of a composite for the preventive conservation in the field of cultural heritage and of packaging.

**Results and discussion:** Results showed that the particles of filler are homogeneously dispersed in each polymer and that the thermal properties depends on the function group and on the concentration.



Fig. 1 - Photo of a MCM-41- carboxymethylcellulose composite.

#### DEGRADATION OF PA11 NANOCOMPOSITES: THE CHEMICAL POINT OF VIEW

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**Concept:** In view of novel PA11 green applications, the thermal and thermo-oxidative degradation processes occurring on PA11 samples and PA11 nanocomposites (Cloisite®30B at 3 and 9%) were investigated. Thermal and thermal-oxidation was performed in a glass vessel at 215°C under N<sub>2</sub> flow or atmospheric air up to 150 minutes. The oxidized materials were analyzed by size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). Data obtained for thermo-oxidized PA11 nanocomposites, ascertained an active contribution of organo-modifier clays in accelerating cross-linking reactions. An elucidation of possible mechanism involved was discussed. Furthermore, a strictly connection between the appearance of a characteristic peak in the MALDI spectra of degraded samples and gel formation was also highlighted.

**Motivations and objectives:** It is well known that polyamides are not intrinsically stable in the presence of oxygen and/or humidity especially at high temperature. The literature clearly identified as most relevant the  $\alpha$ -CH hydrogen abstraction oxidative mechanism followed by the Karsten and Rossbach pathway for the interpretation of residue formation. Contradictory opinions about the degradation processes involving PAs nanocomposites materials were found. Improvement in thermal stability of PA11 and PA12 were observed for nanoclay concentration of 2-4%. On the other hand, was not clear as nanoclays affect the degradation pathways of PAs nanocomposites. We aim to investigate both thermal degradation processes (non oxidative and oxidative) occurring in PA11 nanocomposites and establish the eventual contribution of organo nanoclay modifier on degradation mechanisms.

**Results and discussion:** During thermal oxidation, PA11 nanocomposites samples degraded faster than virgin PA11 material producing an higher amount of insoluble residue. The formation of gel fraction was accomplished by the appearance of a characteristic peak in the MALDI spectra. We suppose

that  $\alpha$  olefins produced by Hofmann elimination reaction from Cloisite®30B were responsible for the increase of rate of cross linking reactions. In fact,  $\alpha$  olefins are very susceptible to air and moisture, producing oxygenated (aldehydes, acids) as final products. During initial step of auto-oxidation, the formation of  $\alpha$  olefin hydroperoxides is accomplished by the capture of available hydrogens; the favourable attack is without doubt to the  $\alpha$  amino methylene positions of PA11 chains. At this point, the well known  $\alpha$ -CH hydrogen abstraction mechanism proceeds, accelerating the formation of amide terminal chain groups and consequently the gel fraction. The amide degradation products were identified and revealed as a characteristic peak in the MALDI spectra.

#### POLYETHERIMIDE BASED NANOCOMPOSITES FOR AEROSPACE APPLICATIONS

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<sup>1</sup>Department of Enterprise Engineering "Mario Lucertini", University of Rome "Tor Vergata", Rome, Italy; <sup>2</sup>MAG-Mecaer Aviation Group, Monteprandone, Italy; <sup>3</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

**Concept:** The aim of our research, following a bottom-up methodology, is to start from the modification of the raw material, to better the performance of the final component. In particular we investigate innovative nanocomposites made of PEI (polyetherimide, a polymer suitable for aerospace "not critical" application) loaded with nanofillers (multiwalled carbon nanotubes (CNT) and nanoclays) to increase specific properties, as mechanical strength, stiffness, vibration damping.

**Motivations and objectives:** Additive layer manufacturing is becoming a key technology for material processing, due to its intrinsic versatility and ease of processing. Nevertheless, at present, still some major issues need to be investigated, mainly regarding processing, quality of the finish, reproducibility, and possibility to process new materials. Regarding the latter, great attention is placed in polymers. At present only a relatively small selection of polymers can be processed, particularly via Fused Deposition Modelling (FDM), limiting their application in engineering and advanced applications, as space.

**Results and discussion:** Multiwalled carbon nanotubes (CNT) and nanoclays are initially characterized and processed (by means of ultrasonication and functionalization) to insure good dispersion and mechanical interlocking to the PEI matrix. Then they are added to the polymers and films are produced and tested by means of: tensile testing, dynamic scanning calorimetry (DSC), and morphology observed by electron microscopy (SEM).

#### THE EFFECTS OF TiO<sub>2</sub> TRAP SITES ON THE INSTABILITY OF DYE SENSITIZED SOLAR CELLS

Chiappara C<sup>1</sup>, Figà V<sup>1</sup>, Di Marco G<sup>2</sup>, Calogero G<sup>2</sup>, Pignataro B<sup>1,3</sup>, Principato F<sup>1</sup>

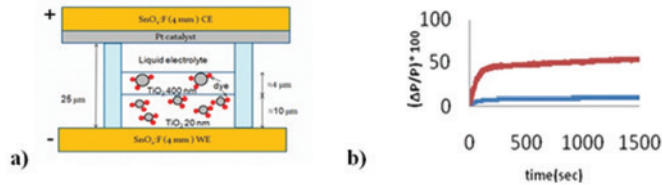
<sup>1</sup>Department of Physics and Chemistry, University of Palermo, Palermo, Italy; <sup>2</sup>Institute for Chemical and Physical Processes (IPCF), CNR, Messina, Italy; <sup>3</sup>National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

**Concept:** The present work is part of the research project (PON-ENERGETIC) for the development of dye sensitized solar cells at low cost. In this work we studied the instability phenomenon present in Ruthenium-based (N719) dye sensitized solar cells (DSSCs). This is mainly observed by the increase of the short circuit current (I<sub>sc</sub>) and the open circuit voltage (V<sub>oc</sub>) when the cell is under illumination, but it occurs even in dark with the decreasing of the dark forward bias current. This phenomenon depends on the charge transport mechanism at the TiO<sub>2</sub>-electrolyte interface and has been investigated by electrical measurements. In particular, the current and voltage transients were measured, both under dark and light conditions, by controlling and monitoring the temperature of the cells. Moreover, the Electrochemical Impedance Spectroscopy (EIS) was used to measure the variations of the electron lifetimes in the TiO<sub>2</sub> during the transients. We show that instability is induced by traps with energy levels in the midgap of TiO<sub>2</sub> and that the kinetics of trapping depends on the type of components present in the liquid redox electrolyte.

**Motivations and objectives:** The instability observed in the investigated DSSC, although it leads to improvement of the cell performance during their operation, it is a crucial point for the development of manufacturing technology of DSC cells and modules. The aim of this work is to investigate the

mechanism occurring at the TiO<sub>2</sub>-electrolyte interface which is responsible of the drifts of the DSSC parameters.

**Results and discussion:** The analysis show that these drifts do not depend on the temperature of the cell and are mainly due to electron trapping by the defects present in the TiO<sub>2</sub> which communicate with ions, such as Li<sup>+</sup>. The trap sites in the oxide limit the recombination of electrons from TiO<sub>2</sub> to the tri-iodide present in the electrolyte. This mechanism has been confirmed by EIS measurements performed at different time intervals, which show the increasing of the electron life-time.



**Fig. 1 - a)** The investigated DSSC, **b)** Variation over time of I<sub>sc</sub> (red) and V<sub>oc</sub> (blue) of the DSSC.

**SUSTAINABLE BIOCOMPOSITES BASED ON POLYMERS AND NATURAL FIBRES FROM RENEWABLE RESOURCES**

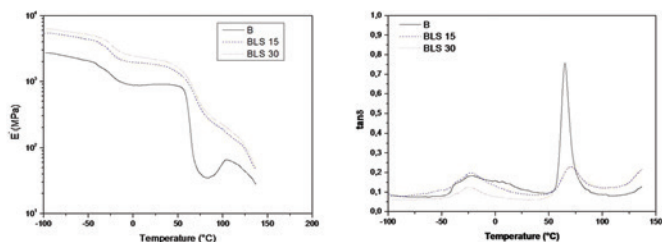
Cinelli P<sup>1,3</sup>, Lazzeri A<sup>1,3</sup>, Del Monte C<sup>2</sup>, Bronco S<sup>2,3</sup>

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**Concept:** The present research is focused on the valorization of natural fibers by products of forest or agriculture industries such as wood fibers or fibers derived by legume by-products. The biobased composites were addressed with different compostable polymeric matrices. We report here the results of biocomposites production with polylactic acid (PLA) as polymeric matrix. PLA was plasticized with biodegradable plasticizer and eventually in presence of other compostable polymers such as poly(butyrate adipate-co- terephthalate) (PBAT).

**Motivations and objectives:** The development of bio-based materials from renewable biomass has become an important challenge. Their use for production of biobased composites has attracted interest of various application sectors ranging from packaging to automotive components and other high value applications. To optimize properties of the materials and maximize the fibers load a good dispersion and matrix to fibers adhesion is required. In particular for production of composites with bio based biodegradable polymers it is important to address fibers pre treatment and use of compatibilizers. The objective of the present research is the selection of formulation for the production of composites with good dispersion of fibers and addressing the production of composite materials by processing on pilot scale.

**Results and discussion:** Fibers from wood, legume and cellulose were used for production of composites with PLA, or PLA and PBAT 50/50 (B). For example wood fibres addition B matrix evidence an increase in modulus composites were prepared with industrial extruder with 30% by weight of natural fibers. Authors acknowledge the financial support from the European Union's 7FP, DIBBIOPACK Development of injection and extrusion blow molded biodegradable and multifunctional packages by nanotechnologies GA: n° 280676, and LEGUAL Valorisation of legumes co-products and by-products for package application and energy production from biomass, GA 315241.



**Fig. 1 -** Dynamic thermal analysis of a PLA/Ecoflex 50/50 matrix (B) with 15% or 30% by weight of wood fibres.

**STUDY OF FIBRE-REINFORCED CEMENT-BASED COMPOSITES CONTAINING EXPANSIVE AGENT**

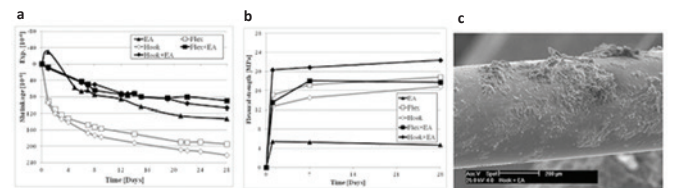
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**Concept:** In this work several Fibre Reinforced Cement-based Composites (FRCCs) were studied, in which CaO-based expansive agent was added in order to help in reducing the risk of cracking induced by drying shrinkage. Two different kinds of metallic reinforcing fibres were tested: flat (and flexible) steel-alloy fibres, and brass-coated hooked steel fibres. All the mixtures were characterized at both fresh and hardened state, by measuring fresh consistency, compressive and flexural strength, as well as length changes under drying shrinkage test. Moreover, FRCC microstructure was investigated by means of Scanning Electron Microscope (SEM) observations. Results obtained confirmed the effectiveness of CaO addition on material stability under drying shrinkage; moreover, it seems to produce a beneficial effect on flexural strength if used with brass-coated fibres. The reason of this synergy probably lies in the improved adhesion at the interface fibre-matrix.

**Motivations and objectives:** The first scope of this paper was to verify the positive influence of CaO-based expansive agent on reducing the autogenous shrinkage of FRCCs prepared with a w/c of 0,30. In fact, a problem involving these cement-based composites with low w/b ratio is the likely tendency to crack at early age, due to autogenous and plastic shrinkages. The second scope was to evaluate the influence of CaO-based expansive agent on the flexural strength of FRCC with high volume of metallic fibres. In fact, some papers are reported in the literature in which an improvement of flexural strength was found thanks to a certain synergy between expansive agent and steel fibres. However, in these papers the mechanism though which this likely synergy is able to develop was not investigated.

**Results and discussion:** The addition of CaO-based expansive agent proved to be effective on counteracting concrete shrinkage (less 60% shrinkage after 28 days of exposure to 50% R.H., Fig. 1a), as well as in terms of flexural strength improvement when used with brass-coated fibres (+60% 24-hour flexural strength, Fig. 1b). The reason of this synergy between CaO-based expansive agent and brass-coated steel fibres probably lies in the formation of calcium- hydroxy-zincate crystals at the interface between fibres and surrounding cement paste; this phenomenon is promoted by dezincification of brass in alkaline environment (due to the presence of high amount of Ca(OH)<sub>2</sub> formed when CaO comes in contact with water): these hydroxy-zincate crystals, as observed by SEM, are likely able to significantly improve the quality of the interface fibre-matrix by increasing the adherence (Fig 1c).



**Fig. 1 - (a)** Drying shrinkage results, **(b)** bending test results, **(c)** SEM observation of brass-coated fiber.

**SUB-MICROMETRICAL 3D PATTERNING FOR LARGE AREAS: FILLING THE GAP**

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**Concept:** Most of the technology to achieve nano scale feature have several limitation due to beam drift, diffraction and costs. We tried to solve this problem with FIB technics developing a method to produce large pattern with reduced costs and process time.

**Motivations and objectives:** Nowadays various technologies are being used for surface micromachining for microelectronics industry and biological application. Patterning with a focused ion beam (FIB) is an extremely versatile tool to realize 3D pattern without require assembling. Nanolithography and



soft-lithography are becoming the most important applications of nanofabrication but large area patterning is still the problem. The main objectives of this work have been to realize 3D pattern on large areas with the Focused Ion Beam. The possibility to create a head print to use as a master in the soft lithography solves several problems correlated with the electron and ion lithography as the beam drift that produces stitching problems or the excessive processing time (more than 24 hr for few mm<sup>2</sup>).

**Results and discussion:** Using homemade scripts, we have developed a method to control and reduce the ion beam drift. We applied this methodology to build a metamaterial for opto-electronic application developing a bitmap template to cover a surface of 20 × 20 mm, Then we have realized a stitched patterned area for 1mm<sup>2</sup> in few hours. Furthermore, a new method has been developed to design 3D patterns because the default tools of FIB can realize only 2D structures and simple 3D ones. This method starts from the 3D model design using a CAD software, then the solid feature is meshed and the coordinates of nodes are saved in a stream file according a specific sequence. In this way, it is possible to modulate the deep of the pattern at sub-micrometrical scale.

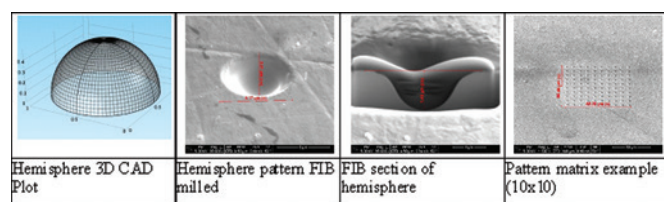


Fig. 1

#### STRUCTURE AND MECHANICAL PROPERTIES OF COPOLYMERS OF SYNDIOTACTIC POLYPROPYLENE WITH BRANCHED MONOMERS

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**Concept:** Syndiotactic polypropylene (sPP) is a superb example of a low cost, high modulus thermoplastic elastomer presenting "polymorphic superelasticity". Highly stereoregular samples, indeed, show elastic behavior in a large deformation range and in a wide range of temperature despite the high degree of crystallinity and high stiffness, thanks to the occurrence of a crystal-crystal phase transition during deformation and relaxation. Copolymers of sPP with other  $\alpha$ -olefins are a new class of elastomers where crystallinity, rigidity and elasticity can be tailored through choice of type and concentration of the comonomer. Incorporation of long branched comonomers, as 1-octadecene and 1-eicosene, allows decrease of the glass transition temperature and development of interesting elastomeric materials.

**Motivations and objectives:** In this communication we report a study of the structure and mechanical properties of copolymers of sPP with branched  $\alpha$ -olefins, as 1-octadecene and 1-eicosene. The effect of the presence of long branches on the crystallization behaviour and elastomeric properties of sPP has been analyzed. The relationships between structure and stress-induced phase transformations and mechanical properties have been clarified. The polymorphic transformations occurring during deformation have been studied by recording X-ray diffraction during stretching and relaxation. This study is motivated by the fact that understanding the effect of constitutional defects, as comonomeric units, on the polymorphic behaviour and mechanical properties of sPP allows tailoring the physical properties of sPP through controlled incorporation of defects.

**Results and discussion:** Samples of copolymers of sPP with 1-octadecene and 1-eicosene have been synthesized with Cs metallocene catalyst and 1-octadecene concentration in the range 1-6 mol% and 1-eicosene concentration in the range 1-9 mol%. All samples show good ductility, high modulus and good elastic properties. Low glass transition temperature is achieved already for low comonomer concentration. In samples with low comonomer content defective crystals of form I partially transform by stretching into the trans-planar form III of sPP, and the elastic recovery is associated with the polymorphic transition of the metastable trans-planar form III into the more stable helical form II and of the trans-planar mesomorphic form of sPP that occurs upon releasing the tension. This transition provides an enthalpic contribution to the elasticity. Samples with higher comonomer concentrations show very low crystallinity and a typical thermoplastic elastomeric behavior. High flexibility is due to the

transformation by stretching of highly defective crystals of form I in the helical mesomorphic form of sPP. In this case, the small crystalline domains in the amorphous matrix act as physical knots of the elastomeric lattice, preventing the viscous flow of the amorphous chains during stretching. The entropic effect of the conformational transition of the amorphous chains from the extended conformation in the stretched state, to the disordered coil conformation assumed when the tension is removed, is mainly responsible for the elasticity.

#### DETECTION OF VOIDS IN STRUCTURAL COMPOSITE LAMINATES AND EVALUATION OF THEIR EFFECTS OVER MATERIAL PERFORMANCES

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**Concept:** Defects in the form of diffused voids are usually present in composite laminates as result of processing procedure. Even efficient techniques for laminate production, commonly employed in aerospace and advanced automotive industry, as vacuum bag/autoclave processes cannot avoid the formation of embedded defects. The presence of voids has detrimental effects over the general performances of the material and should be limited as much as possible. Presence of residual solvent, humidity and/or trapped air is the most common cause of porosity in laminates. A proper choice of processing conditions is crucial for defects limitation and for the optimization of performances. However, reliable experimental methods for voids detection are necessary, which can evidence and quantitatively estimate their presence.

**Motivations and objectives:** Curing cycle parameters and rheological changes occurring during processing are related to void generation during advanced composite production. Laminates with variable amount of voids are thus obtained by a proper selection of production procedure. The detection of actual voids content is subject to remarkable uncertainties, related to the specific analysis method employed. Different void analysis techniques are applied to laminates of variable thickness to compare their quantitative detection capability and their specific advantages and limitations. The relationship between voids and laminates mechanical performance are evaluated.

**Results and discussion:** A direct relationship is found between autoclave pressure and voids presence in carbon/epoxy laminates. The rheological analysis allows to set the proper timing for processing conditions. A comparison between gravimetric, optical, tomographic and ultrasonic methods is presented; results show that SEM-image analysis is an adequate method which produces reliable data provided a sufficient number of images are observed. Tensile, compressive, short beam tests confirm the relevance of voids over mechanical properties (Fig. 1).

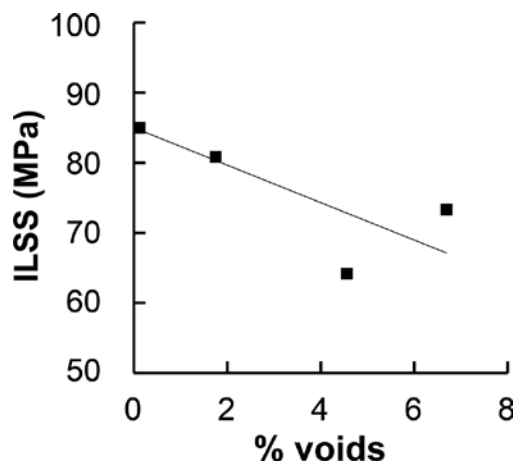


Fig. 1 - Interlaminar shear strength of carbon composite laminates with different void contents.



### DEVELOPMENT AND CHARACTERIZATION OF PHOTOCATALYTIC ANODIC TiO<sub>2</sub> FILMS FOR ENVIRONMENTAL REMEDIATION

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**Concept:** Aim of this work is to develop TiO<sub>2</sub> films by anodic oxidation of metallic titanium to be used in environmental remediation, from wastewater treatment to air purification, and identify operative conditions that maximize their photocatalytic efficiency while maintaining economic viability of preparation to avoid precluding possible technological transfer at industrial scale. Three different anodizing procedures were identified as suitable to produce photocatalytic oxides, each one having different advantages, from fast production, to the concomitant presence of photocatalytic activity and interference coloration for design applications, to the achievement of excellent efficiencies for purification devices. In all cases, the advantage of immobilized photocatalyst over more common treatments employing dispersed particles is huge, because no photocatalyst separation is required after water treatment.

**Motivations and objectives:** The growing attention to environmental problems has pushed scientific research towards more sustainable and environmental-friendly technologies and industrial processes, which often focus on the use of titanium oxides by exploiting their renowned photocatalytic activity in the degradation of polluting compounds. This work aims at developing anodic TiO<sub>2</sub> photocatalysts and optimizing anodizing processes to identify operative conditions that maximize the oxide photocatalytic efficiency. Resulting oxide properties depend on anodizing parameters, such as: electrolyte, anodizing duration, cell voltage, and current density employed. Moreover, TiO<sub>2</sub> photoactivation relies on its crystalline structure and specific surface area, which define the quantity of surface sites available for photocatalytic reactions. In this work, several anodizing procedures were evaluated and the degradation of an organic dye, Rhodamine-B, was chosen as model photocatalytic reaction.

**Results and discussion:** The best anodizing condition for three main groups of TiO<sub>2</sub> photocatalysts, divided according to production methodology, was identified (Fig. 1): anodizing for two minutes at a cell voltage of 150 V in H<sub>2</sub>SO<sub>4</sub> (fast process); anodizing at 110 V + annealing at 500°C (photocatalytic oxides showing interference colors); anodizing at 60 V for 30 minutes in organic solution containing fluorides + 1 h annealing at 400°C (nanotubular oxides, optimal efficiency). Possible applications are described above in the concept section.

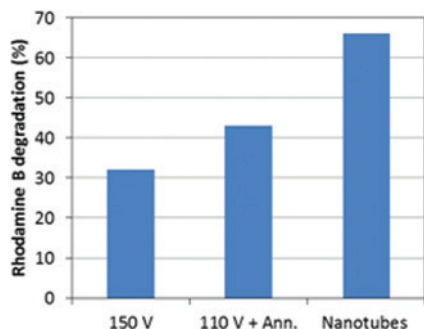


Fig. 1 - Rhodamine B degradation after 6 h irradiation with 3 mW/cm<sup>2</sup> UV/Vis light in presence of different TiO<sub>2</sub> films.

### IMMISCIBLE POLYMER BLENDS HAVING PLATE-LIKE NANOPARTICLES ADSORBED AT THE POLYMER-POLYMER INTERFACE: DYNAMICS OF FILLER ASSEMBLY AND MORPHOLOGICAL IMPLICATIONS

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**Concept:** The assembly of lamellar (clay) nanoparticles in a blend of polystyrene (PS) and poly(methylmethacrylate) (PMMA) with drop-matrix morphology is studied. Besides assessing the effect of the presence of liquid interfaces on the assembly process, the impact of the filler on the morphology of the blend

is also investigated. The PMMA drops anchor the lamellae frustrating their peculiar mobility in the polymer melt. Once the polymer-polymer interface is saturated, a space-spanning particle network builds up. The latter exhibits the same features of networks which form in homogeneous mediums. Contextually, the nanoparticles radically affect the blend morphology, inducing irregularly-shaped drops and drop clustering phenomena. The latter can be exploited to promote co-continuity at low amounts of either of the polymer phases.

**Motivations and objectives:** Multiphase fluid systems having interfacially adsorbed particles offer the possibility to drive and control the material morphology and, through it, the macroscopic properties. Peculiar morphological features, such as drop clusters, non-spherical droplets and co-continuous morphologies can be promoted and stabilized through a clever use of nanoparticles. Although desirable, manipulating the morphology of polymer blends by means of nanoparticles remains a challenging task, and many issues remain unresolved for a truly engineering of new tailor-made materials. The present study fits in this context, as it aims to highlight the complex phenomena which eventually determine the micro- and meso-structure forming in multiphase polymer systems.

**Results and discussion:** At the end of the time scans, the normalized equilibrium modulus,  $G'(t \rightarrow \infty)/G'(t = 0)$ , gradually scales with the filler content,  $\Phi$ , reflecting the inherent mobility of the particle in a homogeneous medium. On the contrary, in the blend the jump at  $\Phi \sim 1\%$  reflects the "off-to-on" switch of the particle mobility once the filler saturates nearly completely the PS/PMMA interface. Morphological analyses on two samples around this threshold (Fig. 1a, full symbols) definitely confirm such a conclusion. Once allowed to freely rearrange in the PS phase, the filler assembles, connecting drops and drops clusters and eventually forming a space-spanning network, whose features resemble those of superstructures forming in homogeneous medium. On the other hand, the presence of clustering phenomena is responsible for the development of co-continuous morphologies at amounts of the minor phase,  $\Phi_{PMMA}$ , lower than in the unfilled biphasic PS/PMMA system (Fig. 1b).

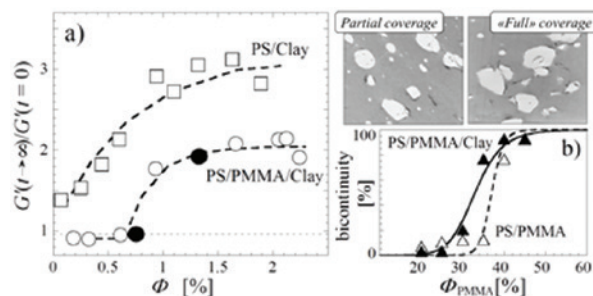


Fig. 1

### TiO<sub>2</sub> COATED PD MEMBRANES FOR PROPANE DEHYDROGENATION

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**Concept:** A TiO<sub>2</sub> film is deposited by nanosol/dip-coating on a Pd/Al<sub>2</sub>O<sub>3</sub> tubular membrane to prevent the deactivation over the palladium layer, during the propane dehydrogenation in a membrane reactor. The TiO<sub>2</sub> film is prepared by sol-gel method carried out by controlled hydrolysis of tetraisopropyl orthotitanate (TIPT), then it is deposited by dip-coating. The palladium membrane is dipped five times at the same speed, each time is dried in vacuum oven at 200°C for 1 hour and finally calcined at 500°C for 1 hour.

**Motivations and objectives:** The use of catalytic membrane reactor (CMR) for propane dehydrogenation enhances alkane conversion by a selective removal of hydrogen from the reaction media. However, hydrogen permeance through Pd-based membranes is strongly affected by Pd-C formation and coke deposition due to the propylene diffusion through the palladium film. In order to prevent the hydrogen permeance decrease, we coated Pd-membrane by a thin oxide layer in order to avoid the propylene diffusion but allow the H<sub>2</sub> one.

**Results and discussion:** We investigated the permeation behavior of the TiO<sub>2</sub>/Pd membrane, and the effect of the propylene decomposition over palladium film, on hydrogen permeance, by using a tubular CMR. A mixture containing a ratio H<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> 1/1 (60N<sub>2</sub>:20H<sub>2</sub>:20C<sub>3</sub>H<sub>6</sub>) was fed in the membrane

reactor at two temperature 400 and 450°C in order to simulate the PDH process, and the  $H_2$  permeate flux was monitored via digital mass flow meter. A decrease in  $H_2$  permeate flux at both temperatures investigated was observed, which means that the  $TiO_2$  layer partially block the  $C_3H_8$  diffusion. Although, a slight improvement was observed respect to the only Pd membrane, the SEM images (Fig. 1) show a very thin (about 200 nm) microporous layer of  $TiO_2$ , but still some cracks are observed, probably due to the grains microstructure of Pd film and its roughness. A  $TiO_2$  layer without cracks and holes, was instead obtained on a glass sample with a very smooth surface. Although, the  $TiO_2$  layer showed promising results to limit the Pd-C formation and coke deposition, some improvements in the preparation method are required, varying for instance, the dip-coating speed and/or calcinations treatments, in order to get a dense oxide layer without cracks. The authors would like to thank the Italy-Israel project MEME "Molten salt heated membrane reactor for propane dehydrogenation. Energy saving new process".

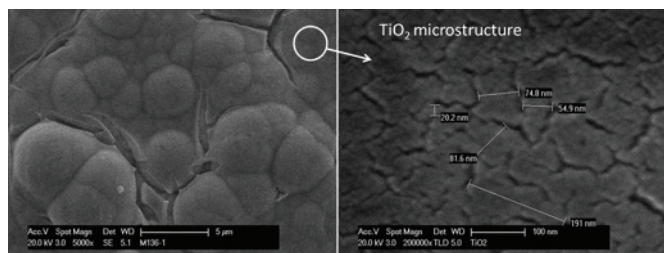


Fig. 1 - Top-view of  $TiO_2$  layer deposited on Pd membrane.

#### BALLISTIC RESPONSE OF SELF-HEALING POLYMERS AND COMPONENTS

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**Concept:** Self-healing (SH) polymers and composites have gained large attention in recent years. Different solutions to get autonomic mending capabilities have been investigated, including dispersed micro-vessels/vascular network containing reactive substances, reversible chemical bonds and supramolecular chemistry. Some thermoplastics, such as ethylene-co-methacrylic acid based ionomers, can autonomously heal impacts in a wide range of ballistic conditions. In these materials, healing results from polymer melting and re-solidification activated by projectile passage. A number of potential applications profiting of such particular behavior have been devised: inflatable and/or inhabited space environments, which are exposed to high-speed micrometeoroids; fuel or dangerous liquid containers, subjected to low energy impacts, are some examples of possible applications of such SH materials. Since autonomic healing polymers usually possess limited mechanical properties, their reinforcement or coupling with stiffer and stronger materials as in multilayer structures is often advisable.

**Motivations and objectives:** In view of cited uses, plain ionomer and aramid reinforced ionomer plates, as well as ionomer/carbon composite panels, were tested under ballistic conditions at various projectile impact speeds and angles. In multilayer materials, the mutual interactions between constituents may lead to adverse effects over impact damage and healing response. The autonomic healing efficiency of different plate/projectile configurations and the importance of the related healing mechanisms were thus investigated and discussed. Similarly, in case of tanks, the presence of a dense internal fluid can remarkably change the deformation behavior and healing response of ionomeric walls as result of a projectile impact. Preliminary results with a tank mock-up are presented.

**Results and discussion:** The results of ballistic campaign show that plain ionomer panels present efficient SH behavior in a range of projectile speed/impact angles. In addition, in tanks, the presence of inner liquid improves mending efficiency, supporting the deformation recover during the healing process. However, in composite and multilayer panels, the presence of

rigid reinforcement or backing remarkably reduces healing chances suggesting that free deformation is required for efficient recovery and healing. Encouraging results were obtained with ionomer/honeycomb-core/composite structures in which the ionomeric skin can efficiently heal (Fig. 1).

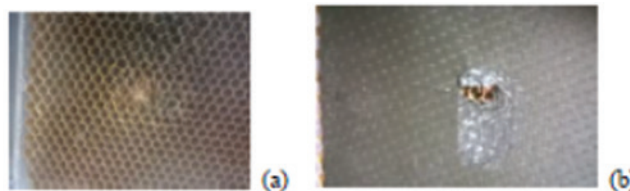


Fig. 1 - Front (a) and back (b) of an ionomer/honeycomb/carbon panel impacted with a 10 mm steel ball at 180 m/s.

#### DEVELOPMENT OF COMPOSITE PIEZOELECTRIC MATERIALS FOR ENERGY HARVESTING

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**Concept:** The main objective of this study is the preparation and characterization of flexible, cheap and easy processable piezoelectric materials. Different 0-3 composites, that consist of a random array of particles dispersed in a matrix, are then prepared by solvent casting and hot pressing techniques, by using barium titanate (BT) as filler. Polyvinylidene fluoride (PVDF) and its copolymers, polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), and polymethylmetacrilate (PMMA) are used as matrices in order to evaluate the influence of polymeric materials with different mechanical and functional properties on the composite behavior. The prepared composites are characterized via X-Ray Diffraction, Differential Scanning Calorimetry and Infrared Spectroscopy, and their microstructures are observed through FESEM. Piezoelectric coefficient is then evaluated by applying a mechanical stress and collecting the generated charge by The Belincourt d<sub>33</sub>-meter. In order to define the composite permittivity, capacitance and losses are measured with a high precision HP4284A LCR meter. In all the cases an improved piezoelectric response is recorded with the increase in BT amount, reaching values that have been measured for composites containing particles made of the most performing piezoceramic, PZT.

**Motivations and objectives:** Piezoelectric ceramic-based devices have long been used for mechanical-to-electrical energy harvesting. However, ceramic materials tend to be stiff and limited in mechanical strain abilities; so for applications with low-frequency and large-stroke mechanical excitations (such as human movement), direct coupling of the piezoelectric ceramic to the excitation source yields a very low input mechanical energy. On the other hand, organic materials are soft and flexible; therefore, the input mechanical energy is considerably higher under the same mechanical force. However, piezoelectric polymers have a much lower piezoelectric coefficient compared to piezoelectric ceramics. The dispersion of piezoceramic particles in polymer matrices should allow to couple the flexibility and the piezoelectric response of these two phases, developing piezoelectric composites. In particular, in this study the influence of the amount of ceramic particles and the nature of the polymers, by using matrices with different mechanical and functional properties, on the composite performances is investigated.

**Results and discussion:** Polymer matrix composites obtained through the hot pressing process presented an optimized microstructure, reaching higher densities and a more homogeneous distribution of ceramic particles. On the other hand, the presence of pores and voids in solvent cast materials implies higher permittivities and lower piezoelectric coefficients with respect to the corresponding hot pressed composites.

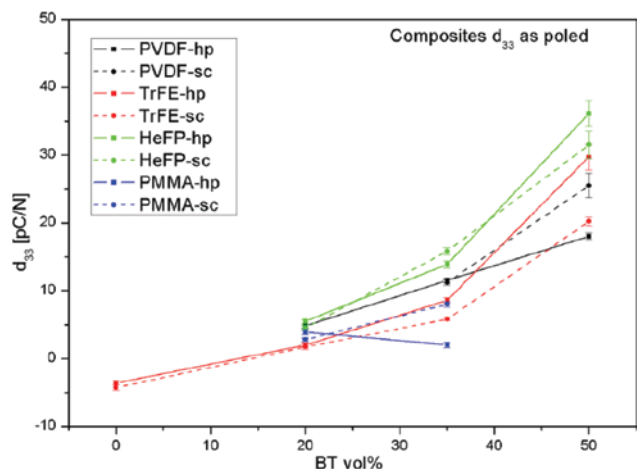


Fig. 1

### BIO-POLYMERIC BASED SPONGES FOR OILY WASTE RECOVERY

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**Concept:** Over the last years, many efforts were dedicated to the development of sustainable sorbent materials. The interest concerns a wide range of applications. Oily products and utilization are increasing all over the world as far as the possibility of spill oily accidents. In this direction, production of sponges showing lipophilic properties allows for the proper disposal of oily waste and does not cause secondary pollution. In this work, it is proposed an eco-friendly technology to prepare a polycaprolactone (PCL) biodegradable sponge for the selective absorption of oil from water. PCL biopolymer matrix was melt mixed with water-soluble porogen agents and then leached in water to obtain a porous 3D structure. The intrinsic lipophilic nature of PCL made the porous device able to selectively absorb oily pollutants showing, moreover, with high efficiency and high reusability potential. Devices are characterized from morphological and mechanical point of view. Oily waste uptake was evaluated by considering 3 different oily waste (olive oil, motor oil, gasoline) and considering 50 recycles.

**Motivations and objectives:** Several materials were proposed for the production of absorbent devices: from polymeric sponges to inorganic devices based on clays or graphite. Recently, polymeric materials obtained by renewable sources and with potential biodegradability, received much interest for their potential in reducing the overall environmental impact. Among these PCL achieved both industrial and academic interest due to its peculiar properties in terms of degradation, biocompatibility and mechanical properties. For these reasons, in this work it has been chosen as polymeric porous device for selective adsorption of oily waste.

**Results and discussion:** The sponge morphology of the biopolymeric device, showed in Figure 1, was characterized by a multimodal pore structure with distinct pore sizes and pore architectures. The macropores associated with salt particles (Fig. 1a), are well interconnected and seems to be homogeneously distributed in the polymer matrix with size ranging from 50 to 100 mm. The micropores (5-10 mm) network, better visible in Figure 1b, was likely created by the extraction of the PEG phase. Pores morphology did not change significantly with the number of waste/cleaning cycles. A mass-based oil uptake up to 500% (with respect to the original weight) can be observed. In particular it was higher for motor oil, gasoline and olive oil respectively. The average absorption capacity of the sponges device as a function of the number of the recycles remains about at that measured after the first cycle even after 50 recycling. Young's modulus of the pristine sponge is 0,63 MPa and it was found to be almost independent from the kind of pollutants up to 25 cycles, while a large reduction of E was visible at 50 cycles for all the systems tested on.

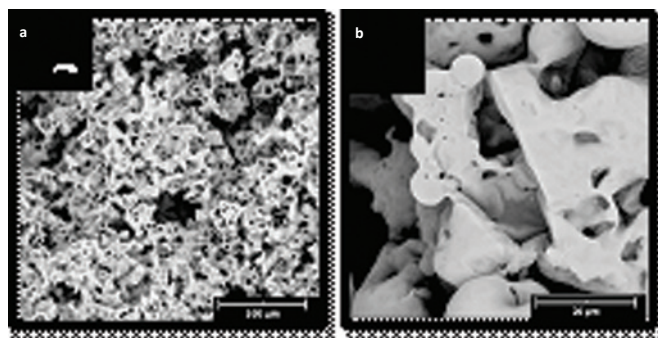


Fig. 1 - SEM images of ORS at different magnifications, scale bar a) 100 m; b) 20 m.

### EVALUATION OF CORROSION BEHAVIOR OF AUSTENITIC STAINLESS STEELS DURING CONVERSION OF WASTE TO BIOFUEL

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**Concept:** The paper deals with corrosion behavior of stainless steels as candidate material for biofuel production plants. The feedstock undergoes a thermal treatment conversion stage at temperatures between 240 and 310°C and autogenous pressure of water to produce bio-oil that can be upgraded into liquid biofuel. Corrosion tests were carried out on AISI 316L and AISI 304L stainless steels. General corrosion rate was measured by weight loss tests. The susceptibility to stress corrosion cracking was evaluated by means of U-bend type A specimens (ASTM G30-97). The specimens were exposed in the conversion reactor either to water/oil phase or humid gas phase. SSR tests were performed at 250°C and 10<sup>-5</sup> strain rate. SEM analysis of exposed specimens was carried out to detect SCC cracks and localized attacks.

**Motivations and objectives:** The sorted organic fraction of Municipal Solid Waste can be converted to bio-oil by several processes. Nowadays, gasification and fast pyrolysis are widespread but liquefaction is also suitable. In such processes, biomass is converted to liquid through a complex sequence of reactions. Depending on process, oil has high Total Acid Number (TAN) and can induce too high corrosion rates on carbon steels. Furthermore, stainless steels may be susceptible to localized corrosion and SCC owing to chlorides and high temperatures. However, the behavior is complex due to different effects of compounds on corrosion. The work deals with the evaluation of the corrosion behavior of austenitic stainless steel in bio-oils produced by the liquefaction process.

**Results and discussion:** Corrosion rates were strictly dependent upon exposure conditions, time and temperature (Fig. 1a). No SCC cracks were observed on U-bend specimens under static loading. Small cracks in the necking cone of the specimens after the SSR tests (Fig. 1b) proves that SCC can occur only for stress values exceeding yield strength.

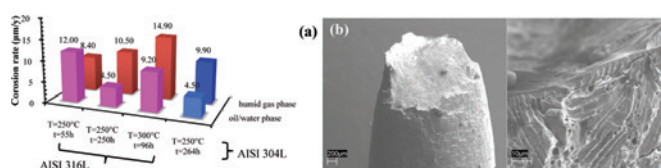


Fig. 1 - General corrosion rates (a) and fracture morphology after SSR tests at 250°C and 10<sup>-5</sup> strain rate (b).

### GRAPHITE AND GRAPHENE OXIDE PAPER

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**Concept:** In this contribution, we present GO papers as prepared after basification of the colloidal GO aqueous suspension (thereafter defined as basified GO paper and shortly b-GO paper). This work also shows that basification of GO suspensions also facilitates processing, because b-GO paper can be easily obtained by solvent casting and vacuum filtration procedure. Spectroscopic analyses of the obtained papers have been conducted aiming to a possible rationalization of the observed behavior.

**Motivations and objectives:** The ability of graphite oxide (GO) aqueous suspensions to form robust and resilient GO paper is largely improved by basification of the suspension prior of processing. In particular, casting procedures, which are generally unsuitable for production of GO paper, become suitable for the case of basified GO (b-GO) suspensions, leading to flexible free-standing papers. Thermal treatments of b-GO paper easily produce graphene oxide paper, i.e. paper with exfoliated GO (eGO), while thermal treatments of GO paper lead to mixed GO, eGO and graphite components.

**Results and discussion:** GO papers as prepared after basification of the colloidal GO aqueous suspension. Differently from usual GO and eGO papers, papers from b-GO suspensions exhibit remarkable resistance to solvents as well as to acids and bases, even in aqueous solutions. The reported spectroscopic characterizations suggest that the achieved filmability by casting, the easier thermal GO exfoliation and the improved solvent resistance of the b-GO paper are due to ether bonds, also forming atomic bridges between individual graphene oxide layers.

### SPUTTERING DEPOSITION OF CuO AND Fe<sub>2</sub>O<sub>3</sub> THIN FILMS FOR HYDROGEN PHOTOGENERATION

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**Concept:** In this work we successfully prepared nanostructured supported film of CuO and Fe<sub>2</sub>O<sub>3</sub> by means of rf-magnetron sputtering starting from metal targets. By modulating the sputtering parameters (i.e., substrate temperature, total pressure, oxygen partial pressure and RF power) we were able to modulate the nanostructure of the deposited thin films in terms of morphology and density. The deposited materials were analyzed with respect to their photocatalytic activity in presence of a sacrificial agent. Thanks to the deep structural and morphological characterization carried out on the CuO and Fe<sub>2</sub>O<sub>3</sub> films (by means of XRD, AFM, SEM, profilometry, XPS), we could correlate the photocatalytic performance with the physical properties of the prepared catalysts. Such systematic investigation allowed us to identify the main parameters positively affecting the catalytic performance.

**Motivations and objectives:** Main motivations of this work is the development of low-cost, environmental-friendly and efficient photocatalyst materials capable of driving the required processes under visible light. Our objective was to find a close correlation between the photocatalyst performance and the growth parameters for nanostructured CuO and Fe<sub>2</sub>O<sub>3</sub> film prepared by means of cost-effective and scalable method such as rf-sputtering.

**Results and discussion:** The main results achieved were the: i) ability of modulating the nanostructure of the CuO and Fe<sub>2</sub>O<sub>3</sub> films by playing with the deposition parameters in a systematic way; ii) correlate such deposition parameters with the photocatalytic activity, and iii) identifying the key features for the optimization of the catalysts.

This work has been supported through the INSTM-RL "ATLANTE" project.

### NEW ECO-COMPOSITES BASED ON POLY(LACTIC ACID) (PLA) FOR AUTOMOTIVE APPLICATIONS

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**Concept:** Poly(lactic acid) (PLA) is one of the most promising renewable polymers to be employed in the automotive sector. The reactive blending with polycarbonate (PC) in the presence of a catalyst was demonstrated to be a successful strategy. The addition of cellulosic fibers having different aspect ratio to these blends allowed the improvement of elastic modulus. The composites were prepared by laboratory extrusion and characterized in terms of chemical, morphological and thermo-mechanical properties.

**Motivations and objectives:** The objective of this work was modulating the Elastic Modulus of composites as a function of the geometric characteristics of the employed fibers.

**Results and discussion:** Different cellulose fibers (Arb I, Arb II and Lyo) were compared in terms of their capacity of increasing the elastic modulus of blends. In Figure 1 the Elastic Modulus of the matrix blend, consisting in recycled PLA and Recycled PC, and of the composites, obtained by using 10% by weight of fibers, is reported. As the aspect ratio increases from Arb I, to Arb II, to Lyo cellulosic fibers, it is evident that there is not a correlation between the value of the elastic Modulus and the aspect ratio.

European NMP FP7 EVOLUTION project financial support is acknowledged.

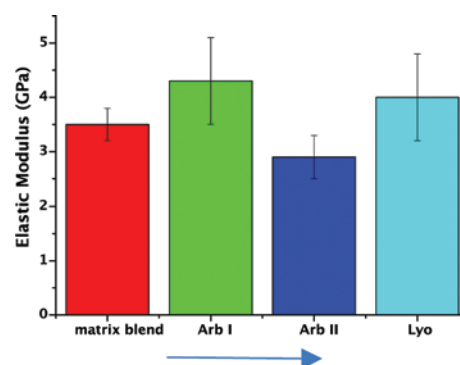


Fig. 1 - Elastic Modulus of matrix blend and composites containing cellulosic fibers.

### MICROWAVE CHARACTERIZATION OF BRICKLAYING MATERIALS FOR NON-DESTRUCTIVE EVALUATION OF RESTORING TREATMENT EFFECTIVENESS

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**Concept:** A novel technique for non-destructive test on bricklaying materials is proposed and described. Such method makes use of microwave devices for materials electromagnetic characterization: vector network analyzers are employed to measure samples microwave reflection, transmission and absorption properties in both free space and waveguide framework. The materials under testing include calcium carbonate- and silicate-based bricklaying stones where conventional artwork-restoring substances are applied on.

**Motivation and objectives:** The usefulness of the present research lies in identifying and developing an innovative non-destructive testing route for cultural heritage restoring, as well as in enhancing the knowledge about the water-microwave interaction and suggesting new fields and modalities of microwave analysis applications.

**Result and Discussion:** The comparison between the microwave results obtained for the naked and the restored materials allows to evaluate the effectiveness of the consolidation treatment. In particular, the electromag-

netic field skin depth retrieved from the measurements of the microwave scattering parameters may be correlated to the effective length of the capillary infiltration achieved by the restoring solutions, thus providing powerful informations about the restoring technique efficacy itself. Moreover, the effects of the moisture on the microwave properties of porous materials are analyzed: the water desorption is monitored by measuring the change of the reflection coefficient, thus establishing a real time correspondence between the microwave absorption peaks shifting and the water content inside the sample. The effectiveness of the consolidation treatment is well established by the different behavior discovered in terms of water absorption/desorption with respect to the untreated materials. Mainly, the asymmetric fashion of the microwave reflection response is directly linked to the axial gradient of porosity due to the gradual penetration of the consolidating solution, thus supplying information about the restoring treatment depth by means of high reproducibility non-destructive testing.

**PRODUCTION AND CHARACTERIZATION OF CARBON-PHENOLIC ABLATIVE MATERIALS MODIFIED WITH NANO-FILLERS**

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**Concept:** Ablative materials represent the traditional approach to protect space vehicles from the severe heating during hypersonic flight through a planet's or the Earth's atmosphere. The Materials and Surface Engineering Lab (LIMS) of Sapienza-University of Rome has developed carbon-phenolic ablative materials with several densities and compositions. This work presents a new methodology for their manufacture adding functionalized nano-fillers. In particular acetic, decanoic and methacrylic acid were chosen as functionalizing group of nano-zirconia. Mechanical (bending and compression tests) and thermal characterization (TGA/DSC) are carried out in order to understand the effect of nano-fillers on the material properties.

**Motivations and objectives:** Ablative materials consist of a rigid felt impregnated with phenolic resin. During the process the resin is diluted and nanoparticles are added to this solution. Nano-filler are introduced in order to improve mechanical and thermo-physical properties of virgin and charred material, but their efficiency is strictly connected to the homogenous dispersion of the particles. An acid surface modification were conducted to avoid the agglomeration of particles according to Chiang et al. The efficiency of the method was proved by FE-SEM photographs, mechanical and thermal tests will enlighten the properties improvement.

**Results and discussion:** The FE-SEM photograph (Fig. 1) of a cured carbon-phenolic ablative material shows that addition of nano-fillers does not decrease the goodness of the distribution of the resin in the sample without density variation. Figure 2 shows that the surface modification and the impregnation procedure does not change the dimension of the nanoparticles (as shown in the inset). Although the particles are well dispersed in the resin. Bending and compression tests will provide a comparison between samples manufactured with and without nano-zirconia.

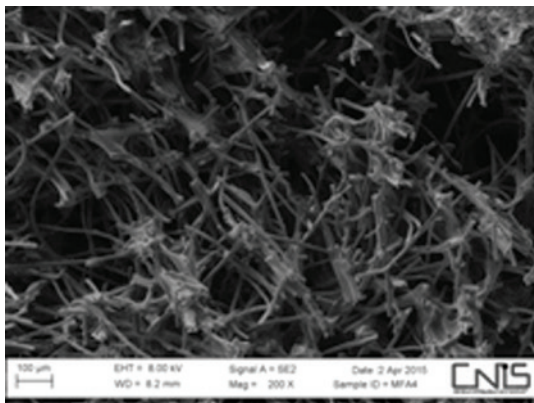


Fig. 1 - Carbon-phenolic ablative material with nano-zirconia.

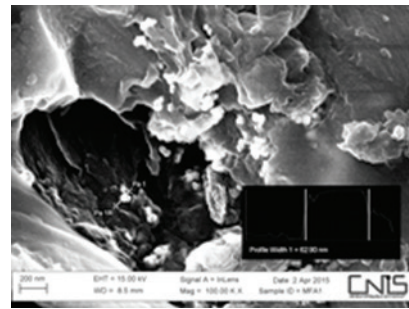


Fig. 2 - Cured ablative material. Nano-zirconia particles (measure on the inset) are functionalized with methacrylic acid.

**SUPER ABSORBENT POLYMER AS AN INTERNAL CURING AGENT FOR REDUCING EARLY-SHRINKAGE OF TRADITIONAL AND HIGH PERFORMANCE CONCRETES**

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**Concept:** The introduction of SAP (superabsorbent polymer) into traditional concrete does not seem to provide improvements in performances. In order to preserve the same strength obtained without SAP addition, no additional water to pre-saturate SAP grains was added; the required workability was obtained by adding a higher rate of superplasticizer admixture. On the contrary, with the high performance concrete (HPC), a slight shrinkage reduction was achieved. Unfortunately, without a preliminary SAP saturation, the slump loss was too high, and the increase in compressive strength was not enough to override the penalization due to SAP addition.

**Motivation and objectives:** Cement materials with low water/cement (w/c) or low water/binder (w/b) ratios are vulnerable to early age cracking due to autogenous deformation caused by self-desiccation. A decade ago, it was suggested and demonstrated that this problem can be solved by mixing superabsorbent polymers (SAP) into fresh concrete, thereby establishing small reservoirs of internal curing water. When a new component like SAP is introduced into the concrete matrix, it becomes important to investigate how this component influences concrete properties such as workability and mechanical properties. In addition, one can examine whether a partial reduction in early hygrometric shrinkage can be achieved, other than the reduction in autogenous shrinkage.

**Results and discussion:** The actual work is related to concretes with two different water-cement ratios, 0.4 and 0.53: the lower ratio is the upper limit of HPC while the higher one is typical of traditional concretes. The rate of SAP addition to the mixture was 0.25% or 0.50% by weight of cement. In order to verify the effect of this admixture, a reference concrete and a concrete with SRA (Shrinkage Reducing Admixture) were also produced. Other researchers have hypothesized the amount of water absorbed by SAP during mixing and casting and they have added some water in the mixture. We preferred not to predict the absorption amount and we did not modify the nominal composition. The slump loss was preserved by increasing the superplasticizer rate. In the case of traditional concrete, the resulting decrease in the w/c overcame the penalization ascribed to SAP addition, and it lead to the same compressive strength as the reference concrete. As regards to HPC, the strength recovery was not complete and the loss in workability, by using a correct (permissible) superplasticizer rate, was not avoided.

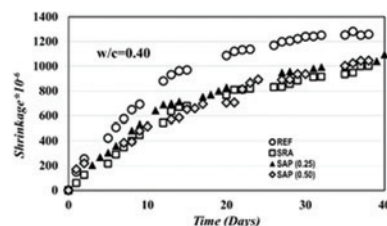


Fig. 1 - Shrinkage (vs time) of the concretes with w/c = 0.4.

**STUDY OF PLASTERS CONTAINING ORGANIC PARTICLES FOR SUSTAINABLE AND ENERGY-EFFICIENT BUILDING**

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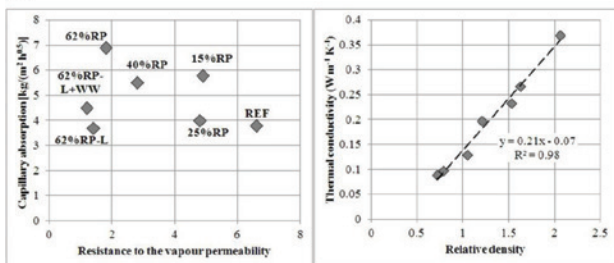
**Concept:** The reduction of energy consumption in construction, the production of thermally insulating materials, as well as the solution of environmental problems by recycling industrial and municipal waste are key challenges for the next future. For this reason several plasters have been studied, in which virgin raw materials such as natural sand and limestone filler were replaced up to 100% by waste polyethylene terephthalate (PET) particles and pulverized Glass Fiber Reinforced Plastic (GFRP) waste, respectively. As supplementary cementitious material silica fume was employed, an industrial by-product obtained from silicon wafer sawing. Finally, in some mixtures even cement was fully replaced by a combination of lime and hydraulic lime in order to further improve the carbon footprint of these plasters. Plasters were characterized by means of compression and bending tests, as well as by means of resistance to vapour permeability, capillary water absorption as well as thermal conductivity tests.

**Motivations and objectives:** The development of composite construction materials with low thermal conductivity by using waste organic particles could be an interesting alternative that might solve simultaneously energy and environmental issues. In this work some plasters have been studied, in which natural sand and limestone filler are totally replaced by waste PET particles and GFRP powder, respectively. The final goal is to find an environmentally-friendly material, which is also energy-efficient in terms of reduced weight and thermal conductivity, without compromising other functional properties able to reduce humidity inside the plaster, which play a key role in assuring comfort indoor. A similar work can be found in the literature, in which PU waste was used, replacing sand, to produce plasters.

**Results and discussion:** Plasters with adequate fresh consistency were obtained. When increasing the amount of organic waste particles the compressive and flexural strengths gradually decreased, however a minimum value of at least 2 MPa in compression and 1 MPa in bending were achieved. In terms of plaster lightness, the use of organic particles and the addition of huge amount of air entraining admixture (AEA) allowed to reduce the weight by 65% (Fig. 1c). In parallel, also thermal conductivity was reduced up to values slightly lower than 0.1 W m<sup>-1</sup> K<sup>-1</sup>. Concerning vapour permeability and water capillary absorption, which play a key role in assuring comfort indoor, these plasters showed to be extremely promising, thanks to the likely presence of many macropores (due the addition of huge amount of AEA), which are able to reduce both the resistance to the vapour passage and the rising damp.



(a)



(b)

(c)

Fig. 1 - (a) PET waste, (b) capillary absorption vs. vapour permeability, (c) thermal conductivity vs. density.

**HYBRID LAMINATES FOR AEROSPACE APPLICATIONS**

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**Concept:** Hybrid laminates were produced by tape casting technique which involves: the preparation and the cast of a ceramic slurry in order to obtain, after drying, the green tapes. The layers were cut and stack according to the proper sequence. Then they were submitted to binder burnout and final sintering without pressure assistance. The aim was to verify the feasibility of laminates integrating 80vol%ZrB<sub>2</sub>-20vol%SiC composite layers in between SiC ones: the processing method has to take into account different factors such as the grain size of starting powder and the thickness of the composite layers. These parameters have great influence on the processing and the properties of this multilayer system. The materials were then characterized from physical and mechanical point of view. Preliminary oxidation tests have been performed in order to compare the oxidation resistance of these kind of laminates with ones with all layers showing the same chemical composition.

**Motivations and objectives:** Silicon carbide is one of the most used material for aerospace applications thanks to its good thermal stability, low density, good strength, high hardness and self passivating behavior in oxidizing environment. Its main limit is the temperature range of use: for temperature higher than 1600°C the surface passive layer melts and can be easily consumed and carried away due to the air friction. Moreover active oxidation can occur damaging the silica layer too. Hybrid laminates integrating composite layers in between SiC ones have been investigated in order to improve the performance of SiC based material at higher temperature. When the SiC layers are damaged the underlying ZrB<sub>2</sub>/SiC layers can protect the underlying structure slowing down the diffusion of oxygen and so improving the oxidation resistance of laminates.

**Results and discussion:** The presence of layers with different chemical composition gives rise to residual stresses which are mainly developed on cooling from sintering temperature due to the mismatch between the different thermal expansion coefficients of the two materials. They cause the formation of cracks propagating in the composite layers, defects in the structure up to delamination. In order to reduce the residual stresses two strategies have been adopted: vary the grain size of starting powder and modify the thickness ratio of layers with different chemical composition. The reduction of ZrB<sub>2</sub> starting powder (milling up to obtain a grain size comparable to SiC one) let to obtain an improvement both in densification degree and mechanical properties of laminates. Increasing the thickness of composite layers (respect to the standard value of 200 μm obtained for the green tape) delamination of multilayer is observed. On the other hand the decrease of 80vol%ZrB<sub>2</sub>-20vol%SiC layers thickness has positive effects on the laminates properties: the cracks formed in the composite layers are very thin and the mechanical properties increase in function of the increasing of composite interlayer thickness. The oxidation resistance of hybrid laminates results improved respect to those of multilayers with all layers with the same chemical composition.

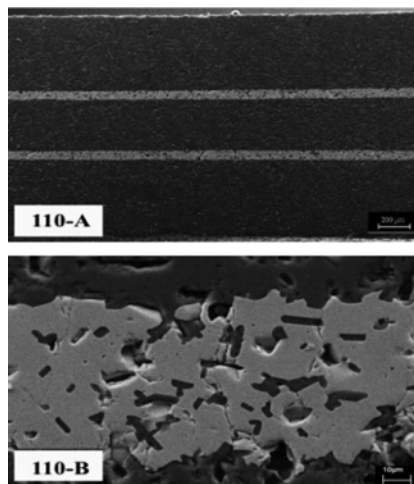


Fig. 1 - A-Microstructure of laminates integrating ZrB<sub>2</sub>/SiC layers (110μm thick) in between SiC ones; B-Zoom of composite interlayer.

### METHANATION OF CARBON DIOXIDE OVER Ni-Fe/BASED $Ce_{0.9}Gd_{0.1}O_2$ CATALYSTS

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**Concept:** This study was devoted to CO<sub>2</sub> methanation over Ni-Fe based catalysts supported on Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2</sub> (GDC). The catalysts were prepared by impregnation and characterized by usual analytical techniques (XRD, TPR-H<sub>2</sub>, SEM-EDX). The effects of metals loading, gas hourly space velocity (GHSV) and reaction temperature ranging from 200 to 400°C. on the catalytic activity and selectivity were examined.

**Motivations and objectives:** In carbon dioxide recycling for prevention of global warming and supply of renewable energy, hydrogenation of CO<sub>2</sub> to methane is an important catalytic process with many benefits from environmental and economical viewpoints. The methanation is thermodynamically favorable but the reduction of the fully oxidized carbon to methane is an eight-electron process with significant kinetic limitations, which thus requires a catalyst to achieve acceptable rates and selectivities. This process has been previously investigated over a number of metal catalysts (Ni, Fe, Co, Cu, Ru and Rh) supported on various metal oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and CeO<sub>2</sub>). Among these catalysts, Ni-based catalyst have been widely employed for CO<sub>2</sub> methanation due to their high catalytic activity and high selectivity for methane.

**Results and discussion:** The catalysts have a total metal loading of 50% wt/wt with respect the support. The high load of metal is due to the foreseen use of the catalyst in Solid Oxide Electrolyzer Cell (SOEC). TPR measurements (not shown) were performed to examine the metal-support interaction and the reducibility of the catalyst. Reduction behavior of metal species in the catalysts was quite different depending on the iron loading. The XRD results indicate that the metal oxide species were completely reduced during the reduction step. The chemical analysis of fresh catalyst confirm the content of metal loading. As shown in figure the CO<sub>2</sub> conversion is affected by iron loading both at low and high GHSV, in fact it is possible to observe a decrease in conversion. Obviously, at low GHSV CO<sub>2</sub> and H<sub>2</sub> conversion have higher values.

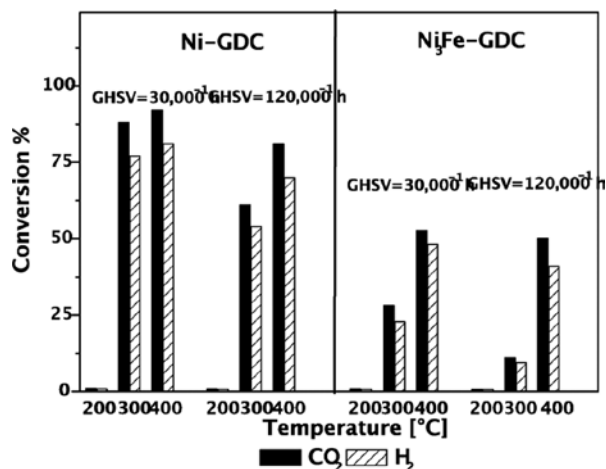


Fig. 1

### DISPERSION OF CARBON NANOTUBES IN POLYPROPYLENE: A COMPARATIVE INVESTIGATION BY OPTICAL MICROSCOPY AND TERAHERTZ TIME-DOMAIN SPECTROSCOPY

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**Concept:** The degree of dispersion of nanosized fillers in a polymer based matrix strongly influences the ultimate properties of nanostructured systems. In this contribution, melt compounded polypropylene (PP) based systems containing 0.5% in volume of not functionalized, carboxyl- and amino-functionalized multiwalled carbon nanotubes (MWCNTs) have been analyzed by optical microscopy and high frequency spectroscopy. Results, confirming the influence of the chemical features on the achieved filler dispersion, highlighted useful correlations between the typical dispersion index (D) obtained by optical microscopy tests and specific spectroscopic parameters as refractive index (n) and absorption coefficients (α) from high frequency tests.

**Motivations and objectives:** Among nanofillers, carbon nanotubes (CNTs) are extremely promising since they combine extremely high stiffness, large electrical and thermal conductivity together with high aspect ratios but their applications are still limited owing to the random disposition and poor alignment usually achieved by conventional processing technologies. Many studies have been carried out to investigate the mechanisms of dispersion by analytical approaches, usually difficult and time consuming to be applied systematically, besides being mostly off-line. Recently, alternative and more versatile techniques as the terahertz time domain (THz) spectroscopy have been developed at this regard. Main aim of this research is to further validate this latter technique.

**Results and discussion:** The main correlation between the dispersion estimated using optical microscopy and the THz refractive index is shown in the following picture in which the dashed curve represent a guide-to-the-eye only. Clearly, the highest D value correspond to the lowest n value. Analogous conclusion has been obtained in terms of the absorption coefficient (α).

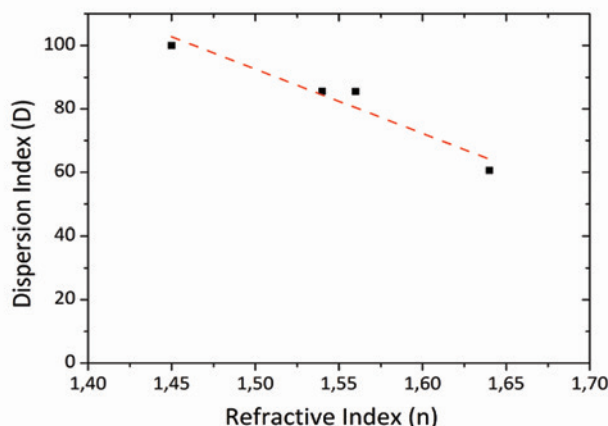


Fig. 1

### Zn-ZrO<sub>2</sub> NANOCOMPOSITE COATINGS OBTAINED BY ELECTRODEPOSITION

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**Concept:** In the present work Zn-ZrO<sub>2</sub> nanocomposite coatings (ZrO<sub>2</sub> 0.2-2.5 wt%) on mild steel substrate have been produced by electrodeposition technique with high current efficiency. Electrodepositions were performed at 35°C by using a chloride bath containing gelatine and yttria-stabilized zirconia nanoparticles (<100 nm); the tests were carried out under galvanostatic control with pulsed direct current, using a cathodic square wave (pulse frequency 1 Hz, duty cycle 50%). The coatings were characterized by means of X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and Vickers microhardness measurement. Corrosion potential and polarization resistance measurements were performed in 3.5% NaCl solution. The composite coatings showed an improvement in hardness and in corrosion resistance with respect to the pure zinc coatings.

**Motivations and objectives:** In the last few years, the electrodeposition of composite coatings, formed by a metallic matrix and ceramic micro or nanoparticles, has been the object of several investigations because the incorporation of the particles leads to an improvement of mechanical properties. Zn-ZrO<sub>2</sub> composites have been electrodeposited by other authors from

sulphate baths. The aim of the present work was to obtain by electrodeposition Zn-ZrO<sub>2</sub> coatings on mild steel from a slightly acidic chloride bath widely used by galvanic industry for the barrel process.

**Results and discussion:** Both pure zinc and Zn-ZrO<sub>2</sub> composite coating electrodeposition from the studied bath occurs with very high current efficiency, due to the presence of gelatine in the bath. SEM observations showed that zinc deposits have very low grain size; ZrO<sub>2</sub> nanoparticles incorporation does not affect markedly the morphology: only a slight increase in deposit roughness was observed. Pure zinc coatings are crystalline; as found previously, the addition of gelatine to the bath causes a strong orientation of zinc deposit, with the reflection from the (110) plane largely predominant. The incorporation of ZrO<sub>2</sub> slightly changes zinc structure, leading to less orientated deposits; this effect increases on increasing the percentage of nanoparticles in the deposit. The composite coatings showed an improvement in the hardness with respect to the pure zinc coating obtained from the same bath without nanoparticles, with also a slight increase in corrosion resistance (Tab. I).

**TABLE I** - Composition microhardness, corrosion potential and polarization resistance in 3.5% NaCl solution of Zn and Zn-ZrO<sub>2</sub> coatings

Coating	ZrO <sub>2</sub> wt%	HV	Ecorr V	Rp kΩ cm <sup>2</sup>
Zn	-	100	-1.060	0.3
Zn-ZrO <sub>2</sub>	0.93	140	-1.045	0.6

#### PROCESSABILITY OF POLYPROPYLENE/INTUMESCENT FLAME RETARDANT/SEPIOLITE SYSTEMS

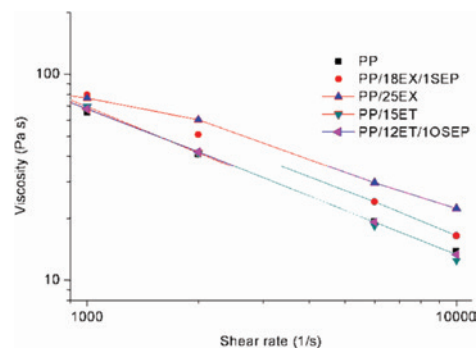
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**Concept:** Intumescent flame retardants (IFRs) are a new and efficient generation of FRs for polyolefines for some of their peculiarities as very low smoke and toxic gases produced during burning and anti dripping behavior. As widely reported in the literature, their efficiency is enhanced by the simultaneous use of synergistic agents increasing strength and stability of the char layer. In this contribution, 0.5 and 1% by weight of neat sepiolite (SEP) or organo-modified sepiolite (OSEP) particles have been included in intumescent polypropylene systems prepared by melt compounding and including two novel commercial IFR additives, herein coded as EX and ET. Capillary rheological measurements show that, especially in presence of surface modified sepiolite, a decrease of the shear viscosity with respect to the reference neat PP is observed all over the examined range of shear rates.

**Motivations and objectives:** Polypropylene has been widely used in many fields due to its excellent properties and easy processability. Considering that the inherent high flammability of PP, as for many synthetic polymers, restricts its application, research efforts to overcome this drawback still remain a challenging task. At this regard, satisfactory results were obtained by using a new generation of additives best known as intumescent flame retardant forming a foamed cellular charred layer on the surface of the product and, consequently, slowing down the heat and mass transfer between the gas and the condensed phase. However the levels of loading required to compete with traditional halogenated additives are so high to compromise, among others, the processability of new materials, unless adequate synergistic agents are simultaneously included. Given the lack of information about this aspect, this contribution is focused on the processability of PP based systems with enhanced flame retardancy.

**Results and discussion:** Shear viscosity flow curves of flame retarded PP based formulations are compared in the following picture. Clearly, the IFR ET is more efficient than IFR EX. Moreover, the IFR ET additive does not involve an increase of the shear viscosity with further slight reduction of the same in presence of 1% by weight of OSEP.



**Fig. 1**

#### BIO-NANOCOMPOSITES BASED ON PECTINS AND HALLOYSITE NANOTUBES LOADED WITH ANTIMICROBIALS FOR FOOD PACKAGING APPLICATIONS

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**Concept:** In this work we prepared nanocomposites based on natural pectins and HNTs filled with antimicrobial natural molecules from rosemary oil. Structural characterization and physical properties were evaluated. The controlled release of rosemary acid was followed as function of time. The prepared systems, with tuneable properties, appears very good candidate for food packaging applications, as eco-friendly materials.

**Motivations and objectives:** In food packaging, a critical issue is extending the shelf life of packed products, preserving all organoleptic characteristics for as long as possible. The development of innovative packaging materials consists in one layer product in which several functionalities are included. Nanotechnology is a very promising strategy to improve physical and barrier properties of polymeric materials. The introduction of nanofillers into biopolymers is a strategy to overcome some critical issues, such as poor water resistivity and low mechanical properties. Bio-based polymeric materials are currently considered the only alternative in the future to petroleum-derived polymers, as fossil resources become exhausted. The use of bio-based polymers with nanofillers in food packaging, can offer many advantages in the formulation of active packaging, because of the possibility to anchor active molecules such as antioxidant, oxygen scavenging or antimicrobial molecules, which can increase the quality and safety of packaged foods. The objective of this work was to use natural pectin, as polymeric matrix, from renewable sources and completely biodegradable, and a new class of fillers: halloysite nanotubes (HNTs). The latter are naturally occurring eco-friendly nanotubes with low cost that are harmless to human. HNTs are unique and versatile nanomaterials composed of double layered aluminosilicate minerals with a predominantly hollow tubular structure in submicron range. They are nontoxic in nature, have tuneable release rates and fast adsorption rates. These nanotubes have got wide range of applications in anticancer therapy, sustained delivery for certain agents, act as template or nanoreactor for biocatalyst, have found use in personal care and cosmetics and even used as environment protective.

**Results and discussion:** TG-DTG analysis showed that the essential oil molecules into the nano-hybrid delay the thermo-oxidation, because some molecules were successfully entrapped into the nanotubes. The degradation of the pectin matrix was not greatly influenced from the nano-hybrid filler, except for the oxidation stage at high temperatures, that resulted anticipated. X-ray analysis on the composites showed that pure pectin presents an amorphous structure. The basal peak of dehydrated HNTs tends to disappear and/or to expand after the intercalation of essential oil and the mixing in water with the pectin matrix. Mechanical properties showed an improvement, or at least a preservation, of all the mechanical parameters of pectin. Barrier properties to water vapor, in terms of diffusion, resulted improved. The presence of the filler increased the tortuosity of the system, leading to a decrease in the value of the diffusion coefficient. A comparison of the molecular release of the rosmarinic acid molecules directly dispersed in pectins and in the nano-hybrid was reported, indicated the much slower release in the latter case.



### PARAMETERS OPTIMIZATION IN POROUS SCAFFOLD FABRICATION PROCESS BASED ON TAGUCHI METHOD AND ANOVA

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**Concept:** Bone defects pose significant health problems. Tissue engineering offers a promising new approach for bone repair by using a three-dimensional porous, biodegradable polymer scaffold that serves as a template for tissue regeneration. The function of a scaffold is similar to that of the natural extracellular matrix that assists proliferation, differentiation, and biosynthesis of cells. Basic requirements for 3D scaffolds are biocompatibility, high porosity, large specific surface, pore interconnection and mechanical resistance. This study involves a systematic procedure for the parameters optimization to maximize the properties of the implant. PLA biopolymer matrix was melt mixed with water-soluble porogen agents, i.e. NaCl or CaCl<sub>2</sub> and PEG; scaffolds were produced by compression molding and then leached in water to achieve a porous 3D structure. Seven controllable factors, each at two levels, are tested by adopting Taguchi method and statistical analysis ANOVA is utilized to search for the statistically significant factors and their optimal level combination.

**Motivations and objectives:** Polymer scaffold is delivered to the desired site in the patient's body. Mechanical properties must be appropriate and should not collapse during movements and activities of the patient. High porosity and high interconnectivity between the pores are necessary to allow cell growth and transport of nutrients. Accordingly, it is necessary to maximize final properties of the device, which depend on materials, fabrication method and process variables. Aim of this research is the optimization of process variables to increase compression modulus and porosity. This work is animated by the absence, in literature, of applications of Taguchi method in tissue engineering.

**Results and discussion:** Devices performance was characterized by rheological, morphological and mechanical tests. The morphological structure of scaffolds is highly porous with well interconnected pores. The macropores associated with NaCl salt particles (variable factor) are roughly cubic in shape (Fig. 1a) while the macropores associated with CaCl<sub>2</sub> salt particles are oval shaped (Fig. 1b). The micropores network arose from the extraction of PEG phase from the PLA matrix. The analysis of variance (ANOVA) revealed that the temperature and the time of melt mixed were the most statistically significant factors in the improvement of elastic compression modulus.

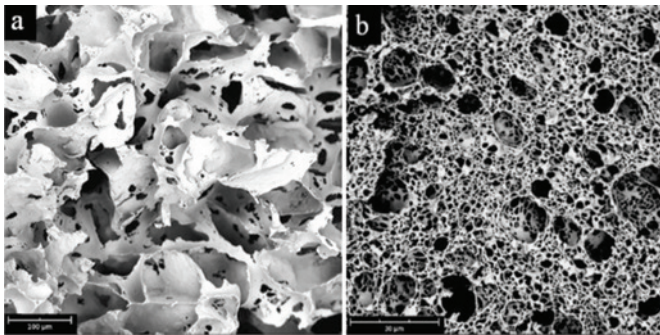


Fig. 1 - SEM micrographs of PLA-PEG-NaCl (a) and PLA-PEG-CaCl<sub>2</sub> (b).

### EFFECT OF $\beta$ AND $\gamma$ RAY STERILIZATION ON THE PROPERTIES OF POLYMERIC MATERIALS FOR BIOMEDICAL APPLICATIONS

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**Concept:** Sterilization processes are necessary for the clinical application of polymeric materials but this practice raises many issues, including potentially harmful effects on the material properties and changes in the device performances. In particular, high energy radiation methods ( $\beta$ ,  $\gamma$  or X-ray) can induce degradation to the polymer by crosslinking and/or photoionization

leading to a loss of mechanical, physical and chemical material properties. In polymers where "cross-linking" prevails, an increase in mechanical properties as elastic modulus (E) and elongation % at break, can be detected; on the other hand, when photoionization predominates, mechanical properties decrease.

**Motivations and objectives:** The goal of this study is to evaluate the effect of sterilization by  $\beta$  and  $\gamma$  radiation on the properties of four different polymeric specimens for biomedical use (Fig. 1): a PVC pipe for connection in dialysis and heart surgery devices; a PVC band for enteral and parenteral nutrition bags, a TRIFLEX pipe (internal PE, middle PE/PVC, external PVC) for connection, a PC rigid pipe for the connection of tubes and bags for infusions. The effect of sterilization was studied by means of tensile mechanical characterization, thermo-gravimetric and morphological analysis and FT-IR spectroscopy. UV-VIS spectroscopy was used to evaluate the yellowing index, determined by radiation exposure. For each specimen, a no-sterilized one was tested for comparison.

**Results and discussion:** From the analysis of the results it can be concluded that: on PVC based materials (PVC-pipe and PVC band), in particular with  $\gamma$  radiation, sterilization generally favors crosslinking processes, detectable by FT-IR analysis, with consequent stiffening as observed with the increase in the modulus of elasticity E; in the case of TRIFLEX pipe, the slight stiffening observed by the tensile tests can be induced by a slight increase of the crystalline phase in the PE inner layer produced by sterilization, as detected by FT-IR analysis; the PC tube, underwent a photo-oxidation process and scission of the chains detectable by FT-IR analysis which explains the loss of rigidity of the material observed during the mechanical tests; in all cases, sterilization has led to a significant variation of the optical properties of materials quantified with a yellowing index increase up to 100%; between the two types of sterilizations,  $\gamma$  radiation is the most aggressive in the material properties change. However, all the modifications produced by radiation exposures are not likely to compromise the use of the items subjected to this investigation, after the sterilization process.



Fig. 1 - PVC pipe, PVC band, TRIFLEX pipe, PC rigid pipe (from left to right).

### STUDY OF THE INTERFACE BETWEEN THE CAPSULE AND THE CONSOLIDATING POWDER MASS DURING HIPING OF Ni SUPERALLOY

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**Concept:** The use of Hot Isostatic Pressing (HIP) technology for directly forming components to a near net or net shape is currently depending on the possibility to limit the interaction between the capsule and the powder mass. The capsule is typically made of metallic material (typically low carbon steel) and its main role is to efficiently transfer the forming pressure at HIP temperature to the consolidating powder mass. During HIP-ping cycle at the interface elements inter-diffusion and partial sintering occur, thus providing altered properties to the superficial layers of the final components. The extension of such alteration defines the possibility to have near net or net conceptual design.

**Motivations and objectives:** The current paper reports of a systematic study on the interaction mechanisms occurring between a low carbon steel capsule and Astroloy Ni alloy. Chemical composition profiles across the interface were derived through the use of Energy Dispersive Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS) and Combustion Analysis to specifically detect the carbon content at different depth layers. Micro and nanohardness measurements were applied to map the mechanical levels across the interface region. Scanning Electron Microscopy (SEM) were used to study the consolidation level achieved at the capsule/Ni alloy interface and in the

sub-superficial layers moving from this interface to the core. To complete the study X-ray micro-diffraction analysis were applied to detect phase distribution from the capsule to the core of the Ni-alloy.

**Results and discussion:** Main observations achieved are the following:

- 1) The powder mass is consolidated already at the capsule/Ni-alloy interface, but its microstructure is characterized at the interface by well identified spherical powder granules sintered without marked shape modifications; between 1 to 2 mm from the interface the powder mass is indeed sintered; here the original powder granules can be identified rarely and the typical polycrystalline structure is formed; nevertheless some isolated grains can still be detected.
- 2) At the capsule/Ni-alloy interface a preferential diffusion of Titanium at powder granule boundary occurs; at the same time carbon diffusion from the capsule into the consolidating Ni-alloy occurs thus forming Titanium carbides preferentially at primary particles boundaries; this results in a decoration with carbides of the regions between consolidate powder particles; this effect disappears as we move from the capsule/Ni-alloy interface to the Ni-alloy core, i.e. as long as the carbon diffusion is progressively limited.
- 3) The hardness profile across the capsule/Ni-alloy interface is highly scattered; this is put in correlation with the effects of preferential segregation of elements in the powder granules of the very first powder mass layer (i.e. the first 1-2 mm) and the related precipitation of carbides; the hardness level becomes uniform at deeper layers from the interface.

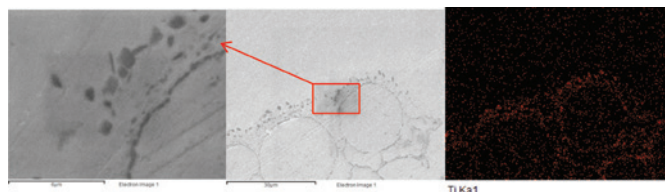


Fig. 1

#### STUDY OF SELECTIVE ABSORPTION OF OIL/WATER AND OF MECHANICAL PROPERTIES OF POLYURETHANE FOAMS FOR OIL SPILL RECOVERY

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**Concept:** Pollution due to spillage of hydrocarbons into the sea represents an environmental problem well known in the last years. In order to recover oils and to clean the sea, containing arms made by polymeric materials can be employed. Polyurethane foams can be considered suitable materials for this purpose since they can recover oils from sea-water easily by squeezing and subsequently re-using them. In this work we studied polyurethane foams filled with carbon fillers, in different amount, in order to enhance the selectivity of the material toward the oils recovery and to improve the mechanical durability of the foam. Wet-ability in water, oils and water/oils mix, absorption measurements, morphological observations and mechanical tests were performed on the foams. Experimental results highlighted as the carbon filler enhance the selective absorption of the foam toward oils and improves the elastic behavior of the foam.

**Motivations and objectives:** In the last years, a problem which has attracted more and more concerns hydrocarbons spillage into the sea. Those events have grown in number by time, growing with petrochemical industry development, bringing extensive environmental damage in the short and long term. The effects, today, are still evident. They hit obviously flora, local wildlife and the economic field, with consequences on tourism and fisheries. To effectively combat oil spillage, it is however necessary, in addition to an immediate action, to choose cautiously the equipment and the materials to be used, according to the type of hydrocarbon and local conditions in which the spillage has happened. The main target of our work was that of designing a porous material which could be used in oils spill recovery operations. Between the possible materials useful for this purpose, we choose to use a polyurethane sponge admixed with carbon filler. This foam was characterized to assess its oleophilic, hydrophobic and mechanical properties.

**Results and discussion:** In this work we have studied nanocomposite foams, polyurethane based, experimentally characterized by physical and mechanical tests (contact angle measurement, absorption test according to ASTM F726-99 standard, optical microscopy observation and compression fatigue tests according to ISO 24999 standard. Results indicated an increase in hydrophobic behavior and a good oleophilic character of the composite sponges beside an improved selective absorption of the foam toward oils in mixed water/oil media. The better filler amount is around 1% in weight for the homogeneous distribution inside the polymeric foam. Finally, the fatigue test results showed that the elastic behavior of the foam grows the increasing in carbon filler amount.

#### SURFACTANTS CONTROL ON MnO NANOPARTICLES SHAPE AND MnS NANOPARTICLES CRYSTAL PHASE

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**Concept:** We studied how surfactants affect the synthetic outcome of a solvothermal protocol for the synthesis of MnO and MnS NPs, which comprises the decomposition of a Mn carboxylate in octadecene in the presence of sulphur and a long-chain surfactant. We found that appropriate choice of the surfactant allowed us to control (i) the shape of MnO NPs and (ii) the crystal phase of MnS NPs.

**Motivations and objectives:** As an initial step forward our goal of preparing magnetic core-shell AFM-FIM nanoparticles with improved magnetic stability exploiting both shape anisotropy and exchange coupling at the AFM-FM interface, we focused our attention on the synthesis of AFM manganese chalcogenides (MnO and MnS) with the aim of obtaining MnO/MnS NPs with anisotropic shapes, which could subsequently be coated with a FIM shell.

**Results and discussion:** In the case of MnO, we could control the anisotropic NP shape by changing the type of fatty acid surfactant (oleic or stearic) and by varying the surfactant:precursor molar ratio (from 0:1 to 8:1). In the case of oleic acid, we obtained multipode NPs comprising  $n = 1$  to 6 oval lobes, which can make up concave shapes; while with stearic acid, we obtained different multipode NPs comprising  $n = 1$  to 4 jagged-edged linear branches, namely, rods, T's and crosses. HRTEM showed that MnO multipodes are single crystals, grown as such from a single seed or developed by oriented attachment of smaller crystals. We could also show that the nature of the surfactant controls the crystal phase of MnS NPs. We investigated several long chain surfactants comparing two different metal precursors (manganese distearate and  $Mn_2(CO)_{10}$ ). In most cases,  $\alpha$ -MnS NCs are formed (for example, using surfactant such as carboxylic acid, alcohol, thiol or phosphine) but when a mixture of an aliphatic long-chain amine and stearic acid is present in the reaction mixture,  $\gamma$ -MnS NCs are obtained. This chemical control differs from previous reports where the resulting NP phase was controlled by physical means (temperature or pressure).

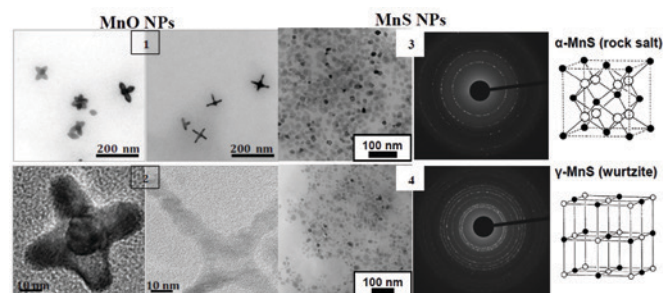


Fig. 1 - (1) Conventional TEM images of MnO NPs: left) oleate:prec 4:1, right) stearate:prec 1:1. (2) HRTEM images of MnO NPs: left) oleate:prec 4:1, right) stearate:prec 1:1. (3) Conventional TEM image and electron diffraction of  $\alpha$ -MnS NPs, surf: oleylalcohol. (4) Conventional TEM image and electron diffraction of  $\gamma$ -MnS NPs, surf: oleylamine.

**CHLORIDES CONCENTRATION AND pH MEASUREMENTS OF CONCRETE STRUCTURE THROUGH IMMERSED SENSORS**

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**Concept:** The present work develops non-destructive measurements of chemical-physical parameters of concrete, in order to evaluate the degradation condition and to monitor, in time, the aging process. This study in particular focuses on the measurement of parameters such as pH, and therefore the carbonation level of the concrete, and salt concentration (i.e. chlorides), and the evolution of these quantities with time. The analysis can be extended to other chemical-physical parameter of interests for which is provided a specific microsensor.

**Motivations and objectives:** This investigation process provides an innovative technique for the measurement, non destructive (NDT) and with remote sensing, of chemical-physical parameters through sensors located in structures in work. With this operating condition is possible to avoid: the taking of samples in situ, through coring or destructive tests; analytical laboratory measurements on samples/dust; the direct intervention of operators to perform the measurements. This experimental procedure allows measuring both chloride concentration and pH, and thus to perform a continuous monitoring of the state of preservation of the structural element, in order to control the degradation processes and to prepare in time maintenance plans.

**Results and discussion:** This project concerns: (i) the realization of appropriate sensors, Ag/AgCl for the chlorides and Ir/IrO<sub>2</sub> for pH, (ii) their installation within the concrete or manufactured articles, (iii) data detection and remote transmission. The sensors are directly embedded within the concrete during the casting stage, leaving out from the manufactured article a copper wire connected to the electrode itself. The latter is connected to a voltmeter. A counter electrode (Cu/CuSO<sub>4</sub>) leaning on the structure allows measuring the electrochemical potential. Using the Nernst equation the potential is converted in chlorides concentration and pH. In the case of existing buildings, the sensors can be inserted after the concrete casting. It is believed that the procedure is extendable to other materials, with appropriate instrumental devices. This method allows also obtaining thematic maps (chloride and pH) using grid of measurements, performed in the neighbor of the sensor.

**THERMOMECHANICAL DEGRADATION OF A POLYPROPYLENE/ GRAPHENE NANOCOMPOSITE**

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**Concept:** In this work the morphology and the rheological and mechanical properties of a nanocomposite made of a polypropylene with graphene nanoplatelets (GNP) have been investigated as a function of the compounding parameters to evaluate the thermomechanical degradation behaviour of this system. The presence of graphene seems to reduce the thermomechanical degradation of the matrix. A better dispersion of the GNP seems the cause of this behaviour.

**Motivations and objectives:** Aim of this work is to investigate the processing and the rheological and mechanical properties of a polypropylene based nanocomposite with graphene in order to evaluate the thermomechanical degradation of this system. In the adopted compounding conditions, an improved morphology is observed with increasing the severity of the processing.

**Results and discussion:** The torque curves measured during compounding depend only on the viscosity of the melt in the processing conditions. The dimensionless torque curves, Fig. 1a), indicate that the decrease of the torque is more relevant for the pure matrix and sensibly lower at low content of the graphene. This behavior is quite unexpected as other nanocomposites show an opposite behavior. However, when the nanofiller can change its morphology because of the compounding, a reduction of the thermomechanical behavior can be observed. In this case, a better morphology due to a better dispersion and some “exfoliation” of the GNP aggregates can be considered responsible for the apparent reduction of the thermomechanical degradation of the system. This hypothesis is confirmed by the elongation at break data, EB, Fig. 1b), that show again a reduced degradation kinetic of the nanocomposite system.

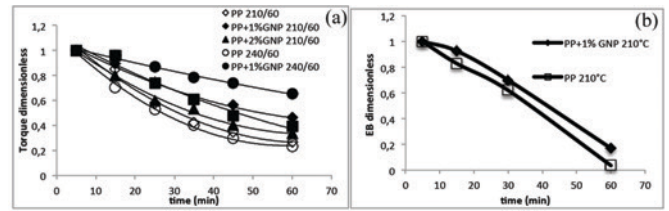


Fig. 1 - Dimensionless torque values (a) and dimensionless elongation at break (b) as a function of time.

**SELECTION TOOL FOR THE USE OF FUNCTIONAL MATERIALS**

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**Concept:** Functional materials, also called “smart materials”, are materials that can “sense environment events, process that sensory information and then act on the environment”. These materials are able to transform a given stimulus into a response. We use the general term “transition phenomenon” to describe this process. These transitions can be as diverse as, e.g.: mechanoluminescence, which is a light emission produced by the application of a strain, or thermoelectricity, the conversion of a temperature difference into an electric potential. We designed a specific database and selection process for functional materials. The data structure is organized around their main functionality: the transition phenomenon. This database is implemented in the Cambridge Engineering Selector software, using the “constructor” functionality.

**Motivations and objectives:** The standard selection framework proposed by Ashby relies on 4 successive stages: translation, limits, objectives, documentation. It is not entirely suited to the selection of functional materials, which has to account for the relation between stimuli and responses.

**Results and discussion:** In our database prototype, we introduce a table of transition phenomena, which is organized by families and sub-families of outputs (Fig. 1). The relationship between materials and transition phenomena is made by linking the tables together and providing specific attributes that describe the stimuli-responsive properties of the materials. Future developments include tables of existing products and processes used to implement functional materials or functionalize existing ones. In this work, as the entry point to the information system is the stimuli responsive behaviour of functional materials, rather than their structure and properties. The emphasis is thus put on user experience and interaction with materials and products.

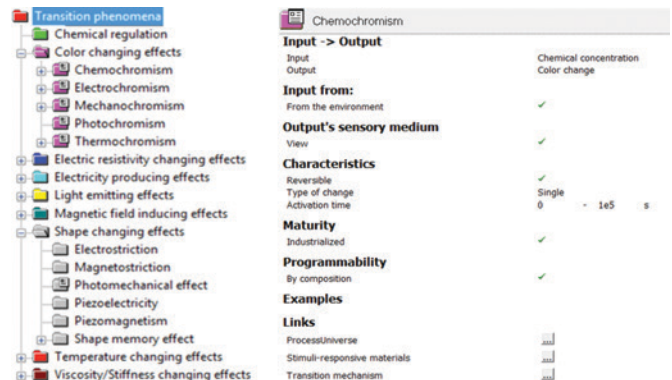


Fig. 1 - Tree structure and datasheet of the transition phenomena table.

**PHOTOSTABILIZATION OF CROSSLINKED EVA AS ENCAPSULANT FOR PHOTOVOLTAIC MODULES**

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**Concept:** EVA copolymer is widely used as encapsulant for photovoltaic modules. This polymer must be stabilized to extend the life time of the material and to avoid the change of permeability to the solar radiation. The work aims at finding new photostabilizing agents to improve the lifetime of this material. **Motivations and objectives:** The aim of this work is to study the photostabilization of crosslinked EVA to be used as encapsulant in photovoltaic cells. In particular, the photooxidation was followed by monitoring the mechanical properties and the IR spectrum as a function of the photo-oxidation time.

**Results and discussion:** The materials used in this work were a sample of film grade, an organic peroxide (Luperox 101) by Atkema and several samples of stabilizers. The compounding was realized by melt-mixing EVA and the additives in a Brabender Plasticorder at a temperature of 110°C and at a rotational speed of 40 rpm for a mixing time of about 5 min. For the preparation of the crosslinked materials Luperox was added at a concentration of 1.5 phr. Accelerated photo-oxidation was carried out in a QUV at 60 °C with a light exposure/condensation cycle of 8/4 hr.

TABLE I

Sample code	Chemical Class	Amount, ppm
EVA+0.6C.NOX	Triazine	6000
EVA+0.6C.SORB	HB Acid	6000
EVA+0.6THT	HALS	6000
EVA+0.6T123	HALS	6000
EVA+0.6T371	HALS	6000
EVA+0.75T371	HALS	7500

The elongation at break-exposure time curves, Figure 1, indicate that the presence of the HALS stabilizers strongly improves the decay of the elongation at break and then the photoresistance of the crosslinked matrix.

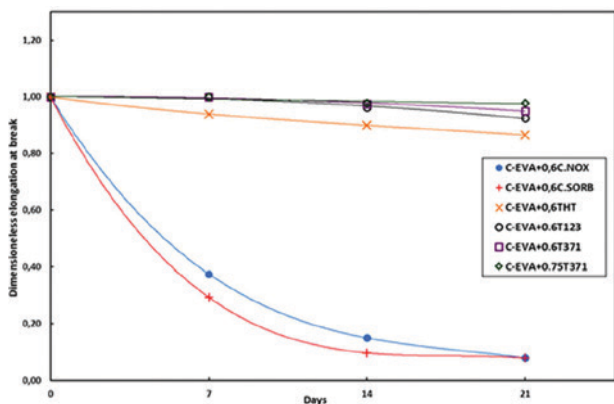


Fig. 1

**INTERLAMINAR ELECTROSPUN THERMOPLASTIC VEILS FOR ADVANCED COMPOSITES: PRO AND CONS**

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**Concept:** The intelaminal region is a key component to control delamination resistance of fiber reinforced composites. The use of nanostructured veils

add the possibility to bring functionalities other than simple mechanical resistance in the interlaminar region. The concept of engineering the interlaminar region by the use of well-designed veils is covered in the paper.

**Motivations and objectives:** Epoxy resins are widely used for structural fiber reinforced composites because of their easy processing and good thermomechanical properties but they are brittle. This brittleness cause delamination in composites. Epoxy resins used in structural prepregs for aircraft primary structures are blended with aromatic thermoplastics to overcome the poor toughness of epoxies but these prepregs cannot be used in resin transfer molding because of their high viscosity caused by the thermoplastic predissolved in. Therefore, a novel approach based on soluble interlaminar thermoplastic veils was developed and is discussed here. Interlaminar toughening with soluble veils is influenced by different parameters such as: thermoplastic type, epoxy monomer type, cure profile, presence of filler etc. The present paper summarize the researches carried out on this topic showing the influence of some design parameters on the efficiency of the proposed approach. The comparison with the use of non soluble interlaminar veils is also discussed.

**Results and discussion:** The epoxy monomers were triglycidyl para-aminophenol (TGAP) and diglycidylether of bisphenol A (DGEBA). The diamine curing agent was methylene bis(2,6-diethylaniline) (MDEA from Lonza). Two lab made thermoplastic modifiers with masses of 9,000 and 20,000 were used as soluble veils in the first trials. Commercial PES were used for scale up testing. Commercial nylon based polymers and carbon fiber veils were evaluated as non soluble veils. All the electrospun membranes were impregnated with epoxy resin and the dissolution behavior study under an optical microscope at different isothermal temperatures. High molecular mass coPES dissolved later that low molecular mass while TGAP was faster to dissolve coPES than DGEBA. Dynamic mechanical analysis and microscopic analysis were carried out on cured neat specimens and lamiates to confirm the full dissolution of the veils. Figure 1 show the comparison, for different coPES concentration, between laminates prepared with the soluble veil and the prepreg route. The comparison confirmed that similar morphologies can be obtained with both routes. Similar viscoelastic properties were also obtained. DCB testing was performed on scale up specimens showing increased in G<sub>ic</sub> of about 15% and 39%. Non soluble veils, in some cases, showed increases of G<sub>ic</sub> of 78% but no possibility for selective dispersion of nanofiller was demonstrated with these non soluble veils. On the other hand, several experiments demonstrated that soluble veils are exploitable to obtain the selective dispersion of nanofiller into composite laminates.

TABLE I

Sample	Max Load/Width [N/mm]	S <sub>0-1</sub> [N/mm]	%Δ	Max G <sub>c</sub> [J/m <sup>2</sup> ]	S <sub>0-1</sub> [J/m <sup>2</sup> ]	%Δ
DGEBA-MDEA	1,79	0,10		544,70	35,27	
DGEBA-MDEA-10NANOVI30500	3,03	0,57	+69,27% +35,27%	757,65	125,74	+39,09% +20,55%
DGEBA-MDEA-20NANOVI30500	2,24	0,16	+25,14% -26,07%	628,51	122,70	+15,39% -17,04%

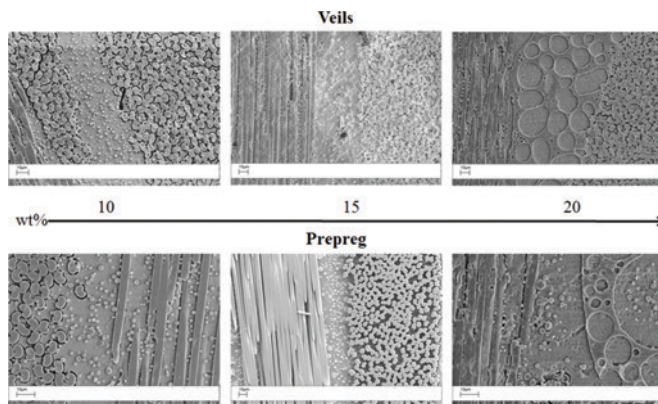


Fig. 1



### FUNCTIONAL ELECTROSPUN MEMBRANES

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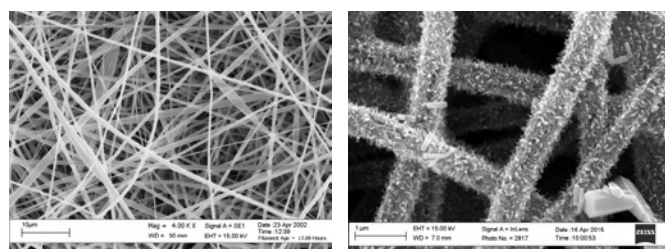
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**Concept:** The present paper is focused on the development of novel functional materials based on the use of hierarchical structuring. Functional nanowires are grown on the surface of electrospun nanofiber to maximize the active surfaces while keeping high permeability to ensure full contact with reagents.

**Motivations and objectives:** Membranes for filtration used nowadays are mostly based on mechanical filtering. However, in some applications it is needed to have an active filtration effect with chemical removal of toxic substances. The present work aims to combine the permeability properties of electrospun membranes with the efficient chemical activity of oxide nanowires. Different grown methods are evaluated to overcome cost limitation for foreseeable industrial scale up.

**Results and discussion:** Polyethersulphone was selected as basic polymer for membrane production because of its widely accepted use in the membrane field. Electrospinning was performed on a laboratory scale machine. The polymer was dissolved at room temperature in DMF: Toluene 1:1. The polymer solution was electrospun at 21KV with a constant flux of 30µl/min. The resulting membrane was free of defects (Fig. 1) and the average fiber diameter is 716 nm ± 365 nm. The membrane showed an average pore diameter of 5.32 µm with maximum values of 6.65 µm. The porosity was 91,4% ± 1,1. The ZnO nanowires were grown by a hydrothermal process. In a first step the electrospun fibers were immersed in a solution of Zn(Ac)/H<sub>2</sub>O (0.5 M) and stirred for 3h. Then they were dried in an oven at 110°C overnight. The second step was a CBD (Chemical bath deposition) process by using Zn(Ac), H<sub>2</sub>O and Etylenediamide (EDA). The resulting active membrane was characterized by SEM analysis. It was fully covered with ZnO nanowires that are characterized by photocatalytic activity. Similar results were achieved by Athauda et al. but their preparation procedure was more time consuming and complex to scale up. However, the presence of ZnO nanowires showed that 82% of the initial methylene blue was photocatalytically degraded. Alternative growing methods were also evaluated to obtain different nanowire structure.



a) PES Electrospun membrane

b) Active PES Electrospun membrane

**Fig. 1 -** Comparison between electrospun membrane (a) and functionalized membrane (b).

### MATERIALS SELECTION TOOLS IN PROFESSIONAL APPLIANCES: HYPOTHESIS TO ESTIMATE MATERIALS' PERFORMANCE AND IMPACT ON INDUSTRIAL PROCESSES

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**Concept:** The use of materials selection in professional appliances increased in recent times, thanks to its potential pre-evaluation of materials' performance and impact on industrial production processes. Materials selection permits cost reduction in preventive tests, introduction of innovative materials and technologies, materials optimization and decreasing of failures. Through a collaboration among Politecnico di Milano (Department of Design and Department of Chemistry, Materials and Chemical Engineering "Giulio Natta") and Electrolux Professional S.p.A. (Global Research & Development, Innovation & Technologies Area), an evaluation of materials' tangible and intangible properties has been developed using non-traditional methods. In the first part, this work evidences the major limits and critical points of the materials' selection tools currently and most commonly proposed in industrial applications. Within these, the main key points highlighted are the translation and connection of quantitative and qualitative properties and the risk associated to the materials selection process reliability. In a second step, some ameliorative hypotheses are built to overcome these limits, using a repeatable and suitable method for different materials selection cases.

**Motivations and objectives:** From the critical analysis of Ashby and Karana materials selection processes emerged a critical issue: the need of a unique language to evaluate the different properties commonly investigated in a materials selection conducted both from engineers and designers. The non-traditional materials selection methodology would offer a complete evaluation of different properties: material's technical properties (e.g. mechanical, thermal and process parameters), durability (e.g. food chemicals and detergents), food-material compliance and intangible properties (e.g. customer perception). The need of a unique materials selection method, able to convert quantitative to qualitative evaluation of properties and to estimate the risk associated to the materials selection reliability, driven the research. A procedure, which evaluates components' life and possible failure modes (based on DOE), is under development in order to integrate these information into the future products development.

**Results and discussion:** The research presents the development of the materials selection methodology under considerations supported by a case study focused on durability properties of materials. Each professional appliance can be seen as an input-output system constituted by materials and components that interact and have an effect on materials and components, generating different outputs. Failures are possible outputs, due to different factors, and decrease the efficiency of the system, reducing the guaranteed performances. As regards the perception of the same professional appliances by the users, their quality is unconsciously rated on the basis of visual, haptic and auditory feedback generated during the user-product interaction. The "Sensory Metrology" has been selected as appropriate method in investigating both physical properties of the materials, and in evaluating the relation with some descriptors (e.g. adjectives) associated to the perception of quality and robustness of the whole appliance.