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ANISOTROPIC PROPERTIES OF NATURAL RUBBER NANOCOMPOSITES WITH sp² CARBON ALLOTROPES

Agnelli S¹, Pandini S¹, Torricelli F², Romele P², Musto S³, Serafini A³, Galimberti M³

¹Department of Mechanical and Industrial Engineering, University of Brescia, Brescia - Italy

²Department of Information Engineering, University of Brescia, Brescia - Italy

³Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

Introduction: It is well known that nanoparticles with high aspect ratio, such as carbon nanotubes (CNT), can provide anisotropic properties in polymeric matrices. In particular their alignment is an effective way to selectively improve the composite properties along a specific direction. However, in soft matrices, such as rubbers, anisotropic effects promoted by nanoparticles have never been thoroughly analysed. Based on structural, mechanical and electrical characterizations, this work provides a comprehensive investigation and analysis of the anisotropic properties promoted by nanofillers in rubber nanocomposites prepared by an easy and common production process.

Materials and methods: Natural rubber based composites are prepared by mechanical mixing, calendaring, and compression molding. 3 mm thick sheets of composites are prepared with three different fillers, i.e. CNT, nanographite with high shape anisotropy (nanoG) and CB, and various filler amounts are used. Electrical and dynamic mechanical properties are measured along different directions. The dependence on strain amplitude (i.e., Payne effect) of dynamic mechanical properties is also studied. Transmission Electron Microscopy (TEM) analysis is used to evaluate preferential filler orientation.

Results and discussion: Both dynamic moduli and electrical resistivity show a strong dependence on the measurement direction for both CNT and nanoG filled composites. Properties are very similar inside the sheet plane and very different in the orthogonal direction, according to the behavior of a transversal isotropic material. The anisotropy level, defined as ratio between maximum and minimum property values, is found to be dependent on filler type and amount.

This behavior could be interpreted as a consequence of a random orientation of the filler particles in the sheet plane, and of their planar piling up through the sheet thickness. Evidence of preferential orientation is further confirmed and quantitatively observed by coupling TEM and Selected Area Electron Diffraction analyses, following a combined approach that is applied to the microstructural characterization of nanofilled rubber for the first time. This work provides interesting insights on the behaviour of nanofilled rubber composites, which can be useful for a better control of functional properties, such as energy dissipation and electrical properties.

EXPLOITING INTERPLAY BETWEEN BACTERIA AND MICROALGAE FOR SIMULTANEOUS WASTEWATER REMOVAL AND BIOREFINERY: A MICROBIAL FUEL CELL PROOF-OF-CONCEPT (EXOTICA)

Angioni S^{1,2}, Bianchetto O^{1,2}, Millia L^{1,2}, Quartarone E^{1,2}, Cavinato G³, Pace G³, Negro E³, Vezzu K³, Bach Delpuech A³, Di Noto V³, Mustarelli P^{1,2}

¹Department of Chemistry, University of Pavia, Pavia - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of Industrial Engineering, University of Padua, Padua - Italy

Introduction: The task to reach a carbon-free society is a primary milestone of the world-wide economy. Bioenergy is an emerging economic field, of wide interest both for heat and power production. It is renewable energy made available from materials derived from biological sources (biomasses), which can be converted into biofuels, biohydrogen, and also directly into bioelectricity.

Materials and methods: In this project, we aim at building-up a PMFC with algae-assisted biocathode for the simultaneous treatment of wastewater and algae growth, necessary for the production and subsequent extraction of technological products. In detail, the project focuses on the development of: i) innovative proton exchange membranes (PEMs) based on polybenzimidazole moieties, both pure and composites, which are cheaper than Nafion™, and also highly resistant to biofouling, less permeable to the substrate and finally less sensible to the bigger cations typically present in the organic substrate (e.g. wastewater). All these aspects will be developed by modulating the morphology and the microstructure of the membrane through the exploration of advanced membrane preparation techniques, as electrospinning; (ii) innovative hierarchical nanostructured supports based on graphene, for anodic microbial fuel cell electrocatalysts (ECs); and (iii) advanced ECs for the oxygen reduction reaction (ORR), for application at the cathode of microbial fuel cells.

Results and discussion: Here we report some preliminary results of the project. Two PMFCs were investigated: i) Pt-electrocatalysed, and ii) Pt-free. They were operated as a microbial carbon capture (MCC) device under continuous illumination, by using a domestic wastewater as the anolyte and *Scenedesmus acutus* strain in the catholyte. The Pt-based cell allowed generating higher volumetric power density (~400 mW m⁻³) after more than 100 operating days. This resulted in improved wastewater treatment efficiency, determined in terms of normalised energy recovery (NER >0.19 kWh/kgCOD⁻¹ in case of Pt). The CO₂ fixation of the PMFC-grown microalgae led to a high production of added-value products, namely pigments and fatty acids. A significant quantity of lutein was obtained, as well as a relevant amount of other valuable carotenoids, as fucoxanthin, astaxanthin and cantaxanthin.

ANTIMICROBIAL BIODEGRADABLE FOOD PACKAGING FILMS BASED ON LAE

Apicella A¹, Scarfato P¹, Di Maio L¹, Hayouka Z², Incarnato L¹

¹Department of Industrial Engineering, University of Salerno, Fisciano (Salerno) - Italy

²Institute of Biochemistry, Food Science and Nutrition, The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot - Israel

Introduction: Antimicrobial packaging represents an innovative technique to inhibit microbial growth in foods while maintaining their quality, freshness and safety.

Traditional techniques, such as the direct addition of antimicrobials in food matrix, results in an immediate reduction of bacterial populations, but doesn't allow controlling the growth of surviving cells after depletion of antimicrobial residues.

The incorporation of antimicrobial substances into the polymer matrix could control the release of the active compound, providing a continuous antimicrobial effect on the food during the exposure and playing a dynamic role in food preservation.

Materials and methods: Ethyl- α -dodecanoyl-L-arginate (LAE) was selected as the active agent, approved by FDA and EFSA as GRAS additive for food contact, effective against a wide range of microorganisms, such as Gram positive and negative bacteria, yeasts and moulds.

Multilayer films were obtained by antimicrobial addition at different percentages of active phase (1, 2.5, 5%) to a PLA coating solution, spread on a BOPET substrate.

The systems were characterized by several techniques (FT-IR, DSC, TGA, tensile tests, UV-Vis, contact angle, colour measurements, weldability tests) in order to obtain information on LAE interaction with the polymer matrix and functional performance of the films.

Finally, preliminary antimicrobial tests were performed to assess the effectiveness of the produced systems in inhibiting microbial growth.

Results: The results on multilayer systems showed that, after the coating layer addition, chemical and physical properties were not substantially modified.

In addition, thanks to the amorphous nature of PLA coating layer, good sealability was obtained for the multilayer films, unlike the original not-sealable BOPET substrate.

Furthermore, the presence of LAE in the coating layer was demonstrated effective in giving to the films antimicrobial activity against bacteria.

Discussion: Results on antimicrobial activity of multilayer samples highlighted the proportionality between the inhibition of microbial strain and the LAE concentration into the polymer matrix. Further research will focus on the optimization of multilayer systems, in terms of layer thickness and antimicrobial content, and on the analysis of the LAE release kinetics.

DIRECT ENERGY DEPOSITION OF AISi10Mg

Aversa A¹, Tusacciu S², Reggio E², Busatto M², Lai M², Manfredi D³, Biamino S⁴, Fino P⁴, Lombardi M⁴

¹ Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

² IRIS S.r.l., Turin - Italy

³ Center for Sustainable Futures Technologies - CSFT@POLITO, Istituto Italiano di Tecnologia, Turin - Italy

⁴ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Direct energy deposition (DED) is a blown powder additive manufacturing (AM) process that allows to rapidly built and prototype complex shaped metallic parts and to clad or repair metallic components. The advantages in terms of microstructures and mechanical properties of DED components have been investigated mainly for steel, nickel-based and titanium-based alloys. Up to now, only a few studies investigated the DED process of aluminium alloys which is very challenging mainly because of the high reflectivity of the powder.

Materials and methods: AISi10Mg gas atomized powders, provided by LPW Technology, were used for all samples. The DED system used is constituted by a 3 kW IPG fiber laser located on the top of an ABB anthropomorphic robot arm. The laser melts the metal powders, which are blown by means of GTV powder feeder through a lateral nozzle which anticipates the laser path. An inert shielding gas protects the melt pool from oxidation. The main parameters varied in these experiments were the focus position with respect to the building platform, the laser power and the powder flow rate. The scan speed rate was kept constant at 60 mm/s for all samples.

In this preliminary study, single scan tracks (SSTs) were produced in order to select the most suitable power, powder flow rate and focus position. This approach will allow the definition of optimized process parameters in view of the production of massive components.

Results: Optical micrographs revealed that the focus position has a strong effect on the stability of the scan and that relatively low power must be used for the obtainment of stable tracks. High power and negative focus position cause the formation of deep melt pools, which contain pores in their lower part indicating a keyhole melting. FESEM micrographs showed that DED samples are characterized by fine α -Al cells surrounded by the eutectic structure.

Discussion: It was possible to produce dense and stable DED aluminum SSTs by means of the selection of the optimized building parameters. Measurements of SSTs dimensions allowed the selection of the most suitable distance between nearby tracks for the obtainment of dense massive samples.

MATERIALS FOR HYDROGEN STORAGE: PROPERTIES AND ENVIRONMENTAL IMPACTS

Belmonte N¹, Dematteis EM¹, Castellero A¹, Pistidda C², Agostini A³, Luetto C⁴, Sgroi M⁵, Rizzi P⁵, Moretto P⁶, Dornheim M⁶, Baricco M¹

¹ Department of Chemistry and NIS, University of Turin, Turin - Italy

² Nanotechnology Department, Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research, Geesthacht - Germany

³ ENEA-Italian National Agency for New Technologies, Energy and the Environment, Rome - Italy

⁴ Tecnodelta S.r.l., Chivasso (Turin) - Italy

⁵ Group Materials Labs, Centro Ricerche FIAT, Orbassano (Turin) - Italy

⁶ European Commission, Joint Research Centre (JRC), Institute for Energy and Transport (IET), Sustainable Transport Unit, Petten - The Netherlands

Introduction: Hydrogen is investigated as the next generation energy carrier for mobile and large scale stationary uses, but its efficient storage is still a bottleneck toward industrial applications. High pressure gaseous storage is the current technology, suffering for high costs and safety issues. Research

focused recently on new solid-state hydrogen storage materials such as borohydrides, owing to their high gravimetric hydrogen content. In this paper, Life Cycle Assessment (LCA) methodology has been employed to evaluate the environmental impact of hydrogen storage technologies and new mixtures of complex hydrides were explored in order to improve hydrogen sorption reactions.

Materials and methods: LCA was performed on a prototype solid-state and commercial type IV gas tank by the GaBi software. Various ternary, quaternary and quinary equimolar combination in the LiBH_4 - NaBH_4 - KBH_4 - $\text{Mg}(\text{BH}_4)_2$ - $\text{Ca}(\text{BH}_4)_2$ system were synthesized by ball milling and characterized by XRD, DSC, TGA-MS. Thermodynamic properties were assessed by CALPHAD (Thermo-CALC software).

Results: A prototype solid-state hydrogen tank with a mixture of metal and complex hydrides ($\text{LaNi}_{4.3}\text{Al}_{1.0.4}\text{Mn}_{0.3} + 2\text{LiNH}_2 - 1.1\text{MgH}_2 - 0.1\text{LiBH}_4$) and a commercial type IV compressed gas tank were compared and evaluated by LCA. Global warming potential is 481 and 33 kg CO_2 eq. for the prototype and type IV tank, respectively. The environmental impact of the solid-state tank is given mainly by stainless steel and the complex hydride, whereas carbon fiber is the most impacting component for the type IV tank. To improve the hydrogen sorption conditions of the complex hydride, we explored new solid-state hydrogen storage materials by mixing different borohydrides. Eutectic mixtures or bimetallic, trimetallic compounds and solid solutions were evidenced. For LiBH_4 - NaBH_4 - KBH_4 binary and ternary mixtures, thermodynamic properties and phase diagrams have been assessed. The occurrence solid solutions and multi-metallic compounds leads to changes in the hydrogen desorption reactions, depending on the interaction among the components.

Discussion: Gaseous storage needs high cost composite materials for tanks and has a low energy efficiency because of compression. Solid-state hydrogen storage needs materials with high costs and strong environmental impacts. The balance between properties and environmental impact of hydrogen storage technologies will be discussed.

MICROSPHERES CHARACTERIZATION: FOCUSED ION BEAM AND NANOINDENTATION

Moscatelli R, Bemporad E

Engineering Department, University "Roma Tre", Rome - Italy

Introduction: The definition "microspheres" includes micro-capsules, cells, beads and all of them represent a wide scientific research area, due to the large industrial applications feasible with these products (life sciences, biotechnology, cosmetics, electronics and environment applications). Morphology and structure of the microspheres are strictly bound to their productive process, for example a polymeric reactions realized in well-defined conditions or the polymers auto-assembly in solution. It is so clear how much crucial is the microspheres characterization in order to study the active principles release depending on the boundary conditions of these materials (environment).

Materials and methods: Hollow polymeric microspheres for cosmetic and cleaning industrial applications with different morphologies and compositions have been deeply analyzed and characterized by several techniques: optical profilometer analysis, SEM, FIB cross-section, nanoindentation (compression).

Results: FIB analysis: determination of several capsules' properties: integrity, dimensions, outer/inner surface morphology, shell thickness. Nanoscale mechanical characterization: development of a robust and reliable procedure to quickly measure stress/deformation of capsules under compression (rupture force, rupture stress and rupture deformation).

Surface free energy evaluation: development of a new theoretical models and new methodologies for free energy measurement via tip approach with nanoindentation.

Discussion: The investigation developed on the tested samples allowed to establish a sort of new characterization protocol for this kind of materials: it has been possible to realize new theoretical models and new measurement procedures overstepping the standard and conventional use of the equipment. In this study a robust and efficient tool for the mechanical characterization (and later industrial selection) has been tested and validated and it is now ready for the industrial implementation. A new technique for the adhesion properties measurement has been explored and tested and it is now under development.

EFFECT OF POLYMER MODIFIED CEMENTITIOUS COATINGS ON CHLORIDE INDUCED CORROSION OF STEEL IN CONCRETE*Bolzoni F¹, Brenna A¹, Diamanti MV¹, Ormellesse M¹, Pedeferra MP¹, Pastore T², Berra M³*¹ Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy² Department of Design and Technology, University of Bergamo, Dalmine (Bergamo) - Italy³ R.S.E. S.p.A. Ricerca sul Sistema Energetico, Milan - Italy

Introduction: Steel reinforcements in concrete are in passive condition. Depassivation may occur in presence of chlorides in contact with steel over a critical content (from 0.4% to 1.0% by cement mass in aerated concrete). Polymer modified cementitious mortars represent an additional method to prevent chlorides induced corrosion of steel in concrete. These coatings show good adhesion, flexibility and "crack-bridging" ability. Nevertheless, while many results of standard and short-term tests are available in the literature, long-term data on the protective effect are lacking.

Materials and methods: Two commercial cementitious coatings, modified with acrylic-based polymer (polymer-to-cement (p/c) ratio of 0.35 and 0.55, mean thickness 2 mm) were tested. Concrete water-cement ratio was 0.5 with 28 days compressive strength 46 MPa. Rebar corrosion potential and linear polarization resistance monitoring was performed in concrete exposed to accelerated chlorides penetration (ponding cycles) for 17 years. Total chloride content, water content, coating adhesion and morphology of corrosion were assessed.

Results: The carbon steel rebars in concrete without coating suffered initiation of corrosion after few months; in concrete with 0.35 p/c coating, the initiation of corrosion was noticed on two (of three) specimens after 3.5 years; with 0.55 p/c coating reinforcement remained passive after 17 years. The coatings were able to reduce the chloride content in concrete and the effect was enhanced for the higher p/c ratio, as expected. Critical chloride content (necessary for the onset of corrosion) was 0.5% by cement mass, not affected by the presence of coatings. Severe pitting corrosion was observed on rebars after the exposure, with mean value of corrosion rate below 10 mm/year.

Discussion: Polymer modified cementitious coating can strongly delay chloride-induced corrosion of rebars, reducing chloride transport in concrete. The protective effect is more pronounced as the polymer content (p/c) increases. After corrosion initiation, in coated concrete, corrosion rate is reduced due to the lower water content in concrete, even if this effect is less important.

REPROCESSING OF PLA BASED NANOCOMPOSITES: EFFECT OF NANOFILLER*Botta L^{1,2}, Scaffaro R¹, Mistretta MC¹, Sutura F¹, La Mantia FP¹*¹ Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Several studies investigated the effect of the reprocessing on the properties of PLA. However, recycling of PLA-based nanocomposites was not been investigated in depth so far. PLA is susceptible to thermo-degradation during melt processing operations. For this purpose, the study of thermo-mechanical degradative phenomena associated to its re-processing is of great concern in order to assess the possibility of recycling PLA-based nanocomposites. This work aims to evaluate the effect of reprocessing on morphology and properties of PLA reinforced with different nanofillers, i.e. hydroxycitric acid (HT) and graphene nanoplatelets (GnPs), pointing out on the role of the nanofiller.

Materials and methods: The matrix used in this work was an extrusion grade sample of PLA. The nanofillers were two commercial HT samples, i.e. a unmodified HT (U-HT) and an organically modified HT (OM-HT), and graphene nanoplatelets (GnPs).

Nanocomposites (containing 5 wt% of filler) were prepared in a co-rotating twin-screw extruder. Reprocessing was carried out using a single screw extruder up to five subsequent extrusion cycles.

The morphology of the materials was evaluated by SEM. The rheological characterization was performed using a rotational rheometer. Tensile tests were carried out on specimens cut off from films prepared by compression molding. The viscosimetric molecular weight (M_v) was calculated by measurements of intrinsic viscosity.

Results: The melt viscosity of all the materials, decreased on increasing the extrusion cycles except the viscosity of PLA + OM-HT after the first extrusion cycle. The SEM micrographs revealed that the reprocessing of the nanocomposites led to an improved dispersion of nanofiller. Both the neat PLA and PLA/HT nanocomposites showed a decrease of M_v on increasing the reprocessing cycles. In particular, the presence of the HT caused an strong decrease of M_v even for not reprocessed materials. On the contrary, the presence of GnPs decreased the rate of degradation due to the reprocessing.

Discussion: The reprocessing affected the properties both of the neat PLA and of the nanocomposites. However, on increasing the extrusion reprocessing cycles, the properties of the nanocomposites showed behavior due to two opposite effects, i.e. chain scission due to thermo-mechanical degradation and filler dispersion improvement resulting from multiple processing.

CATHODIC OVERPROTECTION AND INTERFERENCE CONDITION ON A GAS TRANSPORTATION PIPE ENCASED IN A CASING PIPE IN THE PRESENCE OF WATER IN THE ANNULUS*Brenna A^{1,2}, Beretta S^{1,2}, Brugnetti F³, Ormellesse M^{1,2}*¹ Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy³ Snam Rete Gas, San Donato Milanese (Milan) - Italy

Introduction: The Italian ministerial decree (D.M. 4 Aprile 2014) foresees that, corresponding to rail crossing or parallelism, pipes for liquid and gas transportation shall be encased in a coated steel pipe called casing pipe. The ends of the casing pipe should ensure the perfect watertight seal of the annulus while spacers of insulating material should separate the two pipes. Laboratory tests have been carried out to investigate the protection and interference condition of the gas transport pipe and casing pipe, respectively, in case of a leak in the watertight system with water in the annulus.

Materials and methods: Two coaxial carbon steel tubes were used to simulate the gas transport and casing pipe. The inner tube is a coated pipe (4-inch diameter) with a coating defect of 3 cm² connected to an impressed current cathodic protection system. Different configurations were considered for the casing pipe (8-inch diameter): 1) bare pipe with a passing hole (1 cm diameter) in front of the coating defect of the internal pipe; 2) coated pipe with a 3 cm² defect on the internal and external surface; 3) bare pipe electrically connected to the internal pipe with a 10 Ω shunt. Tests were performed in solution with resistivity 50 and 200 Ω -m, by increasing cell voltage and measuring the current and potential of both tubes.

Results: In the presence of a perfect watertight seal, no interference takes place on the casing pipe, as expected. In presence of electrolyte in the annulus, the external surface of the casing and the internal pipe are cathodically polarized, while the potential of the internal surface of the casing increases in the anodic direction.

Discussion: Interference effects on the casing increase in the presence of a coating with defects, because the interference current concentrates in them, and by decreasing solution resistivity. On the internal pipe, overprotection conditions are reached in all tested conditions without a connection between the two pipes. In the presence of a hole in the casing, interference effects are negligible (bare pipe) but overprotection condition on the internal tube is reached at the lowest cell voltage (2.5 V).

BENCHMARK ANALYSIS ON THE MANAGEMENT OF CATHODIC PROTECTION OF BURIED PIPELINES ACCORDING TO ISO 15589-1*Brenna A^{1,2}, Beretta S^{1,2}, Bolzoni F^{1,2}, Brugnetti F³, Ormellesse M^{1,2}*¹ Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy³ Snam Rete Gas, San Donato Milanese (Milan) - Italy

Introduction: Corrosion of buried carbon steel pipeline transporting methane is controlled by cathodic protection (CP) in combination with a coating. International standards are available giving indications concerning CP crite-

ria, systems, design, installation, commissioning and monitoring. The international standard ISO 15589-1:2015 (Petroleum, petrochemical and natural gas industries – Cathodic protection of pipeline systems – Part 1: On-land pipelines) covers all CP aspects included in the well-known EN 12954 (Cathodic protection of buried or immersed metallic structures) and EN 13509 (Cathodic protection measurement techniques). In 2016, a benchmark analysis was performed in order to understand how international companies manage CP.

Materials and methods: Twenty companies were involved in the benchmark: 13 from Europe, 3 from Asia, 2 from Latin America and 2 from Africa. The benchmark covers three main topics: CP effectiveness, monitoring and services. Concerning the first, each company was requested to describe how the CP system is structured and how CP effectiveness is verified. Regarding monitoring, questions were mainly focused on use of coupons and potential probes. Concerning CP services, the question aimed to verify if maintenance is carried out by corporate personnel or not.

Results: All companies perform the general assessment of CP according to ISO 15589-1, by measuring the ON potential. CP real effectiveness should be verified by measuring the IR-free potential: 90% of the companies declared to correctly measure it, using potential probes. The most used carbon steel coupon surface areas are 1 cm² and 10 cm². Bigger surfaces, used by 5 of the 20 companies, are not recommended. 11 companies declared to measure the OFF potential. Installed test post matches very well the recommendation reported in the ISO 15589-1, which is 1 km or 3 km for urban/industrial or rural areas, respectively. Concerning CP maintenance, there is no a homogeneous organization among the 20 companies.

Discussion: To accomplish ISO 15589-1, CP effectiveness should be verified by IR-free potential reading, using potential probes. OFF-potential, even if permitted, may lead to misunderstanding in the presence of overprotection condition and complex structures. The main conclusion of the benchmark is that companies should improve their monitoring system, by installing proper potential probes.

STUDY OF THE EFFECT OF CYCLIC LOAD ON HYDROGEN PERMEATION IN HIGH STRENGTH STEELS UNDER CATHODIC PROTECTION

Cabrini M, Lorenzi S, Pastore T, Pesenti Bucella D

Department of Engineering and Applied Sciences, University of Bergamo, Dalmine (Bergamo) - Italy

Introduction: Pipelines and offshore applications, operating under cathodic protection to prevent general corrosion, are usually realized with High Strength Low Alloy (HSLA) steels. The risk of hydrogen embrittlement (HE) in pipeline steels due to cathodic overprotection are described in literature. HE is related to absorption and subsequent diffusion of atomic hydrogen through the lattice. On HSLA steels, HE occurs only in dynamic load conditions in the plastic field, such as slow strain rate or corrosion fatigue. Many studies were carried out on the effect of applied stress on hydrogen diffusion and HE mechanism but, at present, the phenomena are not fully understood. In this work, the effect of cyclic load in the elastic field on passivity current (i_p) and hydrogen steady state permeation current (i_{HSS}) is reported.

Materials and methods: The permeation tests were carried out on API 5L X65 steel, according to ISO 17081:2014. The specimen acts as bi-electrode between the two compartments of the Devanathan-Stachurski cell. In the anodic compartment, it is polarized at +340 mV vs Ag/AgCl in a 0.1 M NaOH solution. The cathodic compartment is filled with a borate solution (pH 8.5) and a cathodic current density of 2 mA/cm² was applied once passivity current reached values below 0.05 μ A/cm². Tests in unloaded conditions and under cycling load up to 80% TYS in the frequency range between 10⁻² Hz and 1 Hz were performed.

Results and discussion: Tests realized in unloaded conditions show i_{HSS} around 1 μ A/cm² and hydrogen diffusion coefficients around 7·10⁻¹² m²/s. Such values are comparable to literature data collected on X65 steels. Preliminary tests under cyclic load show that i_p modifies with load, but the response is shifted in phase. The amplitude of Δi_p increases with the load amplitude and frequency. Such behavior can be ascribed to the rupture and reformation of passive film, which is more evident at the highest strain rates (high frequencies). Similar behavior was noticed also for i_{HSS} , but values of Δi_{HSS} are of the same order of magnitude of Δi_p . The average value of the hydrogen stationary permeation flux remains almost constant as the load frequency increases.

EVALUATION OF CORROSION RESISTANCE OF ALSi10Mg AND ALSi7Mg ALLOYS MANUFACTURED BY LPBF

Cabrini M^{1,2}, Lorenzi S^{1,2}, Pastore T^{1,2}, Testa C^{1,2}, Manfredi D³, Calignano F³, Lorusso M³, Fino P^{2,4}

¹ DISE-University of Bergamo, Dalmine (Bergamo) - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Centre for Sustainable Future Technologies CSF@POLITO, Istituto Italiano di Tecnologia, Turin - Italy

⁴ DISAT, Politecnico di Torino, Turin - Italy

Introduction: Laser powder bed fusion (LPBF) is a technique based on fusion of metal powder - layer by layer - by using a laser. This method has advantages in terms of cost reduction and manufacturing time and it is able to eliminate the metal scrap by traditional subtractive machining. However, it leaves rough surfaces and can greatly influence the corrosion behavior of the alloy compared to traditional casting.

Materials and methods: tests were performed on two aluminium casting alloys having different silicon content - AlSi10Mg and AlSi7Mg alloys. The specimens were obtained along two building directions, with the test surface parallel or perpendicular to the deposition plane – i.e. the scanner laser plane – on as-processed or polished surfaces. After manufacturing, the specimens were stress relieved at 300°C for 2 h.

Pitting potential were estimated by potentiodynamic tests at room temperature in Harrison solution at 10 mV/min scan rate.

The susceptibility to intergranular corrosion was evaluated according to ISO 11846 standard.

Results and discussion: The results show modifications of passive film and metal microstructure induced by LPBF, relevant for the corrosion resistance of aluminum-silicon alloys. The results show a marked influence of surface conditions on pitting potential. The lowest pitting potentials measured on both as-processed alloys denotes a worse resistance to localized attack due to the formation of less protective film during manufacturing and heat treatment. The pitting potentials are in any cases similar for both the alloys.

During the LPBF process, the film forms into inert atmospheres with very low oxygen partial pressures and afterwards it evolves during heat treatment at high temperatures – i.e. under conditions quite different from atmospheric exposure. The mechanical polishing removes such poor film and restore the intrinsic resistance of metal matrix.

However, the unique microstructure produced by the LPBF process also affects the corrosion behavior of aluminum silicon alloy. The propagation of localized attack occurred on both the alloys by selective dissolution of aluminum along the border of melt pools, which distinguishes the microstructure of alloys produced by LPBF. Selective corrosion strictly depends upon the presence, distribution and dimensions of silicon particles.

BIOCOMPOSITES BASED ON POLY(LACTIDE) AND AGRI-FOOD WASTE DERIVED CALCIUM CARBONATE

Cacciotti I^{1,2}, Duranti L³, Nanni F^{2,3}

¹ Engineering Department, University of Rome “Niccolò Cusano”, Rome - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Enterprise Engineering Department, University of Rome “Tor Vergata”, Rome - Italy

Introduction: Packaging materials play a key role in worldwide market and sales are forecasted to reach \$975 billion by 2018. Among them, a large percentage is represented by fossil derived polymers whose use has led to dramatic environmental and ecological concerns, being not biodegradable. Therefore, biopolymers have been investigated, even if their industrial application is prevented by their poor mechanical, thermal and barrier properties. In this work, in order to improve the properties of polylactide (PLA) films, natural calcium carbonate, derived from agri-food wastes (e.g. egg and mollusk shells), were exploited.

Materials and methods: Egg/mollusk shells were submitted to a specific protocol of extraction and purification. The obtained cleaned shell pieces were further processed by milling in order to obtain nanometric particles, and by ultrasonication, in the case of mollusk shells, in order to selectively separate the characteristic layers (i.e. nacreous and prismatic). To promote the particles dispersion and to improve the polymer/filler interface, they were functionalised using stearic acid and 12-hydroxy stearic acid. To produce the composite films,

the fillers (1-10% wt/) were disagglomerated in dichloromethane by sonication and then PLA pellets (5%wt/v) were added to the prepared suspensions. All the obtained suspensions were magnetically stirred and then cast on Petri dishes to promote solvent evaporation. As references, neat PLA and PLA loaded with uncleaned milled mussel shells were produced.

Results: The effectiveness of the cleaning and functionalization protocols was verified by scanning electron microscopy (SEM), X-ray diffraction (XRD), infrared spectroscopy, GC-MS analysis and thermogravimetry. The influence of the different CaCO₃ shape, dimension and amounts and of the performed functionalisation on the microstructural, thermal, mechanical and oxygen barrier properties of the produced films was deeply investigated by SEM, differential scanning calorimetry (DSC), uniaxial tensile tests, O₂ permeability.

Discussion: In this work PLA films, loaded with agri-food waste derived calcium carbonate, were successfully prepared by solvent casting technique, replying to the emergent need for ecosustainable alternatives to the traditional polymeric packaging materials and for a smart and sustainable waste management, finding a new reuse of waste materials, in agreement with the "zero waste standard".

MORPHOLOGICAL ANALYSIS OF VAPOR ADSORBENT ZEOLITE COMPOSITE FOAMS BY X-RAY MICROTOMOGRAPHY

Calabrese L¹, Scalici T², Bruzzaniti P¹, Proverbio E¹, Valenza A²

¹ Department of Engineering, University of Messina, Messina - Italy

² Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy

Introduction: Thermally driven zeolite adsorption heat pumps (AHP) are an environment-friendly alternative to conventional electrical heat pumps. In this field several efforts have been done to enhance the volume specific power while maintaining a reasonable thermodynamic efficiency.

In this concern, a new approach by using a composite zeolite-siloxane foam to fill open space in a traditional heat exchanger was proposed. This foam, with large surface area to volume ratio, could be a promising candidate as adsorbent material for adsorption heat pumps applications. Aim of the present work is to assess the influence of morphology and filler amount on the adsorption performances of zeolite filled siloxane composite foams for AHP applications. Digital image analysis and statistical analysis of cell size distribution were performed and on this basis a water vapor diffusion model through foam was proposed.

Materials and methods: Macro-cellular zeolite filled siloxane foams (up to 70% of zeolite filler) were produced following a direct foaming approach. Foam morphology and surface characteristics were evaluated by microtomography.

Results and discussion: The foam is characterized by a mixed open/close cellular structure. By increasing the zeolite content a reduction in pore size and a transition between mainly open porosity to closed-cell porosity was observed. Just after 37% of zeolite content, a reduction of about 50% of cell size diameter was observed. Above 60% of zeolite filler the cell size diameter was about 0.2 mm. Concerning the circularity parameter, a minimum at medium zeolite content was observed. At high zeolite content the bubbles can't coalesce and small isolated bubbles were identified. Conversely at low zeolite content foams a very large amount of bubbles coalesces stimulating a large interconnected porous structure. Morphological aspects were compared with vapor adsorption performances evidencing a good compatibility, indicating, depending on zeolite content, a possible inter-bubble or intra-bubble vapor diffusion mechanism.

CHARACTERIZATION OF GEOPOLYMER-GRAPHENE NANOCOMPOSITES

Candamano S¹, Sgambitterra E², Lamuta C², Pagnotta L²

¹ Department of Environmental and Chemical Engineering-DIATIC, University of Calabria, Arcavacata di Rende (Cosenza) - Italy

² Department of Mechanical, Energy and Management Engineering-DIMEG, University of Calabria, Arcavacata di Rende (Cosenza) - Italy

Introduction: Geopolymers are an innovative class of eco-friendly binders, based on alkali activation of a solid aluminosilicate source. Their fracture properties can be improved by using traditional reinforcing agents, including steel bars, steel fibers, carbon fibers, polymeric fibers and natural fibers. Few recent studies investigated the possibility to produce geopolimetric composite based on in-situ reduced graphene oxide (rGO) into fly ash-based

geopolymers. In this paper the production, microstructures, chemical and mechanical characterization of metakaolin-based geopolymers/GNPs nanocomposites are discussed.

Materials and methods: Graphene nano-platelets (GNPs) have a thickness of a few nanometers, a width of less than 2 microns, and an average surface area of 300 m²/g. Metakaolin particles have a mean diameter of 1.59 μm. An optimized method was used to improve graphene dispersion. The final theoretical composition of geopolymer mortars has Al₂O₃/Na₂O and SiO₂/Al₂O₃ molar ratios equal to 1 and 3.86 respectively, a water/binder weight ratio of 0.56 and a sand/binder of 1.5. Three different GNPs contents 0.1, 0.5 and 1%wt with respect to metakaolin were used. Atomic Force Microscopy, Fourier-transformation infrared (FT-IR), Scanning Electron Microscopy and X-Ray Diffraction, indentation tests and combination of Brazilian disk test and Digital Image Correlation were used to characterize mortars.

Results: The manufactured geopolimetric mortars showed the characteristic broad hump centred at approximately 28° 2θ. The FT-IR transmittance spectra of the geopolymers mortars, at different amount of GNP and cured for 28 days, showed peaks associated to graphene sheets. Negligible variations were recorded for Young modulus, hardness, Poisson's ratio and ultimate tensile strength. In particular, a decrease of these parameters was measured when the GNPs percentage increased from 0.5 to 1%wt.

Discussion: Graphene behaves as inactive fillers in the geopolymerization reaction. Incomplete separation of the GNPs bundles into individual flakes caused, at higher concentration, an incomplete dispersion of graphene Nano-platelets into the matrix. The GNPs microclusters formation negatively affected the composite performances.

ACCELERATED AGING OF THE PAINTED SURFACES OF EARTHEN PLASTERS

Cappai M¹, Meloni P¹, Palomba M², Carcangiu G², Casnedi L¹, Pia G¹

¹ Department of Mechanical, Chemical and Engineering Materials, University of Cagliari, Cagliari - Italy

² Institute of Atmospheric Science and Climate-ISAC, National Research Council (CNR) Cagliari - Italy

Introduction: The accelerated aging is a process used in the materials of science for the study of the resistance of the materials for determining the environmental conditions. There are different methodologies in this regard, some of which are standardized, which allow to simulate environmental conditions and obtain in a short time what is naturally occurring in very long times.

However, due to variability, multitude, and interaction between different environmental phenomena, it is often difficult to set accelerated aging to achieve the desired goals. This paper presents the case of accelerated aging of some earthen painted plasters. The aim was to obtain surfaces with a state of degradation similar to the original manufacturer to be able to consolidate. Particularly, the pathologies that have been recreated on surfaces are the detachment of pictorial film, surface micro-cracking and powdering.

Materials and methods: Earthen painted plasters are used for experimental part. From the study of the environmental parameters, an accelerated aging was performed ad hoc through wet-dry cycles and simulated erosion. To make the simulation, we used the climatic chamber and a simulation device for wind correction.

Effects on the surfaces were verified by using Scotch Tape Test and optical microscopy.

Results: After different tests for the calibration of the environmental parameters involved in the process, in order to obtain the sought pathologies and a degraded condition similar to that studied in situ, an aging process has been designed.

Discussion: The proposed accelerated aging proved to be effective, not only for the degradation process, but above all for the methodological approach employed. Critical analysis of weathering dynamics allows performing experimental tests by improving lab procedure.

MORPHING CARBON FIBER COMPOSITES WITH SELF-ACTIVATED ACTUATION MECHANISM BASED ON INTERNAL HEATERS

Casalotti A, Lanzara G

Department of Engineering, University of Roma Tre, Rome - Italy

Introduction: An innovative concept to exploit self-activated morphing composite materials is presented and demonstrated experimentally. The shape

changes of a carbon fiber composite are achieved by considering proper fiber orientation and temperature-sensitive epoxy resin. The epoxy resin stiffness is controlled with the help of internal heating system represented by the fibers themselves. The proposed mechanism results in a large-scale and cyclic shape-changing capability which, together with the corresponding tunable stiffness, represent the fundamental features of morphing structural materials.

Materials and methods: multiple layers of 90° crossing carbon fibers are embedded into a thermally controlled stiffness changing resin. The thermal contraction descending from the cooling phase at the end of the fabrication process induces internal thermal stresses, which lead to a curved shape. Carbon fibers are adopted, not only as reinforcing element, but also as thermal heaters thanks to the application of a voltage. The thermal gradients introduced into the matrix induce stiffness variations of several orders of magnitude. Consequently, the internal stresses are rapidly released, leading to an overall loss rigidity followed by a shape change of the composite, which goes from its initial curved shape to a flat shape. The so obtained plate is capable to change gradually and cyclically its shape, according to the prescribed voltage.

Results: The experimental campaign comprised a first investigation of the composite plate behavior on a hot plate, thus proving the capability of the material to change its shape according to assigned temperature paths. Further experiments were conducted on a Dynamic Mechanical Analyzer to prescribe not only temperature, but also displacement paths and investigate the mechanical behavior of the samples under different conditions.

Discussion: the results confirmed the capability of the proposed approach to govern the shape and the stiffness of the designed curved plates in different operative conditions.

ENGINEERING POLYMERS FOR FUSED DEPOSITION MODELLING: A RATIONALE APPROACH TO MATERIAL DEVELOPMENT AND APPLICATIONS USE

Cicala G^{1,2}, Pergolizzi E^{1,2}, Latteri A^{1,2}, Abramo G^{1,2}, Recca G³

¹Department of Civil Engineering and Architecture-DICAR, University of Catania, Catania - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Institute for Polymers, Composites and Biomaterials, CNR-IPCB, Catania - Italy

Introduction: Fused deposition modelling is one of the mainly used additive manufacturing technology when functional application is foreseen. The widespread diffusion of desktop FDM machine combined with the desire to tailor material properties gave rise to an increasing number of work focusing on new formulation development. Most of this study focused on reinforced polymers to obtain better mechanical properties. However, when printing samples by FDM the printing parameters can have a significant effect on the measured properties thus jeopardizing the real benefits and potentials of the polymer formulations. The present paper aims to present well conducted experiments to rationalize the effect of printing parameters and experimental conditions on the measurement of mechanical properties. The data from FDM printing are compared to injection moulding counterparts. In addition to that, some example of advanced applications will be discussed.

Materials and methods: A whole range of materials were used from engineering polymers, like PEEK and PEI, to recycled polymers like PE or PLA. All the polymers and the microcomposites were transformed into filaments of 1.75 mm diameters using two pilot extrusion lines depending on the extrusion temperature. Mechanical and thermal data were measured using universal testing machines and dynamic mechanical analyser.

Results: The study showed that engineering polymers, like PEI, show some limitation in processing which can be overcome by the rationale development of specific compounds. The use of recycled polymers enhanced cost reduction by even half of the current price. Finally, the development of soluble polymers showed its potential for mandrels to be used in advanced composites manufacturing.

Discussion: The present work outlined the need for a rationale approach in the developing of polymers for functional applications. The range of properties covered by the developed formulation allowed to exploit different performances. Specific case regarding mandrels for advanced composites demonstrated the potential for new market for the FDM technology.

LIGHTWEIGHT GEOPOLYMER COMPOSITES CONTAINING ORGANIC RESINS AND RECYCLED EXPANDED POLYSTYRENE

Colangelo F^{1,2}, Roviello G^{1,2}, Ferone C^{1,2}, Ricciotti L¹, Molino AJ¹, Messina F^{1,2}, Tarallo O³, Roviello V⁴, Cioffi R^{1,2}, Cheeseman CR⁵

¹Department of Engineering, University of Naples 'Parthenope', Naples - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of Chemical Sciences, University of Naples "Federico II", Naples - Italy

⁴Advanced Services Metrological Center (CESMA), University of Naples 'Federico II', Naples - Italy

⁵Department of Civil and Environmental Engineering, Imperial College London, London - UK

Introduction: Expanded polystyrene (EPS) is a lightweight thermoplastic material with a unique combination of properties including excellent thermal insulation, high durability, easiness of processing and low-cost. However, at end of its life cycle, the recycling options for EPS are limited and it is normally either landfilled or incinerated, causing environmental concern, particularly in countries where environmental standards are not enforced. This research has investigated lightweight thermal insulating materials from geopolymers containing waste expanded polystyrene and a commercial epoxy resin. Epoxy resin was used to improve mechanical properties with respect to the neat geopolymer by obtaining an organic-inorganic composite.

Materials and methods: Two different types of geopolymeric matrices were obtained: a neat one, synthesized from metakaolin and an alkaline activating solution, and an organic-inorganic composite obtained from the neat geopolymer by further addition of an epoxy resin (by adding 10% by weight of epoxy resin to the freshly-prepared geopolymeric suspension). Marble powder was also added to both systems as secondary constituent to act as filler. In particular, for each type of matrix, two sets of samples were prepared: a first one with 65% v/v EPS content and a second one corresponding to 72.5%.

Results and discussion: The geopolymer composites containing EPS were characterized in terms of physico-mechanical properties, thermal performance and microstructure. These materials show improved properties compared to cement-based materials, with reduced shrinkage and creep, improved resistance to high temperatures. In particular, for all the materials prepared, mechanical resistance values were comparable with available commercial alternatives and existing literature data related to EPS-containing cementitious composites.

The lowest thermal conductivity value obtained of 0.121 ± 0.001 W/m·K, involves a reduction 15% compared with cement based existing commercial products with similar density (reference: lightweight insulating concrete-Latermix Cemi Mini-<http://www.laterlite.es/wp-content/uploads/2014/03/General-Catalogue.pdf>).

COMPOSITIONAL GRADIENT SCAFFOLD FOR INTERFACE TISSUE ENGINEERING VIA TIPS TECHNIQUE: PREPARATION AND TUNING

Conoscenti G, Carfi Pavia F, La Carrubba V, Brucato V

Department of Civil, Environmental, Aerospace and Materials Engineering (DICAM), University of Palermo, Palermo - Italy

Introduction: Several tissues in human body are characterized by gradual interfaces, responsible for the functional interactions between adjacent tissues, playing a very important role for the smooth running of the tissue.

Materials and methods: Scaffolds were prepared via Thermally Induced Phase Separation (TIPS) starting from a ternary solution PLLA, 1,4-Dioxane, and distilled water. Hydroxyapatite (HA) was added as a filler in the polymeric solution. PLLA/HA suspension and PLLA solution were hot poured into a HDPE mold in two sequential time steps, respectively (10 min between each step), and then placed in a thermal bath at 30°C (PLLA_30 M) or 60°C (PLLA_60 M) for 30 min. Then the scaffolds were frozen at -20°C, washed and dried.

Results: The internal foam morphology was analyzed via SEM images, while HA distribution inside the scaffold was evaluated by Micro-CT scanner. The pore dimension of the foam is a function of the temperature at which the phase separation takes place: 130 μm ± 22 μm for the PLLA_30 M and 210 μm ± 28 μm for PLLA_60 M. By moving from the bottom of the scaffold to the top, the concentration of HA stays almost constant up to the mid-section of the scaffold, it rapidly decreases in a very narrow zone close to the center and it falls to zero upward.

Discussion: By taking advantage of the scaffold preparation protocol, the gradient scaffold was fabricated in a single step without requiring the junction of multiple layers. A simple, versatile and scalable protocol to produce

compositional gradient scaffolds is reported. The possibility to create compositional filler gradients combined with the accuracy in tuning the scaffold architecture provided by TIPS, suggests this type of scaffold for promising applications in interface tissue engineering.

USE OF FOAMED END-OF-WASTE PLASTIC AGGREGATES AS INTERNAL CURING WATER RESERVOIR INTO A CEMENTITIOUS MORTAR

Coppola B^{1,2}, Courard L², Mistretta MC³, Scarfato P¹, Incarnato L¹, Di Maio L¹

¹ Department of Industrial Engineering, University of Salerno, Fisciano (Salerno) - Italy

² Department of Architecture, Geology, Environment and Constructions, University of Liège, Liège - Belgium

³ Department of Civil, Environmental, Aerospace, and Materials Engineering, INSTM, University of Palermo, Palermo - Italy

Introduction: Shrinkage phenomena represent an important issue for cementitious materials. There are several procedures able to reduce shrinkage phenomena, in particular, external and internal curing. The latter consider the possibility to add water reservoir that are able to release water during the curing period. In this study, porous plastic aggregates were used as internal curing water reservoir.

Materials and methods: Artificial aggregates were obtained by a foam extrusion process, using a post-consumer waste material (polyolefin blend containing PE and PP). Polymer pellets and the chemical blowing agent (2 wt.%) were dry mixed and then added in the hopper of a single screw extruder (Brabender Do-Corder E330) to produce foamed strands. Such filaments were grinded and sieved to produce artificial aggregates that were then water saturated under vacuum. Mortars were prepared using an Ordinary Portland Cement (CEM I 42.5 N) and a standard quartz sand (0/2 mm). Two w/c ratios (0.45 and 0.30) and three natural sand volume replacement (5, 10 and 25%) were investigated. Autogenous and total shrinkage phenomena were monitored for 120 days.

Results: Considering the total shrinkage, the length variation was 0.23, 0.13, 0.11 and 0.14% for the reference mortar and lightweight mortars (w/c = 0.30) replacing 5, 10 and 25% of the natural sand volume, respectively. Also for the w/c = 0.45 was observed the same behavior: the length variation was 0.23, 0.08, 0.06 and 0.07% for the reference mortar and lightweight mortars. On the other side, considering the autogenous shrinkage, it was negligible for the w/c = 0.45 while for the w/c = 0.30, a length variation of 0.07% was measured for the reference sample while the lightweight mortar having a natural sand volume replacement of 10% reported a length variation of only 0.03%.

Discussion: An overall decrease of shrinkage was observed for the mixtures containing artificial aggregates. For both the investigated w/c ratios, the most efficient formulation was the lightweight mortar containing a natural sand volume replacement of 10%. According to the Power's model, the amount of water that such quantity of porous plastic aggregates is able to release is close to the theoretical quantity.

ONE-PART ALKALI ACTIVATED SLAGS FOR CEMENT-FREE REPAIR MORTARS FOR CONSERVATION, RESTORATION AND RETROFITTING OF EXISTING CONCRETE STRUCTURES

Coppola L, Coffetti D

Department of Engineering and Applied Sciences, University of Bergamo, Bergamo - Italy

Introduction: Construction industry – and in particular the cement sector – is considered one of the main natural resources-consuming in the world. The global production of Portland cement, in fact, contributes around 7% to greenhouse gases emissions responsible for climate change and global warming. Hence, it is evident the need in the concrete industry of a forceful turning point towards sustainable development models in economic, environmental and social terms. Replacement of Portland clinker-based cement is one of the main strategies to reach sustainability in the cement sector. This article is aimed to the study of an alkali-activated binder based on ground granulated blast furnace slag (GGBS) as precursor for cement-free mortars devoted to conservation, restoration and retrofitting of existing concrete structures.

Materials and methods: The alkaline activators in powder form were formulated by blending sodium silicate, potassium hydroxide and sodium carbonate. Several activator/precursor ratio – between 2% and 32% by mass – were used in order to investigate the effect of activator dosage on the rheological,

mechanical and physical performances of mortars. The mixing water was adjusted in order to attain the same workability at the end of the mixing procedure, equal to 160 ± 10 mm spreading on the flow table.

Results and discussion: The experimental data show excellent rheological characteristics of different mixtures based on GGBS. Compressive strength increases with the activator/precursor ratio up to 65 MPa at 28 days from casting. In addition, the mortars show a reduced Young's modulus, close to 13 GPa, compared to cement mortars at the same strength class. As a consequence of the low elastic modulus, alkali-activated mortars seems to be very promising in the field of conservation and repair of existing concrete structures, due to a reduction of stress induced by restrained thermal and hygro-metric movements. However, on the other hand, shrinkage is significantly higher than traditional cement mortars, equal to 4 mm/m at 60 days from casting. This means that use of AA mortar in the repair field requires some additional ingredients (expansive agents, polymeric fibers and shrinkage reducing admixture) in order to face the very high hydraulic shrinkage of these innovative materials.

CSA-BASED TERNARY BINDERS FOR SUSTAINABLE MORTARS

Coppola L, Coffetti D, Lorenzi S

Department of Engineering and Applied Sciences, University of Bergamo, Bergamo - Italy

Introduction: Calcium-sulphoaluminate cement (CSA) represents an environmentally-friendly alternative to Portland cement (OPC) due to its lower raw materials consumption, production energy requirement and CO₂ emissions per ton of clinker during production. Nowadays, the use of calcium-sulphoaluminate cements is widespread for CSA – OPC – calcium sulphates (CS, anhydrite) ternary binders, in which OPC is present up to 60% vs binder mass. The purpose of the present study is the evaluation of the rheological, mechanical and physical performances of innovative ternary CSA-based binders designed replacing totally OPC with supplementary green binders (GBCSA) such as fly ashes and ground granulated blast furnace slags.

Materials and methods: Mortars based on OPC CEM I 52.5 R, commercial CSA clinker and technical grade anhydrite were manufactured (fine natural aggregates/binder equal to 3:1). In addition, a ground granulated blast furnace slag and a class F fly ash replaced totally OPC. Tartaric acid in form of powder was used as set retarding admixture (0.4% to 1.2% vs binder mass). Mixing water was adjusted in order to attain the same workability at the end of the mixing procedure, equal to 160 mm \pm 10 mm by means of a flow table. Finally, in mixtures manufactured with GGBS and FA, in order to improve the pozzolanic reaction, 5% vs binder mass of hydrated lime CL90-S class was added.

Results and discussion: A dosage of about 0.8% (with respect to binder mass) of set retarding admixtures permits to maintain the initial workability of GBCSA mixtures up to 75 minutes. Rheological and physical performances of GBCSA mixtures were similar to reference mortars manufactured with OPC at equal set retarding admixture dosage. In addition, the shrinkage is very low and no expansions were noticed at early ages. Experimental data show that the mechanical performances of GBCSA reach about 75% of the reference mortars manufactured with ternary binders containing OPC. Furthermore, the tartaric acid addition strongly penalizes the mechanical performances of mortars, regardless of type and dosage of supplementary cementitious material used. GBCSA are suitable candidates to manufacture R3 class sustainable mortars for reinforced concrete repair according to UNI EN 1504-3.

PHENOMENOLOGICAL APPROACH TO THE STUDY OF HIERARCHICAL DAMAGE MECHANISMS IN COMPOSITE MATERIALS SUBJECTED TO FATIGUE LOADINGS

D'Amore A, Grassia L

Department of Industrial and Information Engineering, University of Campania "Luigi Vanvitelli", Aversa (Caserta) - Italy

Introduction: The strength degradation of fiber reinforced composites subjected to constant amplitude (CA) fatigue loadings can be described by three distinct functions derived from a recently developed two-parameter residual strength model and associated with the sequence of damage mechanisms. Despite the phenomenological prerogative of the model, from the analytical approach it results that under moderate loadings the multiple damage

mechanisms develop with different kinetics and manifest their effectiveness at different time scales, accordingly.

Materials and methods: Fatigue and residual strength data concerning different kind of fiber reinforced composites were taken from literature.

Results: The approach has the potential to reveal the physical aspects of damage sequences with association of analytical functions to the different Stages of damage, despite the phenomenological prerogative of the model. Given its analytical form the model is a promising candidate to test the response of composite structures in terms of damage accumulation and residual strength kinetics when the "in service" variable amplitude (VA) loadings are in play, a case that will be treated in a next work.

Discussion: The three-Stage hierarchical nature of damage accumulation in composites, from diffuse matrix cracking (I), to fiber/matrix interface failure (II) to fiber and ply rupture and delamination (III) can be revealed during fatigue. It is also shown that by increasing the loading severity the timescales of the different damage mechanisms become comparable witnessing their simultaneous co-existence.

PRODUCTION OF MgO NANOPARTICLES FROM Mg(OH)₂ COLLOIDAL SUSPENSIONS OBTAINED BY A COST-EFFECTIVE AND PATENTED PROCESS

Daniele V. Taglieri G, Scoccia G

Department of Industrial and Information Engineering and Economics, University of L'Aquila, L'Aquila - Italy

Introduction: MgO nanoparticles (MONPs) are employed in various areas, as heat-resistant and high-temperature insulating material, toxic waste remediation, or as additive superconductor products. They are obtained from different synthesis methods, which are time-consuming and strict regarding equipment or sophisticated apparatus, and non-promising for large-scale production.

Aim of this work is to produce, by a simple and high yield method, MONPs from Mg(OH)₂ nanoparticles (MHNPs) synthesized by our patented, time and energy saving and scalable route. The MHNPs, used as precursor, are calcinated at different temperatures to investigate the influence of this parameter both on the formation and on particle size of the produced MONPs. The precursor powders and the obtained MO ones are characterized, from structural and morphological points of view, by means of several techniques.

Materials and methods: Materials used are magnesium chloride and anion exchange resin Dowex Monosphere 550A (OH). Deionised water is purified by a Millipore Organex system.

MH suspensions are synthesized by an ion exchange process, that allow us to work at room temperature and ambient pressure, so producing in few seconds MHNPs, without any secondary products. The MH suspensions are dried in oven at 110°C for 24 hours, and then the powders are roughly grounded and calcinated 4 hours at 350, 500 and 600°C, respectively. The obtained nanoparticles are characterized by XRD, FTIR, BET measurements, AFM and TEM observations.

Results and discussion: XRD spectra related to dried powder of MHNPs and MONPs show, for both samples, the formation of only pure and crystalline phase of Mg(OH)₂ and MgO, respectively. Moreover, all diffraction peaks are broadened, thus denoting a small crystalline size. FTIR measurements confirm the phases revealed by XRD analyses, for both MH and MO samples. TEM images, referred to MONPs calcinated at the temperatures of 350°C and 500°C respectively, show as the morphology of the precursor is retained following heating, and the produced MONPs form a two-dimensional network, with roughly spherical and monodispersed nanoparticles ≤10 nm, having a thickness ≤6 nm. By increasing the calcination temperature up to 600°C, MONPs dimension tends to increase, while the highest BET values (178m²/g) are reached at 500°C.

GREEN PACK: SUSTAINABLE MATERIALS FOR PACKAGING

Dastoli C¹, Santi R¹, Piselli A^{2,2}, Diamanti MV^{3,3}, Cigada A^{4,3}, Lucibello S^{4,4}, Scaffaro R^{5,5}, Del Curto B^{3,3}

¹ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

² Department of Design, Politecnico di Milano, Milan - Italy

³ Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

⁴ Department of Planning, Design and Architecture Technology, University La Sapienza, Rome - Italy

⁵ Department of Civil, Environmental, Aerospace and Materials Engineering, University of Palermo, Palermo - Italy

Introduction: Materials for packaging frequently presents unresolved issues about environmental sustainability. A truly sustainable packaging must have a unique separate collection and recycling channel. The aim of the work is to develop biopolymers and composite materials for the realization of a real environmental sustainability composite that allows to produce biodegradable and/or recyclable packaging in paper/cardboard recycling channel.

Materials and methods: The development of different matrixes in order to obtain water-soluble polymers and composites has been carried out. A composite material resulted from fiber of cellulose embedded in a water-soluble PVA has been developed. At the same time studies about biodegradable polymers has been conducted. A PLA biodegradable polymer added with some natural organic loads like sawdust, wood fibers or lignocellulosic loads derived from low-value plants has been realized. The obtained bio-composite materials have been processed by injection processes in order to product sheets of material for stiff packaging realization. Mechanical characterization by several traction tests has been performed.

Results: Injection molding process has allowed to test the best process temperatures for these materials in order to obtain optimal quality results. Temperatures corresponding to 180°C for the barrel and 70°C for the mold have been considered the most appropriate. A good stress-strain behavior has been achieved from mechanical characterization tests. Processability as well as morphological and mechanical aspects are currently being optimized.

Discussion: The obtained results demonstrated the possibility to process bio-composite materials with stiffness and environmental sustainability properties for packaging.

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THERMODYNAMICS OF GLASSY POLY(ETHER IMIDE)-WATER MIXTURES ENDOWED WITH HYDROGEN BONDING INTERACTIONS

De Nicola A¹, Correa A², Milano G¹, La Manna P³, Musto P³, Mensitieri G⁴, Scherillo G⁴

¹ Department of Chemistry and Biology "Adolfo Zambelli", University of Salerno, Fisciano (Salerno) - Italy

² Department of Chemical Sciences, University of Naples "Federico II", Naples - Italy

³ Institute on Polymers, Composites and Biomaterials, National Research Council of Italy, Pozzuoli - Italy

⁴ Department of Chemical, Materials and Production Engineering, University of Naples "Federico II", Naples - Italy

Introduction: This contribution proposes a multidisciplinary approach to understand at molecular level the interactional scenario within a polymer-penetrant glassy mixture (displaying Hydrogen Bondings (HB)), which attains a pseudo-equilibrium of phase state when exposed to a penetrant phase, since the characteristic time of density evolution is extremely higher than the time scale of interest. In particular this methodology is here implemented for the technological relevant case of poly(ether imide)-water system.

Materials and methods: Water vapor sorption data were collected by in situ FTIR spectroscopy and gravimetric tests at 30°C at different water activities. MD simulations and a statistical thermodynamic model ad-hoc developed to take into account the glassy state of the system and the presence of HB interactions, were used as modeling tools.

Results: It was found that the configurations in which water molecules establish water bridges between two carbonyl groups of the polymer repeating unit are strongly prevailing. In addition a second shell of water molecules self HB interacting with the ones involved in the bridge was found.

Discussion: The amount of the different populations of water molecules was determined spectroscopically as a function of water solubility. MD simulations and a statistical thermodynamics model validated against volumetric data of pure polymer and gravimetric solubility data, were used in a predictive fashion to quantify the HBs, showing a significant agreement with experimental data. Furthermore MD simulations showed that in each bridge are involved only carbonyl groups of the same polymer repeating unit. Therefore the proposed procedure has shown that combining experimental and theoretical approaches involving complementary information a comprehensive physical picture of the system is determined.

THEORETICAL AND EXPERIMENTAL INVESTIGATION ON AGGLOMERATION PHENOMENA IN A SRF-FIRED FLUIDIZED BED WASTE-TO-ENERGY PLANT

De Gisi S¹, Pastore F¹, Todaro F¹, Chiarelli A², Tagliente L², Notarnicola M¹

¹ Department of Civil, Environmental, Land, Building Engineering and Chemistry (DICATECh), Polytechnic University of Bari, Bari - Italy

² Appia Energy Srl, Massafra (Taranto) - Italy

Introduction: Several technologies for waste incineration are widespread worldwide such as furnace grate, rotary kiln and fluidized bed. In a fluidized bed combustor (FBC), a bed of sand, combustion ash, or other sand-like material is suspended in an upward flowing airstream. The high turbulence created enhances combustion and promotes an efficient heat transfer and uniform mixing. SRF (Solid recovered fuel) represents the evolution of RDF (refuse derived fuel) and it is generally burned in Waste-to-Energy (WtE) plants.

Among the causes of FBC dysfunction, agglomeration is the most important. It is the result of the in-bed formation of low melting point eutectic mixtures through the reaction of mostly alkali compounds of the waste feed with the silica bed materials. The particle growth of the bed material lead to de-fluidization of the bed with a consequent plant shutdown. Thus, an appropriate prediction of the agglomeration characteristics is essential.

The aim of the study was to investigate the agglomeration phenomena of a FBC by means of a theoretical and experimental investigation. For this aim, the case study of the WtE plant of Massafra (TA) in the South Italy was considered.

Materials and methods: The experimental plan included (i) characterization of the inlet SRF, (ii) analysis of plant shutdown and (iii) chemical characterization of agglomerates and slag.

Results: With reference to the agglomerates, potassium, sodium and silica were among the compounds with the highest concentrations with values of 2990 (± 407) mg/kg, 8696 (± 1322) mg/kg and 13.4%, respectively. These values are indicative of the agglomeration and are the result of the burned SRF in terms of chemical characteristics.

Discussion: The use of detection devices and suitable countermeasures, as well as of most complete analysis of the inlet waste (i.e. in terms of alkaline earth metals), could substantially contribute to a better management of the FBC technology. Furthermore, the pre-treatment of the inlet SRF by means of a mechanic-chemical process could reduce the content of alkaline earth metals, among the main causes of agglomeration.

SYNTHESIS AND CHARACTERIZATION OF PHB-COMPOSITE BASED FILM FOR AGRICULTURE APPLICATIONS

Demitri C, Carofiglio VE, Stufano P, Centrone D, De Benedetto E, Cataldo A, Sannino A

Department of Engineering for Innovation, University of Salento, Lecce - Italy

Introduction: In the last years there has been a growing interest about the use of bio-based and biodegradable plastics, made of renewable resources. A common biodegradable polymer, microbial-derived, is Poly-3-hydroxybutyric acid (PHB). An interesting approach is blending PHB with other compounds in order to improve its physical properties and reducing the production costs of the finished products. The olive mill wastewater (OMW) is an organic-rich residual that arises from the production and refinery of olive oil, mainly composed by aromatic and aliphatic compounds, proteins, sugars and lipids.

Materials and methods: PHB (Mw 437.000 g/mol) was purchased from Sigma-Aldrich. Glycerol, used as plasticizer, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were obtained from Thermo Fisher Scientific Inc. Solution-cast film samples of PHB with natural filler were prepared in different ratio w/w of PHB/OMWR (100:0, 70:30, 60:40). The PHB/OMWR based films were dissolving in HFIP under mild stirring. A fixed amount of plasticizer (10% of glycerol w/w) was added. The solution was then casted onto glass dishes to generate films after solvent evaporation at room temperature conditions.

Results: The obtained PHB/OMWR films presents a thickness of about 50 μ m and weight of about 0,2 g. The results demonstrated that PHB/OMWR based films had a weight loss after 6 days in a range from 20% to 30% compared to PHB based films lacking of plasticizer. This behaviour is partially attributed to the solubilisation of glycerol about 10%, but also to the degradation of the whole matrix. The weight loss was emphasized in PHB/OMWR based 70:30 and 60:40 films, where it is possible to observe respectively 25.3% and 28.9% at 37°C and 23.6% and 31.1% at 80°C. The PHB/OMWR 100:0 films were subjected to loss of approximately 21.8% (37°C) and 20.5% (80°C).

Discussion: The results of PHB/OMWR composite films suggest that the novel combination between PHB and natural filler, especially those from renewable resources, open new perspectives for their application in various fields. Bioplastic-based films with natural filler from OMW have numerous advantages such as low cost, renewable nature, aqueous and soil fast degradability but there are serious disadvantages as low mechanical resistance and difficult manufacture.

SYNTHESIS OF POLYURETHANE FOAMS WITH CO₂ AS PHYSICAL BOLWING AGENT

Di Caprio MR¹, Di Maio E¹, Cavalca S², Parenti V², Musto P³, Iannace S⁴

¹ Department of Chemical Engineering, Materials and Industrial Production, University of Naples "Federico II", Naples - Italy

² Dow Italia s.r.l., Polyurethanes R&D, Correggio (Reggio-Emilia) - Italy

³ Institute for Polymers, Composites and Biomaterials, National Research Council, Pozzuoli (Naples) - Italy

⁴ Institute for Macromolecular Studies, National Research Council, Milan - Italy

Introduction: In the field of thermosetting polyurethane foams (PUFs) obtained by the curing reaction between polyol and isocyanate, the selection and the amount of the blowing agents is very important to the final cellular structure and properties of the foam.

In particular, to address the recent interest in combining the CO₂ (physical) foaming with the classical (chemical) polyurethane foaming, a novel instrumented pressure vessel was designed for investigating: i) sorption under high gas pressure on the two, separate, components of the polyurethane foams, ii) synthesis under high gas pressure after the two components mixing, and iii) foaming upon release of the pressure.

Materials and methods: A formulated polyol and a polymeric methylene diphenyl di-isocyanate (PMDI) were supplied by DOW Italia S.r.l. (Correggio, RE, Italy) and used "as received". High purity grade CO₂ was supplied by SOL (Naples, Italy).

Foaming tests were carried out at 35°C and 40 bar of CO₂ pressure, by changing CO₂ amount, in a pressure vessel that makes use of a sample holder with a flexible impeller that allows to keep polyol and PMDI separated during the sorption stage until saturation and to mix the two reactants to start the PUF curing reaction, at any stage of it physical foaming occurs due to pressure release. Furthermore, pressure vessel makes use of a sapphire window for FT-NIR spectroscopy monitoring of CO₂ sorption in both reactants and curing reaction, by using Frontier™ NIR spectrometer equipped with a fiber optic reflectance probe.

Results: PUFs obtained, at 35°C and 40 bar of CO₂ pressure, by increasing CO₂ amount show the final morphology to change from an inhomogeneous to more homogeneous one until to become a pulverized product for higher CO₂ amounts.

From NIR spectra collected during CO₂ sorption in polyol and PMDI, it is possible to detect the CO₂ combination bands, while, during PUF formation, it is possible to follow the isocyanate band decrease and the urethane band formation and increase.

Discussion: The synthesis of PUFs in presence of CO₂ was investigated in terms of final morphology and NIR spectroscopy investigation.

PRODUCTION AND CHARACTERIZATION OF POLYETHYLENE/CLAY MULTILAYER NANOCOMPOSITE FILMS FOR FOOD PACKAGING

Di Maio L, Coppola B, Scarfato P, Incarnato L

Department of Industrial Engineering, University of Salerno, Fisciano (Salerno) - Italy

Introduction: Polymer/clay nanocomposites have become useful materials also in the field of food packaging thanks to several advantages such as enhanced mechanical, thermal and barrier properties. To avoid the problem of possible nanoparticles migration, the nanocomposite layer can be incorporated between neat polymer layers. Moreover, due to the importance of nanocomposites morphology, processing parameters are important and, for non-polar polymers like polyolefin, compatibilizers are necessary to obtain exfoliated/intercalated morphologies.

Materials and methods: A layered organoclay (D67G) was compounded, using a twin-screw extruder, with a linear low density polyethylene grafted with maleic anhydride (LLDPE-g-MA) and a non compatibilized LLDPE, for comparison. Three different clay wt.% were investigated: 2, 4 and 6%. The resulting

organoclay/polyethylene nanocomposites were then blown into monolayer and multilayer films, including a neat PE film as reference. XRD, FTIR, DSC and tensile tests were performed for films characterization.

Results: FTIR evidenced the occurrence of stronger polymer/organoclay interactions for LLDPE-g-MA nanocomposite films. DSC analysis reported a slight decrease of the crystallinity degree at increasing clay content. Oxygen Permeability (OP) tests indicated a reduction in oxygen transmission with increasing clay content, compared to the reference. Elastic modulus increases at increasing nanoclay content for both PE matrixes because of the reinforcing effect of the clay in the machine direction. Two types of multilayer nanocomposite films were produced: symmetrical (A/B/A) and unsymmetrical (A/B/B) configuration, where A is the neat LLDPE-g-MA layer and B is the LLDPE-g-MA nanocomposite layer with different clay concentrations.

Discussion: A total exfoliated phase was not obtained for both polymer nanocomposite films but LLDPE-g-MA nanocomposite films had a better intercalation and exfoliation of the clay particles thanks to the grafted maleic anhydride. LLDPE-g-MA/clay monolayer nanocomposite films exhibited a considerable improvement in the OP thanks to the increase in tortuosity of the gas path: at increasing clay content the OP decreased of 26%, 31% and 37%, respectively. Considering multilayer films: the maximum decrease in permeability was exhibited for the film (A/B/B) with 6% clay content. In conclusion, multilayer nanocomposite films represent a good solution for the improvement of mechanical and barrier properties of polyethylene/clay films.

SURFACE AND BULK HYDROPHOBIZATION OF MORTAR AND CONCRETE BY ADDITION OF RECYCLED RUBBER FROM END-OF-LIFE TYRES

Di Mundo R, Amodio P, Gaudio M, Petrella A, Notarnicola M

Department of Civil, Environmental, Land, Building Engineering and Chemistry, Politecnico di Bari, Bari - Italy

Introduction: Concrete, versatile and diffused construction material, being porous and hydrophilic, absorbs water, which moves in the artefacts and, under freeze-thaw cycling, leads to progressive deterioration and failure. Standard procedures for protecting concrete structures are mainly based on impregnation and coating methods, involving, therefore, only the modification of exterior layers and leaving the concrete bulk hydrophilic. Recently (2015), the addition of polymeric fibers to the paste mixture, combined to the use of a hydrophobic coating, has been reported to reduce water penetration and to turn to hydrophobic or over-hydrophobic this building material.

Our objective is to develop a concrete with an effective hydrophobic behavior in every part of its structure, i.e. both in the surface and in the bulk, so that the use of coating procedures could be completely avoided. In particular, this objective can be pursued by adding recycled rubber from end-of-life tyres to the paste mixture.

Materials and methods: Mortar specimens were prepared by using a commercial Portland cement, tap water and tyre rubber grains according to standard UNI formulation with rubber grains replacing, in terms of volume, the standard aggregate (sand). Topography (SEM), chemistry (EDX), roughness (conscan), porosity, and wetting (water contact angle, WCA, and drops penetration) of cured specimens were measured i) on the side surface and ii) on the fracture surface of the specimens.

Results and discussion: Standard concrete, analysed for comparison, shows hydrophilicity (low WCA) and high water penetration, especially on the fracture surface. Side and fracture surfaces of rubber grains added concrete appear very different in terms of aggregate distribution and roughness. However, this material shows hydrophobicity (high WCA) and no water penetration on both the tested surfaces. This has been observed on all the rubber added specimens, but with still better performances in the case of finer grain size.

The recycling of rubber from end-of-life tyres as mortar and concrete aggregate, already proposed in the past for other possible functions, really seems to be much more advantageous also for an industrial exploitation.

TUNABLE RADICAL SCAVENGING ACTIVITY OF CARBONACEOUS STRUCTURES AND THEIR ANTI-OXIDANT BEHAVIOUR IN POLYMER BASED NANOCOMPOSITES

Dintcheva NT¹, Arrigo R¹, Teresi R¹, Gambarotti C²

¹Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Palermo, Palermo - Italy

²Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

Introduction: Carbon nanotubes (CNTs), due to their electronic properties, show radical scavenging activity toward the radical formed during the degradation processes of polymeric materials. In this work, we propose a novel strategy to control the CNTs anti-oxidant features through the application of an ultrasound treatment (us).

Materials and methods: Ultra high molecular weight polyethylene (UHMWPE); multi-walled carbon nanotubes (CNTs); CNTs have been sonicated at room temperature for different time intervals. Nanocomposites have been prepared through hot compaction and fully characterized.

Results: The content of CNTs structural defects, evaluated through Raman spectroscopy, increases with increasing the us-time and the last can be invoked as responsible for the amplified radical scavenging efficiency of us-CNTs, estimated through DPPH assay.

The us-CNTs containing nanocomposites have been subjected to thermo- and photo-oxidative treatment and the progress of the degradation processes has been followed by analyzing the evolution in time of the FTIR spectra collected on nanocomposite thin films at regular time intervals. The nanocomposites show progressively improved thermo- and photo-oxidative stability with increasing the us-time, indicating that the oxidative resistance of the nanocomposites is strictly dependent on the CNTs defect amount.

Discussion: CNTs have been subjected to us treatment with the aim to capitalize the structural defects induced by sonication, to obtain nanofillers with controlled radical scavenging activity. Nanocomposites containing us-CNTs show a photo- and thermo-oxidative resistance significantly improved with respect to that of UHMWPE/untreated CNTs, indicating that us treatment is effective in enhance the reactivity of CNTs toward macroradicals coming from the polymer degradation reactions.

In all, polymer-based nanocomposites with modulated photo- and thermo-oxidative resistance can be achieved, tuning the CNT radical scavenging properties, which can be rationally controlled by the ultra-sound assisted defects formation.

ELECTRICAL AND MECHANICAL PROPERTIES OF CEMENTITIOUS MORTARS CONTAINING RECYCLED CARBON FIBERS

Donnini J, Merlonetti G, Bellezze T, Corinaldesi V

Department of Materials, Environmental Sciences and Urban Planning, Università Politecnica delle Marche, Ancona - Italy

Introduction: Advances in concrete technology in the last decades have led to the development of innovative cementitious composite materials with enhanced properties. The addition of electrical conductive particles, fibers or fillers in cement-based mortars is able to significantly reduce their electrical resistivity. The objective of this research is to examine the electrical resistivity and mechanical properties of cement based matrices through the addition of different amounts of recycled carbon fibers.

Materials and methods: Four different mixtures have been studied, one reference mortar and three other ones with the addition of 2, 3 and 4% of recycled carbon fibers by weight of cement. Mechanical properties have been evaluated at 28 days by three-point bending tests and compressive tests. Electrical resistivity was measured by AC impedance measurements, using two stainless steel wire meshes as electrodes, embedded in the cementitious mortars. Resistivity was evaluated every 7 days up to 70 days of curing at 20°C, 50% RH.

Results: The addition of carbon fibers produced an increase of the flexural strength from 4,85 MPa for the reference mortar up to 10,96 MPa for the mortar reinforced with 4% of fibers while compressive strength remained unchanged.

After 28 days, the resistivity of the reference mortar was equal to 5773 Ω·cm while the resistivity of the carbon reinforced mortars was 221 Ω·cm, 67 Ω·cm and 97 Ω·cm for the mixture with 2%, 3% or 4% of carbon fibers, respectively. After 70 days the mortar without fibers showed an extremely high resistivity (greater than 25000 Ω·cm) while the reinforced mortar maintained lower values (122 Ω·cm for the mortar containing 3% of recycled carbon fibers).

Discussion: The addition of recycled carbon fibers showed to be promising in decreasing the electrical resistivity of the cementitious mortar. Resistivity increased over time due to the progressive drying of the cementitious matrix. However it remained fairly low (below 400 Ω·cm) in the mortars containing carbon fibers. With regards to the mixtures presented in this study, 3% of carbon fibers seemed to be the upper limit beyond which a further addition did not produce a correlated decrease in electrical resistivity.

PHASE CHANGE NANOCOMPOSITE MATERIALS WITH LOW TEMPERATURE THERMAL ACTIVATION

Dorigato A^{1,2}, Canclini P^{1,2}, Unterberger S^{3,4}, Pegoretti A^{1,2}

¹ Department of Industrial Engineering, University of Trento, Trento - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Unit for Material Technology, University of Innsbruck - Austria

⁴ Christian Doppler Laboratory for Cement and Concrete Technology, Innsbruck - Austria

Introduction: Latent heat thermal energy storage (TES) systems are characterized by high energy storage density at constant transition temperature. Among them, paraffinic waxes are the most widely investigated, because of their wide phase transition temperature range and limited costs. Paraffins with melting temperatures below ambient conditions could be useful for winter sport clothes, but only few papers dealing with the use of such these materials can be found in literature. The objective of this paper is that to prepare and characterize nanocomposites based on crosslinked poly(cyclooctene) (PCO) and a paraffin with a melting temperature of about 10°C, containing different amounts of carbon nanotubes (CNTs).

Materials and methods: Nanocomposite samples were prepared through melt compounding in an internal mixer at 70°C for 10 minutes. The resulting blends were prepared with a PCO/paraffin relative weight ratio of 60/40, keeping a constant DCP content at 1.5 wt%. The resulting materials were then hot pressed at 180°C for 30 minutes in a hydraulic press, in order to perform the complete crosslinking of the PCO matrix and to obtain nanocomposites at different CNT amounts (from 1 to 10 wt%).

Results and discussion: Optical microscope and FESEM images revealed the presence of paraffin domains inside the PCO phase, with a strong CNT aggregation. DSC tests evidenced for all the compositions the presence of the crystallization peak of the paraffin at -10°C, while that of the PCO could be detected at about 6°C. Melting/crystallization enthalpy values between 98 and 116 J/g were obtained for all the samples. CNT introduction led to important enhancements of both the elastic modulus and of the yield stress, with an heavy decrease of the strain at break values. With CNT contents of 5 and 10 wt%, resistivity values of $3 \times 10^2 \Omega\text{-cm}$ and $5 \times 10^0 \Omega\text{-cm}$ were respectively obtained. Moreover, important enhancements of α and λ could be detected with the CNT concentration. Modelization through finite element analysis confirmed the effectiveness of these nanocomposites in increasing the time required to cool the material and/or the temperature of the materials after a certain time interval.

DEVELOPMENT AND CHARACTERIZATION OF POLYLACTIC ACID-HYDROXYAPATITE COMPOSITES FOR LOW-COST FUSED DEPOSITION MODELING 3D PRINTER

Eposito Corcione C, Gervaso F, Scalera F, Montagna F, Sannino S, Maffezzoli A
Department of Innovation Engineering, University of Salento, Lecce - Italy

Introduction: The need of reconstructing complex bone defects in the maxillo-facial region as a result of trauma, tumour surgery or congenital malformation has become a hot topic in the field of tissue engineering. Digital tools such as 3D CAD systems and rapid prototyping (RP) machines are a useful tool to realize custom-made bone scaffolds. RP techniques allow the construction of complex physical models based on 3D clinical images elaborated by suitable software and CAD systems. Hydroxyapatite (HA) is one of the most used materials for bone restoring because of its composition very closed to human bones and teeth. Producing a custom-made scaffold in a ceramic material directly by RP is therefore an exciting challenge. The aim of the present work was to investigate the potential of RP processes as a manufacturing method for products intended for personalized treatments by exploring the production of novel hydroxyapatite-based feedstock materials for RP purposes.

Materials and methods: The material used is a poly-lactic acid (PLA) Ingeo Biopolymer 2003D and a commercial hydroxyapatite (HAP) powder purchased from Plasma Biotol PB260R, North Derbyshire, UK. The possibility of building polylactic acid-nanohydroxyapatite (PLA/HA) composites by 3D printing was systematically evaluated. PLA/HA filaments for low-cost 3D printers were produced by a multistep solvent-free procedure and characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry, and rheometry.

Results and discussion: TGA analysis confirmed the presence of the HA amounts used in the composites, equal to 50 wt%. The glass transition

temperature and degree of crystallinity of PLA are not influenced by presence of HAP, which remains substantially amorphous. The morphological analysis and compression testing on printed samples showed that HAP was uniformly dispersed within the PLA matrix, improving, in turn, the PLA mechanical properties without changing the rheological performance.

IMPROVING THE MECHANICAL PROPERTIES OF UNIDIRECTIONAL FLAX FABRICS REINFORCED EPOXY COMPOSITES BY SODIUM BICARBONATE TREATMENT

Fiore V, Scalici T, Valenza A

Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy

Introduction: Despite their beneficial effects on the adhesion between natural fibers and polymeric matrices, chemical pretreatments have become less attractive since they are expensive and harmful to environment. The present paper deals with the effect of an eco-friendly and cost effective treatment, based on the use of a sodium bicarbonate solution, on the mechanical performances of flax reinforced epoxy composites.

Materials and methods: A commercial epoxy resin and unidirectional flax fabrics (190 g/m² areal density) were used as matrix and reinforcement, respectively. The fabrics were soaked in 5 and 10 wt% solutions of sodium bicarbonate for 5 days at 25°C, then dried at 105°C for 1 day. By using untreated and treated fibers, three epoxy laminates reinforced with four fabrics were manufactured through resin infusion. Quasi-static mechanical tests and dynamic mechanical tests were performed to evaluate the effect of the treatment on the mechanical performances of the composites.

Moreover, morphological analysis of the fractured surfaces was performed through a scanning electron microscopy and the voids fraction of each laminate was evaluated by comparing the theoretical and real densities.

Results: The results showed that all the properties increased with increasing the concentration of the sodium bicarbonate solution: i.e., the tensile strength and modulus of the 10% treated composites were 20% and ~45% higher than untreated composites. The improvements in flexural properties were equal to ~21% and 12.5% for strength and modulus, respectively. As concerns the DMTA results, the $\tan\delta$ curves of all the laminates showed two peaks: the first one (at ~80°C) related to the epoxy glass transition and the second one at higher temperatures related to the fiber-matrix interphase. By increasing the solution concentration, a slight variation of the temperature and a significant decrease of the height of the second peak were found.

Discussion: All the results are due to the beneficial effect of the treatment on the fiber-epoxy adhesion. This improved compatibility was confirmed by the SEM analysis of the fractured specimens: No pull-out phenomena affected the fiber-matrix interface and thin layers of matrix surround the fiber surface even after the composite failure.

MESOPOROUS GLASSES DOPED WITH THERAPEUTIC IONS AS PLATFORM FOR HIGHLY TARGETED THERAPIES IN TISSUE REGENERATION

Fiorilli S, Bari A, Pontremoli C, Molino G, Vitale-Brovarone C

Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

Introduction: In the field of advanced bioceramics, mesoporous bioactive glasses (MBGs), which combine the textural parameters of ordered mesoporous matrices with the properties of bioactive sol-gel glasses, have received increasing attention as tissue regeneration systems. Recently, the ambition is to impart other biological functions, including anti-bacterial activity, stimulation of osteogenesis and angiogenesis, by incorporating metallic elements and drugs, to develop a smart platform technology for highly targeted therapies for regeneration of hard and soft tissues.

Materials and methods: SiO₂-CaO based MBGs containing different doping ions (Cu²⁺, Sr²⁺, Ce³⁺, Ag⁺) were prepared both by batch sol-gel (SG) method and by aerosol-based spray-drying (SD) process, to obtain spherical nano- and micro-sized particles, respectively. The structural and morphological features were investigated by several techniques (TEM and FE-SEM coupled to EDS, N₂ adsorption-desorption), as well as their ability to form hydroxyapatite (HA) in vitro. The release profiles of the therapeutic ions in different media were measured by ICP-AES. Ibuprofen incorporation into the porous structure of doped-MBGs was carried out and the release properties were investigated by UV-Vis.

Results: FE-SEM observations of SD MBGs doped with Cu^{2+} , Sr^{2+} , Ce^{3+} , showed micro-sized spherical particles. Doped MBGs prepared by SG showed spherical shape and size of ca 200 nm. The EDS mapping analysis revealed a homogenous distribution of the doping ions. TEM observations showed particles containing mesopores in the form of a worm-like system. Doped MBGs show high specific surface areas, ca 200 m^2/g for SD MBGs and ca 400 m^2/g for SG MBGs, homogeneous pore size and excellent bioactivity. Sustained release of ions and ibuprofen were obtained in different media.

Discussion: Novel MBG matrices doped with controlled amount of therapeutic ions, characterized by high surface area, fully accessible nanopores, excellent bioactivity and sustained ion/drug release properties, were prepared by different synthesis procedures. These nanomaterials can find various applications as multifunctional therapeutic agent for tissue regeneration.

THERMOPLASTIC STRUCTURAL COMPOSITES WITH THERMAL ENERGY STORAGE/RELEASE CAPABILITY

Fredi G^{1,2}, Meneghini T^{1,2}, Dorigato A^{1,2}, Pegoretti A^{1,2}

¹Department of Industrial Engineering, University of Trento, Trento - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Thermal Energy Storage (TES) systems are gaining interest in many fields, because of their ability to store excess heat and release it when needed, thus filling the gap between energy demand and supply. In applications where weight and volume saving are a key issue, it is advantageous to embed TES capability into the structure, by developing new multifunctional polymer composites. Paraffin is the most common phase change material (PCM) in TES applications, as it can store a high amount of heat per unit mass due to its high specific melting enthalpy. This work aims at developing thermoplastic structural composites that also show TES features. This was achieved by embedding two paraffinic PCMs in a polyamide 12 (PA12) based, glass fiber reinforced composite.

Materials and methods: The following PCMs were considered: (1) Paraffin wax ($T_m = 4^\circ\text{C}$) shape stabilized with carbon nanotubes (15 wt%); (2) Commercial microcapsules (size 20 μm) with a melamineformaldehyde shell and a paraffinic core ($T_m = 43^\circ\text{C}$). Each PCM was added to PA12 in various weight fractions (up to 60wt%) by melt compounding. The resulting matrices were utilized to produce composite laminates by including 5 laminae of a bidirectional E-glass fabric via hot pressing (200°C, 5 minutes). The matrices and the laminates were thoroughly characterized microstructurally, thermally and mechanically.

Results and discussion: The MFI of both matrices decreased with an increase of PCM fraction, but the decrease was less evident for the capsules filled matrices than for the paraffin filled materials. DSC tests showed that the melting enthalpy of the capsules filled matrices was almost proportional to the PCM fraction, thus indicating that the thermal properties of the PCM were preserved. Young's modulus and tensile strength of the matrices and the composites slightly decreased with an increase of PCM fraction, but the mechanical performance is still suitable to develop composite laminates with adequate structural properties.

These results show potential for the development of multifunctional structural composites with TES capability. Future work will be focused on a deeper thermal and mechanical characterization of the laminates. The thermal stability of the matrices, the fiber-matrix interfacial adhesion conditions, as well as the TES features of the composites will be comprehensively investigated.

UTILIZATION OF COFFEE SILVERSKIN IN WATER REMEDIATION

Frontera P^{1,2}, Bonaccorsi L^{1,2}, Panzera G^{1,2}, Malara A^{1,2}, Paone E¹, Mauriello F^{1,2}

¹Department of Civil, Energy, Environment and Materials Engineering (DICEAM), "Mediterranean" University of Reggio Calabria, Reggio Calabria - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: With a global market of more than 147 million of bags in crop produced in 2016, coffee is one of the most consumed beverages in the world. As a consequence, coffee industry generates large quantities of waste, with spent coffee grounds (SCG) and coffee silverskin (CS) being the most significantly generated.

In the last years, a lot of research efforts have been directed to the valorization of SCG for several industrial applications. Among others, SCG have

been proved to be a valid material for the removal of heavy metal ions in contaminated water. CS was less investigated even if its chemical nature is very similar to that of SCG. In this contribution we show, for the first time, the reutilization of CS in water remediation. The results were compared with those obtained with SCG.

Materials and methods: The physico-chemical characteristics of spent coffee grounds (SCG) and coffee silverskin (CS) powders were investigated by TGA-DSC analysis and SEM microscopy.

Quantitative estimation of metal ion removal was performed by means of ICP-OES analysis.

Results and discussion: For the water removal study, 20 mL portions of different aqueous solutions of Cu^{2+} , Fe^{3+} , Zn^{2+} , Ni^{2+} (100 ppm) were prepared. Then, 0.2 g of the CS (or SCG) was immersed in the metal ion solution and kept under stirring at RT. Aliquots were collected from the solutions at specific time intervals for ICP analysis.

With all investigated metal ions the removal efficiency (%) increases with increasing interaction time, until a plateau is reached. With the exception of Ni^{2+} , CS was found to be more active than SCG in water remediation.

CS is able to efficiently remove Cu^{2+} , Fe^{3+} , Zn^{2+} , Ni^{2+} ions from contaminated water being therefore a good candidate for water remediation.

FIBERS REINFORCED FLY ASH BASED GEOPOLYMER COMPOSITES

Galzerano B¹, Formisano A³, Liguori B^{1,2}, Durante M³, Caputo D¹

¹ACLabs-Applied Chemistry Labs, Department of Chemical, Materials and Industrial Engineering, University of Naples "Federico II", Naples - Italy

²Institute of Polymers, Composite and Biomaterials, National Research Council, Naples - Italy

³Department of Chemical, Materials and Industrial Engineering, University of Naples "Federico II", Naples - Italy

Introduction: The requirement for environmentally friendly construction materials for sustainable development is nowadays an important issue. The introduction of fly ash based geopolymers as an alternative binder to ordinary cement materials promises to be a good choice for green building. Despite fly ash based geopolymer has good strength and excellent material greenness, applications have been limited due to the inherent brittleness. The addition of short fibres can change geopolymer brittle behaviour to ductile or quasi-ductile with significant improvement in tensile strength, tensile strain, toughness and energy absorption capacities.

For this purpose, three different types of short fibres (such as vegetal, inorganic and organic) were selected and their influence on microstructural and mechanical properties of the fly ash based geopolymer composite were studied.

Materials and methods: Fly ashes (FA) supplied by ENEL (Brindisi, Italy) have been used as raw materials to produce geopolymer matrix. The alkaline activator solution, added to the dry powder, has been prepared mixing a sodium silicate solution (SS - Na_2O 8.15%, SiO_2 27.40%) with 10 M sodium hydroxide solution. The weight ratio SS/NaOH/FA was 1:1:3. As fibres reinforcement of the geopolymer matrix, hemp, glass and aramid short fibres were used. The mixtures were placed into sealed moulds and cured at 60°C. After curing, the specimens, removed from the moulds, were stored at room temperature. The morphology of fibres and composites and the evaluation of the matrix/fibres adhesion were examined by Scanning Electron Microscopy. For each mixture, different types of specimens were prepared to carry out quasi-static and dynamic tests.

Results: The results from the mechanical tests highlight that the use of a small quantity of short fibers of different materials, allows significantly improving mechanical properties like strength and toughness of the investigated fly ash based geopolymer composites.

Discussion: Short fibres reinforcement can provide geopolymer composites with enhanced ductility. The use of hemp fibers constitutes a compromise solution between the increase of mechanical properties and the preservation of the environment. Nevertheless, more research is needed in order to better control the workability depending on the type of fibre and to optimize the amount of fibres addition.

EFFECTS OF SURFACE PREPARATION ON CORROSION BEHAVIOUR OF 1.4462 STAINLESS STEEL IN CHLORIDE CONTAMINATED CONCRETE

Gastaldi M, Lollini F

Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan, Italy

Introduction: Stainless steel reinforcement can be a suitable preventative measure to guarantee the durability performance of reinforced concrete structures exposed to chloride bearing environments. The resistance to pitting corrosion of the stainless steels depends on their surface condition. For reinforcement production, generally hot rolling is used. After this process, an oxide scale is present on the surface of the bars and this affects the corrosion resistance of the steel. Oxide scale removal can be performed with sandblasting, pickling or combined processes. This note presents the results of a research that aims at evaluating the influence of surface conditions, obtained by means of different types of surface treatments, on the corrosion behavior of 1.4462 stainless steel reinforcement produced by a hot rolling.

Materials and methods: 1.4462 duplex stainless steel reinforcement (22%Cr-5%Ni-3%Mo) with a diameter of 16 mm was used. Three different surface conditions, provided by the manufacturer, were analyzed: sandblasted, sandblasted and pickled and without any surface treatment after hot rolling. The corrosion behaviour of the duplex stainless steel reinforcement with different surface condition was studied in concrete with 5% of chloride by cement mass, and in saturated calcium hydroxide solutions, with chloride concentrations up to 10% by mass. In concrete specimens, corrosion potential and polarisation resistance of the bars were monitored during exposure at 20°C and 40°C and 90% R.H. and, then, potentiostatic anodic polarization tests were performed (increasing stepwise the potential each 24h until corrosion initiation occur). In solution potentiodynamic polarisation tests were carried out.

Results and discussion: During the exposure of concrete specimens in free corrosion condition no significant variation of corrosion rate and potential was observed. 1.4462 stainless steel, with different surface conditions, showed to preserve the passive state in concrete with 5%Cl⁻, also at 40°C. During anodic polarization tests in concrete, pitting corrosion initiation was observed on concrete specimens with reinforcement with the oxide scale and sandblasted, at a potential slightly higher than the free corrosion potential. No corrosion was detected on the reinforcement sandblasted and pickled, also if a polarisation of +600 mV was reached. These results were confirmed also with tests in solution.

LIGHTWEIGHT MATERIALS FOR INDOOR APPLICATION: THE WAY TO INCREASE COMFORT AND HEALTH OF OCCUPANTS

Giuseppe C^{1,2}, Yu Q³, Tittarelli F^{1,2,4}, Ruello ML^{1,2}, Brouwers HJH³

¹Department of Materials, Environmental Sciences and Urban Planning (SIMAU), Università Politecnica delle Marche, Ancona - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of the Built Environment, Eindhoven University of Technology, Eindhoven - The Netherlands

⁴ISAC-CNR, Bologna - Italy

Introduction: The application of nanotechnology in construction materials for indoor applications has an important role in the comfort and health of occupants. In particular, Photocatalytic Oxidation by adding nano-TiO₂ in mortars for indoor plasters represents an optimum option to improve Indoor Air Quality (IAQ). Moreover, in order to obtain more sustainable mortar, the study of alternative binders by partially replacing cement with industrial by-product is of great interest.

The aim of this research is to develop a new sustainable lightweight mortar for indoor applications, able to fulfill the conventional requirements of mortars for finishes and also to improve IAQ for the comfort of occupants.

Materials and methods: Mortar mixes are prepared using both cement or natural hydraulic lime as binders, in a binary composition with coal fly ash. The water content is kept constant in the mixes. Two different types of lightweight aggregates are compared: natural expanded silicates and recycled expanded glass. Mortars are tested in terms of mechanical properties, capillary water absorption coefficient C (UNI EN 1015-18), thermal transmittance and NOx removal capacity under visible light (ISO 22197). Indeed, different dosages of visible length responsive photocatalyst (TiO₂) are added in mortar formulations.

Results: The best mortar shows the lowest dry density of 810 kg/m³, for a mechanical resistance of about 4 MPa and total porosity of 60%. C is 1.7 kg/(m²min^{0.5}). This mortar has a thermal conductivity of about 0.15 W/(mK). The depollution efficiency increases with the increase of the dosage of TiO₂. It is 18% in the case of 2% addition of TiO₂ and 46% in the case of 4% addition of TiO₂.

Discussion: Mortar mixes are prepared following a particle grinding model to ensure a denser packed mix. Meanwhile, lightweight mortars are obtained,

thanks to the use lightweight aggregates. The high porosity of mortars gives a high value of C but it guarantees a low value of thermal transmittance. There is a correlation between the pore size distribution of mortars and depolluting properties: high specific surface available, due to higher porosity with 1 μm diameter, exposes the pollutants to a greater number of available catalytic sites.

NEW DSCS GENERATION FROM TA INSTRUMENTS (APPLICATIONS TO POLYMER NANOCOMPOSITES)

Gracia-Fernández CA¹, Coletti M²

¹TA Instruments-Waters Cromatografia, Madrid - Spain

²TA Instruments-Waters Spa, Milan - Italy

Introduction: The intense development of new nanocomposites, consisting of a polymer matrix and an inorganic phase, converts the study and characterization of the organic-inorganic interphase in an increasingly recurrent topic in polymer science. Its study is justified since the proper characterization of the composite-interphase is crucial to understand the properties and behavior of the final material.

For this reason, in the present work, a new approach based on the utilization of modulated temperature differential scanning calorimetry technique, is suggested for identifying and characterizing the organic-inorganic interphase produced in a nanomaterial such as fumed silica epoxy composite. In the next slide we'll see the composite components.

Materials and methods: These are the composite components: a two-component epoxy system and fumed silica were used. This fumed silica is a by-product derived from the silicon production in electrical melting furnaces by the reduction of high purity quartz at 1800°C. It is a fine powder consisting of amorphous SiO₂ with a mean particle size of 0.15 micron.

Results: We present the heat flow derivatives and phase angle, and the table with the peak temperatures corresponding to each relaxation for different filler contents.

The temperature trends are very similar for the two peaks, decreasing when the filler content is increased to 20 and 30 percent and increasing when the filler content is greater.

This trend change is related to the presence of agglomerates of silica when the silica content is less than 30%. It has been observed that the agglomerates disappear for a 40 percent filler content. The shear stress produced during the resin and particles stirring-mixing is much higher due to the increasing viscosity.

SELF LEARNING HEALTH MONITORING ALGORITHM IN COMPOSITE STRUCTURES

Grassia L¹, Iannone M², D'Amore A¹

¹Department of Industrial and Information Engineering, University of Campania "Luigi Vanvitelli", Aversa (Caserta) - Italy

²Leonardo Aircraft, Pomigliano d'Arco (Naples) - Italy

Introduction: The paper describes a system that it is able of monitoring the health state of a composite structure in real time. The hardware of the system consists of a wire of strain sensors connected to a control unit. The software of the system elaborates the strain data and in real time is able to detect the presence of an eventual damage of the structures monitored with the strain sensors. The algorithm used to detect the presence of a damage on the structure is based on the Leonardo property concept (TO2012A000588 - Method for performing diagnostics of a structure subject to loads and system for implementing said method, filed 4/7/2012, patent pending). Specifically, it requires as input only the strains of the monitored structured measured on real time, i.e. those strains coming from the deformations of the composite structure due the working loads. The health monitoring system does not require any additional device to interrogate the structure as often used in the literature, instead it is based on a self-learning procedure. The strain data acquired when the structure is healthy are used to set up the correlations between the strain in different positions of structure by means of neural network. Once the correlations between the strains in different position have been set up, these correlations act as a fingerprint of the healthy structure.

Materials and methods: Multi-axial mechanical tests were realized at Leonardo laboratories on a real frame equipped with strain gauges.

Discussion: In case of damage the correlation between the strains in the position of the structure near the damage will change due to the change of the stiffness of the structure caused by the damage. The developed software is able to recognize the change the transfer function between the strains and consequently to presently able to detect the damage.

POLY(LACTIC ACID) PLASTICIZED BY CARDANOL DERIVATIVES

Greco A, Ferrari F, Maffezzoli A

Department of Innovation Engineering, University of Salento, Lecce - Italy

Introduction: This paper is aimed to study the suitability of cardanol derived plasticizers for toughening of poly-lactic acid (PLA). The plasticizers, which have already successfully used for plasticization of PVC, were melt mixed with polymer. Different chemical modifications of cardanol were considered, including acetylation of hydroxyl group and epoxidation of the side chain double bond, as well as neat cardanol. For comparison purposes, a polyethylene (glycole) plasticizer was also used. The produced plasticized PLA were characterized by means of tensile testing and differential scanning calorimetry (DSC).

Materials and methods: The material used is a poly-lactic acid (PLA) Ingeo Biopolymer 2003D. A poly-ethylen-glycole (PEG) characterized by a molecular weight MW = 400 g/mole, purchased by Sigma-Aldrich, was used as PLA plasticizer. Cardanol (C), cardanol acetate (CA) and epoxidated cardanol acetate (ECA) were kindly supplied by Serichim srl (Torviscosa, Udine, Italy). Plasticized PLA samples were produced in a Haake Rheocord mixer at a temperature of 190°C, with a rotor speed of 60 rpm for 10 minutes, using three different plasticizer content, i.e. 10, 20 and 30 phr. Injection molded samples were tested by tensile testing and DSC.

Results: DSC analysis revealed that addition of the plasticizers involves a reduction of the glass transition of the material. However, addition of PEG and CA involves a limited reduction of the T_g (down to 30-35°C for a plasticizer content of 30 phr), whereas addition of C or ECA involves a reduction of the T_g down to 15°C, indicating a better plasticizing effectiveness. In terms of mechanical properties, addition of PEG plasticizer involves a reduction of the modulus from the value of PLA (1.7 GPa) to 0.5 GPa, and an increase of the elongation at break from 0.04 to 0.4. Addition of cardanol derivatives, and in particular of cardanol in its natural form, involves a reduction of the modulus down to 45 MPa, and an increase of the elongation at break up to 1.

Discussion: Cardanol plasticizer, either modified or in its natural form, shows a much better plasticizing effectiveness towards PLA than commercial plasticizers. Compared to PEG, another distinct advantage of cardanol is its natural derivation.

EXPERIMENTAL INVESTIGATION ON TENSILE AND SHEAR BOND PERFORMANCE OF BASALT-FRCM COMPOSITE

Iorfida A¹, Candamano S¹, Verre S², De Fazio P³, Crea F¹, Ombres L²

¹ Department of Environmental and Chemical Engineering (DIATIC), University of Calabria, Arcavacata di Rende (Cosenza) - Italy

² Department of Civil Engineering (DINCI), University of Calabria, Arcavacata di Rende (Cosenza) - Italy

³ Department of Energy Technology, DTE BBC, C.R. Trisaia-ENEA, Rotondella (Matera) - Italy

Introduction: In recent years basalt fabric reinforced cementitious matrix (FRCM) composites have attracted great attention because they result to be effective and cost/environment efficient. Nevertheless, their mechanical performances are still under investigation in order to provide reliable values of parameters for design purposes.

Direct tensile tests and single-lap shear bond test on masonry, have been, thus, carried out on such a composite.

Materials and methods: The FRCM composite consists of a balanced, coated, bidirectional fabric made out of basalt fibres and stainless steel micro-wires and a mineral-NHL mortar. Tensile tests were carried out, at different loading rates, on specimens of nominal dimensions equal to 500 mm × 43 mm × 10 mm with clamping grip. Two LVDTs measured strains in the whole gauge length. Direct shear test were performed with different bonded length. The global slip was measured by two LVDTs. Five specimens for each configuration were tested. A push-pull configuration was used.

Results: Ultimate tensile strength and strain at failure are 413 MPa (CoV = 13.02%) and 2.04% (CoV = 3.70%) respectively, and the tensile modulus in cracked stage up to failure is 33 GPa (CoV = 6.25%). The shear bond tests provided the effective bond length that appeared to be about 200 mm with applied load of about 1100 N.

Discussion: All specimens under tension exhibit a tri-linear behaviour with an extended lengthwise and transverse crack pattern throughout the gauge length before failure of the fibre bundles. The tensile response curves were unaffected by tested loading rates. In shear bond test, longitudinal and transversal cracks generally formed near the composite loaded end, then additional cracks formed progressively towards the composite free end with increasing global slip. Specimens failed by debonding at the fabric to matrix interface with brittle detachment of the fabric strip and external matrix layer.

USE OF AMINO-FUNCTIONALIZED MIL-101(Cr) FOR Cr(VI) REMOVAL FROM AQUEOUS SOLUTIONS: A BATCH STUDY

Jalayeri H¹, Aprea P², Caputo C², Gargiulo N², Peluso A², Pepe F¹

¹ Department of Engineering, Università del Sannio, Benevento - Italy

² Department of Chemical Engineering, Materials and Industrial Production, University of Naples "Federico II", Naples - Italy

Introduction: Metal organic frameworks (MOFs) are crystalline hybrid porous solids consisting of metal clusters connected by organic linkers to form tridimensional structures. These material are known to have very large pore volumes and surface areas, and can be appropriately functionalized for specific applications. Recently, water resistant MOF-based materials have been proposed by different authors for the adsorptive removal of various hazardous materials from aqueous solutions, among which heavy metals. In the present paper, a chromium-based metal organic framework, MIL-101(Cr), functionalized with amino-groups, was used for the adsorption of Cr(VI) from aqueous solution under batch conditions, with the aim of evaluating this material for industrial wastewater treatment. Batch experiments were carried out in order to evaluate both the kinetics and the thermodynamics of the Cr(VI) adsorption process.

Materials and methods: Amino-functionalized MIL-101(Cr) was prepared by a one pot synthesis by hydrothermal treatment of 2-aminoterephalic acid and [Cr(H₂O)₆](NO₃)₃·3H₂O. The resulting material was characterized by XRD, FTIR, and nitrogen adsorption porosimetry. Kinetic experiments were carried out by contacting the amino-functionalized MIL-101(Cr) with K₂Cr₂O₇ solutions under stirring at 25°C, and by sampling the solutions at different times. Adsorption isotherms were obtained with a similar approach, at four different temperatures ranging from 25°C to 80°C.

Results and discussion: XRD confirmed the crystalline nature and structure of the synthesized material. FTIR revealed the presence of amine groups on the surface of the material. Porosimetric analysis indicated a very high specific surface area (BET area: 2300 m²/g). Kinetic curves were analyzed using different models, and data were best fitted by the pseudo second order kinetic model. This suggested that adsorption might be chemically, rather than physically, controlled. Analysis of equilibrium isotherms at T = 25°, 40°, 60° and 80°C indicated a weak dependence on temperature, with a slight positive effect of temperature on adsorption capacity. The maximum capacity of functionalized MIL-101(Cr) turned out to be 34.1 mg/g at 25°C, and the experimental data were fitted with the Langmuir isotherm. In all, the experimental results indicate that amino-functionalized MIL-101(Cr) has a good perspectives for application to the removal of hexavalent chromium from water.

PYRO-RESISTIVE EFFECT OF GRAPHENE ON FERROELECTRICS ENABLING UNCOOLED PHOTODETECTORS IN THE MID-IR

Janner D

Politecnico di Torino, Turin - Italy

Introduction: Great effort is devoted to the development of sensitive light detectors for the midinfrared (mid-IR) spectral region (~3-25 μm). These photo-detectors (PDs) are essential components in many applications, e.g. vibrational spectroscopy and thermal imaging. Because of its transparency in the mid-IR and its good electrical conductivity graphene is a promising material for detectors in such optical range. Indeed, Hsieh et al used it in an opto-thermal field effect transistor (FET) on lead-zirconate-titanate (PZT) substrate. Baeumer et al recently reported spatial carrier density modulation

in graphene on periodically poled LiNbO_3 (LN) demonstrating a p-n junction PD gating graphene across the domain inverted structure. Moreover, Kulkarni et al used graphene as transparent electrode in a conventional pyroelectric detector based on PVDF working from 1.9 to 7.5 μm .

Beyond these approaches, graphene on pyroelectric substrate can be an ideal material combination for mid-IR PDs. Indeed, when the temperature changes due to heat generated by light absorption, surface charges are generated in the pyroelectric substrate producing a pyroelectric-induced change in electrical resistance of graphene thus generating a “pyro-resistive” effect. **Materials and methods:** To demonstrate the pyro-resistive effect, CVD graphene was deposited on the surface of a ferroelectric ceramic (LiNbO_3) and contacted with gold contacts to monitor the sheet resistance against a variation in temperature. The measurements of the pyro-resistive effect used in photodetectors in the Mid-IR was realized by impinging a 10 mm laser radiation and monitoring the resistance change thus evaluating the PD performance.

Results: Fundamental characterization of “pyro-resistive” effect gave ~500% change in resistance within 40K temperature change. The photodetector reached a detectivity of $10^5 \text{ cm}^2\text{V}/\text{Hz}/\text{W}$, which is almost comparable to some commercial PDs. A theoretical model was developed to account for the pyro-resistive effect in graphene with excellent agreement to experimental data.

Discussion: Obtained results prove the fundamentals of the pyro-resistive effect on graphene and demonstrate its usefulness for mid-IR PDs. Such results open the way for a promising new class of devices considering that a 3 order of magnitude enhancement in the PD performance is expected by the optimization of graphene fabrication and device geometry.

MONITORING, CONSOLIDATION, CONSERVATION AND PROTECTION FOR CULTURAL HERITAGE

La Mantia FP^{1,2}, Pedeferra MP^{2,3}, Tulliani J-M^{2,4}, Legnaioli S^{2,5}

¹Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of Chemistry, Materials and Chemical Engineering “G. Natta”, Politecnico di Milano, Milan - Italy

⁴Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

⁵Applied Laser Spectroscopy Laboratory, National Research Council of Italy - Institute of Chemistry of Organometallic Compounds, Pisa, Italy

Introduction: Mistakenly, the term Cultural Heritage is often associated only to ancient artistic artifacts. In fact, there are many examples of objects and artworks that can be fully considered among the cultural heritage of the nation and which require the same attention as to their degradation and conservation. These artifacts are nowadays made in different materials, even combinations of them, which have often been recently introduced and therefore little is known in terms of degradation and, above all, of conservation and restoration.

The purpose of the research project “MONITORING, CONSOLIDATION, CONSERVATION AND PROTECTION OF CULTURAL HERITAGE” is to investigate some classes of materials - polymers, metals, cement and concrete conglomerates – focusing the attention on their monitoring, conservation, durability.

Materials and methods: Four research units operating in Italy (University of Palermo, Politecnico di Milano, Politecnico di Torino and CNR) are involved in the project and they will collaborate in a complementary and synergetic way to define new protocols. Smart and innovative sensors able to monitor in real time the artifact condition according to environmental variables will be studied, modeled and designed. Finally, new materials, their application and methods for conservation and restoration will be proposed.

Results and discussion: Smart sensors and new materials developed within the project will have a positive impact not only in the field of cultural heritage but also in civil and industrial field. The aim of the project is to deepen the scientific issues related to the degradation mechanisms of new materials of modern and contemporary art with the possibility of targeting recovery and protection measures, thus increasing the durability of its artworks.

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ACTIVE AND PASSIVE POLYIMIDE FILMS WITH A MINIATURIZED CELLULAR STRUCTURE

Lanzara G, Chen Y

Department of Engineering, University of Roma Tre, Rome, Italy

Introduction: Morphing materials are becoming strategic in recent years because they have the potential to improve significantly performance of the devices or structures in which they are integrated. In particular mechanical flexibility, light-weight and synclastic morphing capability are desirable for passive materials and low actuation power, fast response, independent and multiple shape changes in 2D, 3D, are necessary for active materials. Here, new designs of active and passive polyimide films that reflect all of the above mentioned properties are presented.

Materials and methods: The active and passive films are characterized by a miniaturized cellular structure. The unit cell in both materials is formed by a polyimide micro-scaled skeletal structure. In the passive case, this structure is such to allow for synclastic shape changes thanks to its intrinsic negative poisson ratio, while in the second case, the polyimide films becomes active (through temperature actuation) thanks to the addition of Poly(vinylalcohol) elements that are strategically interconnected with the polyimide skeleton. With increasing temperature these materials interact within each other in such a way to induce internal stresses that make the film either expand or contract. 3D Morphing is reached by means of a multilayer configuration.

Results: Numerical and experimental campaigns were performed to validate the proposed material design concepts. Novel microfabrication methods were successfully implemented in a clear room environment. The passive polyimide film was tested under various conditions to highlight the influence of surface tension onto the auxetic capability of the film. This is because the miniaturized nature of the cellular structure makes it extremely sensitive to this type of surface forces. The active material was tested in single and multilayer configuration to validate its actuation capability under different temperature conditions.

Discussion: The results confirmed the predicted responses and highlighted the high potential of the proposed polyimide films to improve performance in morphing applications.

A NEW SUSTAINABLE EXTERNAL WALL SYSTEM FOR CIVIL ENGINEERING APPLICATIONS

Lorusso P, Manzi S, Montecchi M¹, Motori A²

¹ CMF_Greentech s.r.l., Pavullo (Modena) - Italy

² Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), School of Engineering and Architecture, University of Bologna, Bologna - Italy

Introduction: This research investigates an external wall system made with hemp-based composites for a possible application in the civil engineering. In particular, the wall system is realized with panels of two different densities. First of all, physical and mechanical properties of the panels are studied, together with fire reaction and resistance behavior. Then, the external wall system is investigated by means of impact energy of the external surface, thermal and acoustic properties.

Materials and methods: The hemp-based panels are made of hemp hurds bonded with a hybrid organic-inorganic admixture, a mineral oxide, a proper aqueous salt solution and a reactive vegetable fraction. In particular, low and high-density panels (i.e., 350 and 1000 kg/m^3 , respectively) are here investigated.

The physical (moisture content, swelling in thickness, water absorption and water vapor resistance factor) and mechanical (bending strength, modulus of elasticity in bending, compressive strength, compression modulus of elasticity and resistance to axial withdrawal of screws) behavior of panels is investigated. Moreover, the impact energy of the external surface, thermal and acoustic properties are studied. Correlations between properties are made.

Results: The high-density panel shows remarkable physical and mechanical properties if compared with panels present in the market with the same application. The low-density panel provides good thermal and acoustic properties to the wall system.

Discussion: The composite materials exhibit an outstanding and not common combination of properties. This research shows first preliminary results aimed at implementing sustainable processes in the constructions industry. Extended studies are ongoing in order to fully prove the suitability of the external wall system for civil engineering applications.

SUPPORTED Ni-CATALYSTS FOR CO₂ CONVERSION

Macario A¹, Frontera P², Candamano S¹, Crea F¹, Antonucci P²

¹ Department of Chemical and Environmental Engineering, University of Calabria, Cosenza - Italy

² Department of Civil, Energy, Environment and Materials Engineering, "Mediterranean" University of Reggio Calabria, Reggio Calabria - Italy

Introduction: Dry-reforming of methane, as well as CO₂ methanation, are two processes that represent promising solutions for CO₂ mitigation and for alternative energy production by low-carbon fuels. This work summarizes the importance of nanostructured catalysts and their properties with respect to the main catalytic processes for sustainable energy supply.

Materials and methods: Suitable catalysts should have high metal dispersion, easy to reduced and preserved from sintering. These are aspects in common for catalysts design and optimization, both for dry-reforming and CO₂ methanation. Oxides such as SiO₂, Al₂O₃, TiO₂, ZrO₂ and CeO₂, are the most studied supports for nickel. Zeolites, mesoporous materials and delaminated structures represent synthetic materials with surface properties tunable to improve nickel catalytic performance. Hydrothermal synthesis is the main procedure to obtain zeolites and related materials, such as Silicalite-1, Ferrierite, MCM-41 and ITQ-6; the method used to deposit active metal on a support is the incipient wetness impregnation. Numerous analytical techniques are employed for a detailed characterization of catalysts.

Results and discussion: CO₂ conversion by dry-reforming and by methanation represents, today, a potential solution to greenhouse gases emissions control. Both reactions can be catalyzed by supported nickel nanoparticles. The type of support plays a pivotal role in the catalytic performance of metal, both for dry-reforming and CO₂ methanation.

Particularly, highly defective supports or lamellar structure, such as ITQ-6 and FER zeolite respectively, favor nickel particles dispersion, producing active species that are preserved from sintering effects and coke deactivation. Cesium addition improves the catalytic performance due to the increasing basicity of the support that leads to an enhanced adsorption of CO₂.

CO₂ methanation performance of mono-metallic nickel and of bi-metallic Ni-Fe catalyst are improved by the gadolinia doped ceria support. This material is able to combine two positive effects for CO₂ hydrogenation reaction: to produce active and stable nickel nanoparticles and to generate surface oxygen vacancies that increase the CO₂ dissociation, resulting in a superior activity and selectivity to CH₄ with respect to other supports most commonly used (ZrO₂, Al₂O₃, SiO₂).

SELECTIVE LASER MELTING OF ALUMINUM ALLOYS: RELATIONS AMONG PROCESS, MICROSTRUCTURE AND MECHANICAL PROPERTIES

Manfredi D¹, Biaino S^{1,2}, Lombardi M^{1,2}, Pavese M², Fino P^{1,2}

¹ Centre for Sustainable Future Technologies CSFT@PoliTo, Istituto Italiano di Tecnologia, Turin - Italy

² Applied Sciences and Technology Department (DISAT), Politecnico di Torino, Turin - Italy

Introduction: The aim of this study is to summarize the results of an extensive research activity focused on processing Al-Si-Mg alloys aluminum alloys through the Additive Manufacturing (AM) technique commonly known as Selective Laser Melting (SLM). This process is gaining worldwide interest thanks to the possibility of obtaining a freeform fabrication coupled with high mechanical properties. The extremely rapid interaction between a concentrated laser source and micrometric metallic powders that occurs in SLM process generates very fast melting and subsequent solidification on each layer and on the previously consolidated substrate, opening *de-facto* to a new metallurgy. For this reason, the effects of the main process variables and of post process heat treatments on the microstructure and mechanical properties of the final parts must be deeply investigated.

Materials and methods: Two aluminum alloys with a different Si content, AlSi10Mg and AlSi7Mg, corresponding to a A360 alloy and to a A357 alloy respectively, were used. The starting powders were characterized in terms of particle morphology and size distribution, through scanning electron microscopy and laser granulometry. Then they were processed by an EOSINT M270 Dual Mode machine. Post process heat treatments were carried out in a Proba oven in air. Cubic samples were used for density measurements, microstructure observations by optical and electron microscopy, and Vickers microhardness. Tensile samples were also fabricated perpendicular and parallel to the building direction.

Results and discussion: The SLM samples in both aluminum alloys exhibited a very high yield strength and hardness in comparison to the corresponding as-cast alloys, due to an extremely fine microstructure created by the rapid melting and solidification phenomena involved in the process. As-produced samples showed the highest properties compared to heat treated ones.

FRACTURE BEHAVIOUR OF SILICA FILLED POLYISOPRENE BASED COMPOUNDS

Marano C, Racconi L, Rink M

Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

Introduction: The fracture behaviour of silica filled polyisoprene rubber was evaluated carrying out uniaxial tensile tests on notched pure shear (PS) specimens up to rupture. Because filled rubbers show a "stress softening" phenomenon - the *Mullins effect* - when subjected to a cyclic deformation process, tests were performed on both pristine material and on material that has been previously cyclically deformed at a given strain value. It was thus possible to evaluate the effect of strain-induced structure modification on the compound's fracture toughness for different values of the strain applied in the "demullinization" process.

Materials and methods: Polyisoprene rubber based compounds differing in silica content were kindly provided by Pirelli S.p.A.. ZeoSilica1165 was used as filler and silica volume fraction of 0, 0.09, 0.145 and 0.172 were considered. The fracture mechanics approach was applied evaluating the value of J integral at fracture onset ($J_c = \eta U_c/A$: η is a shape factor equal 1 for the PS specimen, U_c is the deformation energy at fracture and A is the specimen cross section at the notch plane). Tearing energy at fracture onset, T_c , was also evaluated as follows: $T_c = w_c h$ (w_c is the strain energy density stored in the pure shear region of the specimen at fracture onset). Digital image correlation analysis was performed or strain measurements.

Results and discussion: The main results obtained are: (i) for each material critical values of J_c and T_c are similar, suggesting that both ways of determining fracture toughness are valid for these materials; (ii) J_c of the filled compounds is always lower than that of the unfilled rubber but it increases with the filler content, suggesting that filler contents higher than the ones used in this work should be considered for an effective rubber reinforcement; (iii) the "demullinization" process decreases the fracture toughness of the filled compounds only if it has been performed at relatively high strains; (iv) the strain at fracture onset of the filled compounds resulted to be lower than that of the unfilled rubber, fairly constant with the filler content and not affected by "demullinization process" suggesting that fracture is mainly controlled by a deformational criterion.

MONITORING, CONSOLIDATION, CONSERVATION AND PROTECTION FOR CULTURAL HERITAGE: CO₂ SENSORS FOR CONCRETE CARBONATION MONITORING

Marchisio A, Tulliani JM

Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

Introduction: When ageing, the concrete alkalinity can be reduced by the chemical reaction (carbonation) between calcium hydroxide in the concrete and carbon dioxide from the surrounding atmosphere, which may cause depassivation of the embedded steel and trigger corrosion. Thus, it is hypothesized that within concrete CO₂ concentration will increase with time as concrete cover will carbonate, therefore in this project metal oxide semiconductors usually studied for monitoring carbon dioxide in air will be investigated as sensing materials in low-cost solid-state gas sensors. To this aim, a screen-printed CO₂ sensor will be developed from nanopowders of BaTiO₃-CuO.

Materials and methods: Barium carbonate powder (Fluka) was mixed with titanium dioxide one (Degussa P25) in ethanol in a planetary mill for 5 hours. Then, the powder was dried overnight and pellets were uniaxially pressed at 290 MPa and fired at 1200°C for 6 hours to synthesize barium titanate. Copper oxide powder were prepared from copper sulfate after thermal decomposition at 700°C for 2 hours. A equimolar BaTiO₃: CuO mix, was made in ethanol and in a planetary mill for 5 hours. After drying overnight, powder was screen-printed onto commercial alpha-alumina substrates with platinum interdigitated electrodes, dried in oven and fired at 900°, 1000° and 1.100°C

for 1 hour. The powder was characterized by means of X-ray diffraction, laser granulometry and scanning electron microscopy (SEM). SEM observations were done also on screen-printed films.

Results and discussion: BaTiO₃-CuO thick-film screen-printed sensors were successfully produced through a simple solid-state method. The adhesion of the powder was good only for the higher temperature thermal treatment, at 1.100°C. To unravel the potentialities of this mixed oxide for CO₂ detection, the sensors were tested in a wide CO₂ concentration range (from environmental actual concentration to few thousand ppmv) at the temperature of 250°C. Very preliminary tests carried on some sensors showed a limited sensitivity to CO₂ in the adopted experimental conditions: improvements to increase sensors response and sensitivity like photo-activation of BaTiO₃-CuO films are ongoing.

COMPUTATIONAL TOOLS AND METHODOLOGIES FOR THE SUSTAINABLE USE OF MATERIALS IN ENGINEERING AND DESIGN

Masi L, Fredriksson C

Education Division, Granta Design Ltd., Cambridge - UK

Introduction: Sustainability is a broad topic that engineers need to consider when developing new products as well as improving existing products. It involves resources, material and energy flows, alongside societal and economic aspects. Increasingly, sustainability is of concerns among professionals, researchers, and educators from any engineering field, making it an interdisciplinary but complex topic.

Materials and methods: In this talk, we present an interactive computational tool and unique database of material properties that enables rational and sustainable material selection in engineering design. These are based on a methodology developed by Prof. Mike Ashby at the University of Cambridge and enable cost, manufacturability, mechanical performance, and eco-properties such as embodied energy or CO₂-footprint to be taken into account in a visual and interactive way. Life-cycle implications can be estimated at the early design stage and guidance provided to the designer or the student on ways to change the design for improved environmental performance.

Results: Examples based on a recently developed Sustainability Database and Eco Audit function will be used to show how these tools can be used to support resource and criticality aspects in teaching as well as product development.

Discussion: This computational tool now provides an initial framework for sustainable assessment in product development. The database and tools, alongside a set of teaching resources are used today in a growing number of universities worldwide to educate the engineers of the future.

INORGANIC BINDERS BASED ON FIRED LIMESTONE-CLAY RAW MATERIALS

Mavilia L

Department of Heritage, Architecture and Urban Planning, "Mediterranean" University of Reggio Calabria, Reggio Calabria - Italy

Introduction: Limestone-clay based natural or artificial mixtures are investigated as inorganic materials for the production of sustainable inorganic binders as hydraulic lime or belite cement. From preliminary tests it has been found that it necessary to pay much attention to both the nature and composition of the starting material in order to maximize the content of hydraulic active components. This because some mineral phases among them mainly the gehlenite have been mistakenly considered and computed as an active component of the fired product by others researchers.

Materials and methods: Calcium carbonate, aluminum hydroxide kaolin and amorphous silica pure for analysis reagents (Sigma-Aldrich) and non-commercial types of natural raw materials classified as limestone, siliceous limestone, clay marl and calcareous marl were used in this study. The first set of reagents were employed to prepare binary and ternary mixtures of pure chemicals with a widely weight ratio ranging from 90/10 to 20/80. Characterization procedure by thermal analysis and powder X-ray diffraction techniques were made both before and after the thermal treatment performed in a platinum crucible at 1000 ÷ 1100 Celsius degree for a reaction time of 2-3 hours.

Results: Experimental findings have clearly shown that thermal treatment of both pure mixtures of limestone and kaolin with largely variable CaCO₃/Al₂(OH)₄Si₂O₅ weight ratios and natural raw materials based on these two minerals gives rise to the formation of a mixture of several minerals always including besides lime and larnite the gehlenite. The same has also found in the fired products derived from raw materials characterized by the presence of kaolinite clays. Gehlenite and other calcium silicate and calcium aluminosilicate as wollastonite and anorthite, respectively were not found when Al₂O₃ and SiO₂ are provided from two separate sources.

Discussion: The study proposed has highlighted that sustainable firing cycle on raw materials such as clayed limestone, marl and marly clays can lead to feebly hydraulic binders characterized by a content of active part (lime + belite) ranging from 15 to 65%. Otherwise ternary mixtures of calcite, aluminum hydroxide and amorphous silica processed under the same experimental conditions can lead to strong hydraulic limes and belite cement.

MECHANICAL CHARACTERIZATION OF BIORESORBABLE PHOSPHATE OPTICAL FIBERS

Milanesi D^{1,2,3}, Pugliese D^{1,2}, Ceci-Ginistrelli E^{1,2}, Boetti NG⁴, Renga F¹, Janner D^{1,2}, Sglavo VM⁵

¹ Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ CNR-IFN, Trento - Italy

⁴ Istituto Superiore Mario Boella, Turin - Italy

⁵ Department of Industrial Engineering, University of Trento, Trento - Italy

Introduction: Phosphate glasses can be properly engineered to fabricate bioresorbable optical fibers. Such fibers have been employed for diffuse optics experiments and dissolution in simulated body fluids was demonstrated with a rate of 2 μm/day. In the present work, step-index 125 μm diameter optical fibers were manufactured by rod-in-tube technique starting from two slightly different bioresorbable phosphate glasses. The prepared fibers underwent morphological and optical characterization, followed by the measurement of their mechanical properties.

Materials and methods: The investigated phosphate glass compositions included the following components: P₂O₅, CaO, Na₂O, SiO₂, MgO. The core and cladding glasses were fabricated by melting a powder batch of high purity chemicals inside an alumina crucible at a temperature of around 1200°C, followed by casting into preheated brass molds. The core glass was cast into a cylindrical mold to form a rod, while for the cladding glass rotational casting was carried out to obtain a tube. Capillary fibers were obtained by directly drawing the cladding glass tubes. The optical fiber was characterized by measuring the optical loss by cut-back method at the wavelength of 1300 nm. Mechanical tests on the fibers included tensile tests both in dry and humid environments with the aim of determining their elastic moduli and tensile strengths.

Results: The prepared fibers were homogeneous and in the case of the optical fiber a very good core/cladding interface was observed, leading to an optical loss of 3.4 dB/m. Tensile tests were carried out on fibers with gage length from 10 to 150 mm, this allowing the determination of a failure stress ranging from ~200 MPa to ~400 MPa and an elastic modulus of about 53 GPa. This latter was also determined on capillaries produced by the glasses constituting the core and cladding. This provided the evidence of higher stiffness of the cladding glass composition, whose elastic modulus (around 53 GPa) determines the stiffness of the entire fiber.

Discussion: The core and cladding glasses and fibers were successfully fabricated, and the tensile tests carried out revealed a surprising limited fatigue susceptibility although the fibers are relatively soluble in water based solutions.

EFFECT OF COMMERCIAL AND WASTE CARBONACEOUS FILLERS ON THE MECHANICAL AND ELECTRICAL PROPERTIES OF INNOVATIVE MORTARS

Mobili A^{1,2}, Belli A^{1,2,3}, Giosuè C^{1,2}, Mancini R^{1,2}, Mazzoli A^{1,2}, Bellezze T^{1,2}, Tittarelli F^{1,2,4}

¹ Dipartimento di Scienze e Ingegneria della Materia, dell'Ambiente e Urbanistica (SIMAU), Università Politecnica delle Marche, Ancona - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ DIASEN® s.r.l., Sassoferrato (Ancona) - Italy

⁴ Institute of Atmospheric Sciences and Climate (ISAC), CNR, Bologna - Italy

Introduction: The addition of nano/microfillers can improve the mechanical performance and durability of mortars, thanks to a microstructure refinement. Moreover, carbonaceous fillers can enhance the electrical properties of hardened compounds, thanks to their high conductivity. However, commercial carbonaceous fillers (nanotubes or graphene) are very expensive.

In this work, the effect of commercial carbonaceous fillers on the mechanical and electrical performances of a binder paste, was compared with that of carbonaceous fillers with zero embodied energy, as industrial by-products.

Materials and methods: Pastes were manufactured with hydraulic lime at water/binder ratio of 0.32, naphthalene sulfonate superplasticizer (1% by binder weight) and different amounts of carbonaceous fillers (0.25%, 0.5% and 1% on binder weight). As commercial fillers, graphene nanoplatelets (GNP) and activated carbon (AC) were used. As wastes, a char from biomass gasification (CH) and a used foundry sand (FS) (particle size <75 μm for both) were used. As reference, a paste without fillers (R) was manufactured.

Previously fillers were dispersed with an ultrasonicator for 10 minutes in water with superplasticizer, then lime was added. The obtained pastes were cured at 20°C and RH = 100% for 7 days, then at RH = 50%.

Specimens were subjected to compression and tensile splitting tests after 28 days. Electrical resistivity was determined by electrochemical impedance measurements through two AISI 316 electrodes after 7, 14, 21 and 28 days.

Results: At 28 days, R tensile strength was 0.82 MPa; 1% of GNP or AC enhanced it of 40% and 25%, respectively. The other additions did not affect significantly the results.

Under compression, all types and amounts of filler improved mechanical behavior of about 30%.

The electrical resistivity of pastes increased during time, reaching $2 \cdot 10^4 \Omega \cdot \text{cm}$ for the reference. However, all additions decreased it: GNP and AC of about 55% and 50%, respectively, but CH and FS at 1% of about 65%.

Discussion: The investigated waste carbonaceous fillers, even if cheaper than the commercial ones, can comparably enhance the mechanical properties and electrical conductivity of mortars. These preliminary data are encouraging for developing mixtures to test also the electromagnetic shielding effectiveness.

FUNCTIONALIZATION OF STAINLESS STEEL USING SBA-15 MESOPOROUS SILICA

Pasqua L¹, Leggio A²

¹Department of Environmental and Chemical Engineering, University of Calabria, Rende (Cosenza) - Italy

²Department of Pharmacy, Health and Nutrition Sciences, University of Calabria, Rende (Cosenza) - Italy

Introduction: Aminopropyl-functionalized SBA-15 mesoporous silica is covalently and electrostatically anchored on the surface of stainless steel plates. The anchoring is carried out through the use of a nanometric spacer and two different spacers are proposed (below 2 nm in size). Sample A is obtained by anchoring, to the stainless steel amino functionalization, a glutaryl dichloride spacer. This specie forms an amide linkage with the amino group while the unreacted acyl groups undergo hydrolysis giving a free carboxylic group. Sample B is prepared using 2-bromo-methyl propionic acid as spacer. Successively the carboxylic group, in both cases, is linked to the aminopropyl derivatization on the external surface of the mesoporous silica particle through electrostatic or covalent bond respectively.

Materials and methods: The starting mesoporous materials have been characterized by XRD, N₂ adsorption, SEM and TEM while the obtained plates have been studied by XRD, SEM, XPS analysis and FT-IR spectroscopy.

Results: The employed SBA-15 particles present spherical morphology with quite homogeneous diameters always below 2 microns in size. The TEM micrograph shows both the hexagonal order of SBA-15 and the curved channels. In both cases a continuous deposition (coating thickness is around 10 μm) is obtained, in fact, XPS data do not reveal the metal elements constituting the plate. The XRD powder diffraction pattern of the coating shows the typical behavior expected for SBA-15 mesoporous silica.

Discussion: The coating thickness resulted to be around 10 μm in both the plates and it corresponds to several layer in SBA-15 particles. The formation of a network of particles can be attributed to the interaction via the aminopropyl linkers on the external surface of different APMS particles.

BENDING STIFFNESS OF POROUS CERAMICS. NEW IFU MODEL EMBEDDING PORE SIZE DISTRIBUTION

Pia G, Casnedi L, Brun M, Sanna U

Department of Mechanical, Chemical and Engineering Materials, University of Cagliari, Cagliari - Italy

Introduction: Porous Ceramics are a class of materials used in numerous industrial and engineering fields. The remarkable applications are due to their unique characteristics as high mechanical properties. This last aspect needs to be investigated in connection with morphology features. For this reason, in this work, a new fractal model capable of reproducing porous microstructure and predicting mechanical properties of porous ceramics has been proposed.

Materials and methods: Ceramics porcelain tiles have been obtained by a compaction technique. Pore forming agents have been used for inspiring porosity into the microstructure. Porosity and pore size distribution have been measured by MIP technique. Three-point bending strength measurements were selected to evaluate the mechanical resistance.

Bending stiffness depends on second moment's statistical information about the microstructure distribution. Intermingled Fractals Units (IFU) models have been implemented in a Matlab algorithm capable of computing the bending stiffness of a beam structure. The numerical model embodies the multi-disperse pore size distribution obtained from different IFU realizations and the geometrical distribution of the pores.

Results: Pore volume fraction obtained by MIP is between $15.7 \div 17.0$. Bending stiffnesses for different types of microstructure have been computed and compared with experimental results for classes of ceramic beams. Experimental results show a bending stiffness in the range of $54 \div 60$ MPa for different porosities and size distributions, while the numerical results give an interval between $56 \div 59$ MPa.

Discussion: Comparison between experimental results and numerical models shows a good agreement. The proposed morphological model is capable of describing the stiffening and softening effects of the internal microstructure. Mercury intrusion porosimetry is a standard experimental procedure that describes pore size distribution but is not capable of determining spatial and morphological distribution of the microstructure. The proposed model, which depends on morphological information, can be also used to determine upper and lower bounds of the effective mechanical properties, which are associated to the internal microstructure and are shown to be sufficiently close.

CAN VOC ADSORPTION BE ENHANCED BY AN EXTERNAL ELECTRIC FIELD?

Pierpaoli M, Ruello ML, Fava G

Department of Materials, Environmental Sciences and Urban Planning, Università Politecnica delle Marche - Italy

Introduction: The term "Plasmacatalysis" describes the synergistic effect of coupling two processes: plasma and catalysis although, the word "Electro-adsorption" refers to the adsorption of a specie on the surface of an electrode in an electrolyte solution. Both phenomena refer to an augmented process (catalysis and adsorption, respectively) thanks to the presence of charged electrical species. Given the lack of existing literature describing the influence between adsorption and an external-applied electric fields for gas phase adsorption, in this study a discharge electrode (at the potential of 3-11kV) was placed over a grounded activated carbon fibre cloth. The adsorption kinetic of several organic compounds on the activated carbon cloth was evaluated in the presence and in the absence of an electric field. Results suggest that its application enhances the adsorptive process.

Materials and methods: A thin wire electrode (discharge electrode) is set to positive polarity, whereas the opposite electrode (activated carbon cloth) is earthed and a fan induces an air flux quasi-parallel to the sample. Acetone, Acetaldehyde, Benzene, Cyclohexane, Ethanol, Methyl Ethyl Ketone, Toluene, 1-Propanol were used to study the removal efficiency with and without electric field.

Results: Results suggest that the application of an electric field on an activated carbon cloth can enhance the adsorptive process, which depend from the applied potential and from the adsorbate itself. Two interesting correlations were found by plotting the removal enhancement along the specific heat of fusion and with the chemical hardness of the adsorbate.

Discussion: The enhanced disappearance rate of selected organic compounds can be explained (1) by the generation of reactive oxidative species, which take part in the degradation of such compounds, (2) by the modification of the sorbent surface, and (3) by the electric polarization of the com-

pounds. Further studies are intended to better understand the nature of such augmented process.

VISUAL EXAMINATION OF METAL-LOOK FINISHES STABILITY AFTER ACCELERATED AGING TEST ON POLYMERIC COMPOSITES APPLIED IN THE PROFESSIONAL KITCHEN ENVIRONMENT

Piselli A^{1,3}, Simonato M³, Del Curto B^{2,4}

¹Department of Design, Politecnico di Milano, Milan - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³The Research Hub by Electrolux Professional, Pordenone - Italy

⁴Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

Introduction: In the professional appliance industry, materials selection for metal replacement represents an opportunity for the design of the components characterized by manual interaction with the user. It allows, indeed, to fulfill ergonomic design and safety requirements (e.g., electrical and thermal insulation). Although, as professional appliances are characterized by an intense use in harsh environments, the materials and finishes' durability in time have to be studied.

Materials and methods: Polymer samples, characterized by six different metal-look finishes, have been prepared by accelerated aging. The samples were exposed to temperature and the most present chemical solutions in the professional kitchen environment (5 food chemicals and 4 surface cleaners). The stainless steel-look finishes that were selected, were developed by bulk-technology, water transfer printing, painting, and aluminum and stainless steel PVD coating.

Results: A visual evaluation of the finishes colour alteration was performed, both by spectrophotometric analysis (Konica Minolta CM-2600d) and stereomicroscopy (Leica model M165 C). One metal-look painting finishing (Z), already applied in the professional kitchen environment, was used as the reference sample. The analysis showed that the highest values in ΔE (colour variation) was registered in the case of PA composite coated by water transfer printing (C) (38.978) and by aluminium PVD (S) (30.938), both immersed in vinegar solution. Chlorine monofluoride demonstrated to be the most aggressive surface detergent solution regarding both C sample (34.707) and S sample (34.960). The same solution sensibly interacted also with the ABS painted sample (R) (21.876).

Discussion: On the basis of the data collected by the experimental tests, we can conclude that some finishes exhibit an evident chemical incompatibility with the chemical solutions present in a professional kitchen environment. PVD coated Aluminium and water transfer printed PA composite samples have been significantly degraded by both surface cleaners and food chemicals, in particular by vinegar and chlorine monofluoride. Moreover, some colour alterations were detected also on painted samples, when tested with some detergents. Further studies at different aging conditions (time, temperature, chemical solution) should be conducted to examine the degradation of composites materials and finishes in such environment.

MONITORING RESIDUAL STRESSES IN CFRP COMPOSITE USING EMBEDDED DISTRIBUTED OPTICAL FIBRE SENSORS AND SIMULATION

Poggetti I¹, Dyson J¹, Corinaldesi V², Soutis C²

¹Department of Materials, Environmental Sciences and Urban Planning (SIMAU), Università Politecnica delle Marche, Ancona - Italy

²School of Materials, The University of Manchester, Manchester - UK

Introduction: The broad objective of this research is aimed at understanding experimentally and theoretically the factors affecting the formation of residual stresses that occur during the curing of carbon fiber composite laminates. One of the key parameters to find the residual stresses analytically or numerically is the cooling of the laminate after it has been cured. Exact prediction of cure-induced distortions and residual stress in composite structures can effectively obtain better design within specified shape tolerances.

Materials and methods: An LY564/HR2954 epoxy resin has been characterized by DSC experiment, both isothermal and dynamic, after which an optical fiber geometry has been embedded into a satin 5HS carbon fiber panel and subjected to a vacuum assisted resin infusion moulding (VARIM) manufacturing process. The total strain induced through manufacture of the panel is extracted in real time during manufacture.

Time dependent viscoelastic analyses of the entire cure process are carried out to predict and investigate the evolution of strains inside the material.

Results: The experimental work shows that the manufacturing process has two key thermodynamic phases: the first is the fluidic action of the resin upon the 5HS weave with limited coupling to the 5HS. The second phase details the thermodynamic and engineering behaviour of the fully cured composite, with a high degree of coupling between the 5HS weave and the cured resin matrix.

Discussion: The monitoring of the total stress state of the 5HS composite during and after cure develops a detailed picture of the various physical processes during the manufacturing process. The stress state during the various thermodynamic phases is accurately verified through multiphysics modelling using data collected in the experiments. We demonstrate the possibility of an isotropic action from the resin in the early stages of cure, which gradually decays into a strongly anisotropic material state upon cooling.

INFLUENCE OF ANODIC OXIDATION TREATMENT ON TITANIUM CORROSION RESISTANCE IN BROMIDE RICH ENVIRONMENT

Prando D^{1,2}, Brenna A^{1,2}, Diamanti MV^{1,2}, Ormellesse M^{1,2}, Peddeferrì MP^{1,2}

¹Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Titanium has an outstanding corrosion resistance in a large variety of environments, due to its protecting oxide, which is spontaneously formed when the metal is exposed to air. Corrosion resistance is guaranteed as long as the integrity of the film is guaranteed, however, concentrated halides may attack the film and cause localized corrosion. To enhance titanium corrosion resistance in these aggressive environments, surface treatments able to tune thickness and morphology of the oxide are developed. Among them, anodic oxidation is the faster, simplest and most effective.

Materials and methods: Commercially pure titanium (grade 2 ASTM) was anodically oxidized with potentials ranging from 10 V to 200 V in H₂SO₄ 0.5 M electrolyte. Two different anodizing regimes were used regarding to the final potential obtained. Constant current density (20 mA/cm²) up to 120 V, and constant potential ramp from 120 V to 200 V (2 minutes ramp). Anodized samples were tested with potentiodynamic tests in NH₄Br 0.5 M, scanning from 0.1 V below open circuit potential, up to 9 V, or until localized corrosion occurred. SEM analyses were performed to determine surface morphology and oxide thickness.

Results: A great improvement in term of localized corrosion potential was observed in all the anodized sample, with an increase of at least 2.5 V compared to non-treated titanium. Localized corrosion potentials was close to 4 V up to anodization potential of 80 V. Then it increased to 5 V at 120 V anodization. At higher anodic oxidation potentials no localized corrosion was observed up to 9 V. SEM analyses showed a thickness increases of order of magnitude when anodic spark deposition regime was achieved; maximum thickness was some μm .

Discussion: The homogeneity of localized corrosion potentials up to 80 V, and the change at 120 V, when anodic spark regime happens, suggests a higher dependence of corrosion resistance on oxide morphology instead of oxide thickness, which monotonously increases with increasing anodizing potential. Further researches is in progress in order to determine the influence of both the porous structure obtained at higher potentials and the effect of bromides ions on corrosion occurrence.

CORROSION BEHAVIOUR OF REINFORCEMENT IN SEAWATER CONCRETE

Redaelli E, Carsana M, Gastaldi M, Lollini F, Torabian Isfahani F, Bertolini L

Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

Introduction: The use of seawater for mixing concrete for reinforced concrete structures is prohibited, since it can promote steel corrosion. However, the use of seawater would contribute to decrease the environmental impact of the concrete, in particular in those regions where potable water is a precious resource. The project SEACON-INFRAVATION between University of Miami and Politecnico di Milano, with various industrial partners, aims at investigating the use of seawater for the construction of sustainable and du-

able reinforced concrete structures and infrastructures. Within the project, a reinforced concrete culvert was built next to A1 motorway, close to Piacenza Sud. This note presents some of the preliminary results of the corrosion behaviour of various types of reinforcement embedded in seawater concrete.

Materials and methods: Seawater concrete was prepared by mixing 335 kg/m³ CEM II/A-LL 42.5R, 30 kg/m³ fly ash, 1795 kg/m³ aggregate, 175 kg/m³ seawater and admixtures. Four types of reinforcement were considered: ordinary carbon steel, austenitic grade stainless steel (SS304), duplex grade stainless steel (SS23-04) and GFRP. The corrosion conditions (except for GFRP) are monitored by means of potential measurements. Also resistivity measurements of concrete are carried out.

Results: All the metallic reinforcements were characterized by an increasing potential in the first months after construction and, after 6 months, the corrosion potentials were -175 mV/SSC for carbon steel, -60 mV/SSC for SS304 and -20 mV/SSC for SS23-04. The resistivity of concrete was 18-24 Ω·m.

Discussion: The values of corrosion potential of carbon steel are relatively high and seem to indicate that corrosion has not initiated yet. This is in agreement with results from similar laboratory specimens. As expected, stainless steel reinforcement of both grades are characterised by an even higher corrosion potential. Long-term measurements of potential together with measurement of concrete resistivity and analyses of chloride content in concrete will allow a better understanding of the corrosion conditions of all reinforcement in contact with seawater concrete.

CHEMICAL TREATMENT FOR IMPROVED ADHESION OF MAGNESIUM ALLOY

Rotella G¹, Candamano S¹, Alfano M², Crea F¹

¹Department of Environmental and Chemical Engineering (DIATIC), University of Calabria, Arcavacata di Rende (Cosenza) - Italy

²Department of Mechanical, Energy and Management Engineering, University of Calabria, Arcavacata di Rende (Cosenza) - Italy

Introduction: Magnesium alloys are growingly employed in the production of lightweight structural components for automotive industries, where the need of reduced fuel consumption and emissions is strict. Magnesium alloys are chemically active, easily oxidizable, forming a loose oxide film on the surface that can cause poor mechanical performance when joining procedures are necessary. Thus, techniques able to properly overcome these difficulties are required. This work compares the results of different pretreatment used to improve the strength of bonded magnesium joints.

Materials and methods: 1.5 mm thick Mg AZ31B alloy was used in this study. The samples were first degreased with acetone and then polished with grit abrasive papers up to 1 mm. The samples were subsequently immersed for 2 minutes at 70°C in a solution of 15 g/L NaOH, 40 g/L Na₃PO₄, 15 g/L Na₂SiO₃, 15 g/L Na₂CO₃ and rinsed with deionized water. Immediately after they were immersed for 10 min at 70°C in the phosphate permanganate solution of 40 g/L KMnO₄, 140 g/L K₂HPO₄, 8 g/L Na₂SiO₃, 0.5 g/L NaF and then rinsed in water and dried at 60°C. The samples were then immediately bonded using a dual component epoxy resin forming a T joint with a length of 60 mm and a width of 25 mm. The bonded length was set equal to 30 mm. The adhesive bond-line thickness was controlled to be 0.2 mm using polymeric wires as spacers. Another batch of material was laser treated prior bonding in order to compare the results. Tensile tests were carried out using an electromechanical testing machine with a displacement rate of 1 mm/min.

Results: The total absorbed energy of the chemically treated T peel joints increased of several folds compared with the laser ablation.

Discussion: Chemical pretreatment improved joint performance by chemically bonding the AZ31B surface to the epoxy resin. The surface modification induced by laser treatment resulted less efficient than chemical one.

LIGHTWEIGHT COMPOSITE MATERIALS BASED ON GEOPOLYMERS AND POLYSILOXANES

Roviello G^{1,2}, Menna C³, Tarallo O⁴, Ricciotti L¹, Messina F^{1,2}, Ferone C^{1,2}, Asprone D³, Cioffi R^{1,2}

¹Department of Engineering, University of Naples "Parthenope", Naples - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of Structures for Engineering and Architecture, University of Naples "Federico II", Naples - Italy

⁴Department of Chemical Sciences, University of Naples "Federico II", Naples - Italy

Introduction: Porous materials are widely used in several applications including membranes, high-efficiency adsorption materials, catalysis, as insulating sound-proof panels or for lightweight structural components. In the case of high temperature applications, as an alternative to polymeric foams, inorganic materials can be used. Particularly, the geopolymer-based porous materials developed to date exhibit very interesting properties in terms of thermal and acoustic conductivity but the presence of pores and the extremely heterogeneous structure affecting their mechanical properties. The present study reports on the preparation and characterization of new organic-inorganic geopolymer-based hybrid foams obtained by reacting an aluminosilicate source and an alkalisilicate solution with mixtures of dialkylsiloxane oligomers, by using different amounts of SiO powder as in situ foaming agent. These new materials are characterized by remarkable mechanical properties, good fire resistance and low thermal conductivity, significantly better than those shown by neat geopolymeric foams reported in the literature and comparable or even better than those of typical (not geopolymeric) inorganic foamed materials with similar densities.

Materials and methods: Geopolymer-based foamed hybrids were obtained by adding 10% by weight of an oligomeric dimethylsiloxane mixture to the freshly-prepared geopolymeric suspension. As foaming agent, silicon powder was then added with different wt% ratios, ranging between 0.03 and 0.24%.

Results and discussion: These foamed materials have average compressive strength up to 5 MPa with a density range of 0.2-0.5 g/cm³, which represents an important range for technological applications of lightweight materials. Moreover, within the same density range, the hybrid materials exhibit good fire resistance and low thermal conductivity with λ values in the range 0.101-0.105 W/mK.

Thus, these properties are significantly better than those shown by neat geopolymeric foams reported in the literature and comparable or even better than that of typical (not geopolymeric) inorganic foamed materials with similar densities.

For these reasons, it can be reasonably concluded that these new hybrid materials could represent a valid alternative to commonly used inorganic foams (e.g. Portland Cement foams) for insulation and lightweight applications, since they combine performance benefits and operational energy savings.

NICKEL-BASED COATINGS WITH IMPROVED MECHANICAL ABRASION AND LONG-LASTING HYDROPHOBIC CHARACTERISTICS

Salehi Kahrizsangi P¹, Calabrese L², Proverbio E², Raeissi K¹, Karimzadeh F¹

¹Department of Materials Engineering, Isfahan University of Technology, Isfahan - Iran

²Department of Engineering, University of Messina, Messina - Italy

Introduction: The wetting characteristics as well as corrosion resistance of a metallic coating can be altered by modifying its surface roughness. Recently, corrosion resistance of hydrophobic metallic coatings compared to their hydrophilic counterparts has been in the center of attention. In the literature, a considerable increase in the corrosion resistance of the metallic coatings by increasing their water repellency has been proposed. Since the loss of surface roughness can result in changes in hydrophobicity and corrosion performance of these coatings, investigation of durability of these surface microstructures in static and agitated corrosive mediums, should be of importance. Mechanical robustness of surface structures should be improved so that the underwater hydrophobic performance can be prolonged. The present research suggests development of hydrophobic nickel based coatings with improved mechanical abrasion and corrosion resistance. These coatings are suitable for more realistic future applications in oil and gas industries.

Materials and methods: Nickel and Nickel-Tungsten coatings were electrodeposited from electrolytic baths containing NiCl₂·6H₂O, Na₂WO₄·2H₂O, NiSO₄·6H₂O as the main ingredients. Electrodepositions were performed using a three-electrode deposition cell (platinum as reference, titanium as counter and copper as working electrodes). The deposited coatings were stored at constant temperature in air for two weeks before performing the wettability tests. The erosion-corrosion (3.5 wt% NaCl + 40 wt% 200-300 μm SiO₂ powder, 500 rpm) and corrosion tests (3.5 wt% NaCl) were performed on hydrophobic nickel and nickel-tungsten coatings. Microstructural investigations were performed by using SEM, AFM, EDAX and XRD analysis.

Results and discussion: Severe loss of the microstructural features of hydrophobic nickel coating was observed during very early stages of erosion-

corrosion. After 30 minutes of erosion-corrosion, the average roughness of the nickel coating decreased from 107.5 nm to 86.9 nm. This was followed by a decrease in water contact angle from 125° to 115°. The microstructure of the hydrophobic nickel-tungsten coating is more resistant during erosion-corrosion. The effect of tungsten on maintaining the microstructural features as well as the hydrophobic performance of the nickel coating was confirmed.

PHOSPHATE-BASED TREATMENTS FOR PRESERVATION OF CULTURAL HERITAGE: THE HAP4MARBLE PROJECT

Sassoni E¹, Graziani G¹, Scherer GW², Franzoni E¹

¹ Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Bologna - Italy

² Department of Civil and Environmental Engineering (CEE), Princeton University, Princeton, NJ - USA

Introduction: Protection of marble artworks from dissolution in rain is one of the main goals of materials science applied to cultural heritage preservation. Forming a coating of hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂) over marble surface is expected to provide remarkable protection, given the lower solubility and slower dissolution rate of HAP compared to calcite. HAP can be formed by reacting marble with an aqueous solution of diammonium hydrogen phosphate (DAP), also containing millimolar quantities of a calcium source. However, the presence of micro-cracks and pores in the HAP layer has been found to limit its effectiveness. In this study, we present some recent results on the possible reduction of cracks and pores by adding ethanol to the DAP solution. **Materials and methods:** Carrara marble was treated with aqueous solutions containing: (a) 1 M DAP and 1 mM CaCl₂; (b) 0.1 M DAP and 0.1 mM CaCl₂ in 10 vol% ethanol. The presence of cracks and pores in the coating was assessed by observing cross sections using a FIB-SEM. The acid resistance was assessed by exposing samples to acidic solutions simulating rain and measuring the pH increase over time.

Results: Treatment (a) led to the formation of an apparently continuous coating, however affected by pores and drying cracks (originated from DAP high concentration). Consequently, its protecting ability was limited. Treatment (b) led to the formation of a thinner and much denser coating, thanks to the reduction in the DAP concentration and to the weakening effect of ethanol molecules on the hydration shell of phosphate ions in the DAP solution. Accordingly, a better acid protection was achieved.

Discussion: Although reduced, dissolution of marble is still not completely inhibited, because the coating is sensitive to the crystallographic orientation of the underlying calcite grains. In fact, some grains with an unfavorable orientation remain bare after treatment, even if they are entirely surrounded by perfectly covered grains. Further research is in progress to optimize marble coverage, for instance by identifying alternative organic solvents with higher effectiveness.

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PLA/PCL NANOFIBROUS BLENDS VIA MULTI-JET ELECTROSPINNING: PROCESSING-MORPHOLOGY-PROPERTY RELATIONSHIPS

Scaffaro R, Lopresti F, Botta L

Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy

Introduction: Electrospinning permits to prepare ultrafine fibers with micro- to nano-meter range diameters. Multi-jet approaches can be used to fabricate blend nanofibrous mats composed by two or more polymers presenting different properties such as degradation rate, mechanical properties and so on. In this study, a series of PLA/PCL blend nanofiber mats were prepared by dual-jet electrospinning. The relative weight ratio of PLA and PCL in blend was controlled by changing the flow ratio of the two syringe pumps containing the polymer solutions.

Materials and methods: PLA and PCL solutions were poured into two different glass syringe fitted with a stainless steel needle. The appropriate flow rates for the two solutions were chosen in order to obtain PLA/PCL blend nanofiber mats at different PLA:PCL weight ratio (1:0; 3:1; 1:1; 1:3; 0:1). The surface chemical composition of the samples were characterized with FT-IR ATR. The morphology of the blend nanofiber mats were investigated with SEM while tensile tests were carried out with a dynamometer.

Results: FT-IR ATR showed that the chemical composition of the mats is strongly affected by the PLA and PCL flow rates. The SEM analysis highlighted that the fibers of all the samples were in nanoscale with a similar diameter size distribution. Mechanical properties showed that the E value of the PLA/PCL blend nanofiber mats increase linearly with the increase of the PLA amount while the ϵ_b increase almost linearly with the increase of PCL content.

Discussion: The repeatability of FT-IR ATR analysis confirmed that it is possible to control the composition of the PLA/PCL blend nanofibrous mats by tuning the relative flow rate of the polymeric solutions. SEM analysis showed that PLA and PCL fibers are not morphologically distinguishable. Mechanical properties showed that it is possible to tune and predict the E and the ϵ_b of the PLA/PCL blend nanofiber mats by controlling the composition of the blends.

PROCESSABILITY AND PHYSICO-MECHANICAL PROPERTIES OF ECO-FRIENDLY POLYPROPYLENE COMPOSITES

Scarfato P¹, Di Maio L¹, Coppola B¹, Garofalo E¹, Incarnato L¹, Pasquali M^{2,3}, Bontempi E^{2,3}

¹ Department of Industrial Engineering, University of Salerno, Fisciano (Salerno) - Italy

² Chemistry for Technologies Laboratory, University of Brescia, Brescia - Italy

³ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Polypropylene (PP), largely used in many applicative fields (e.g. automotive, electrical/electronics, packaging, construction) thanks to its good balance of performance properties, processability and cost-effectiveness compared to other resins, requires additivition to improve some of its limitation (i.e. sensitivity to UV light degradation, limited upper working temperature and high thermal expansion coefficient, easily flammability). In this work we developed new eco-friendly PP composites, by melt compounding the resin with a new low-cost sustainable filler, produced from municipal solid waste incinerator (MSWI) residues by COSMOS technology. The systems were tested to verify the effects of the filler addition on PP processability and on its thermal and mechanical properties. Moreover, in order to investigate the possibility to use the filler as adjuvant or as a replacement for conventional flame-retardants, ternary PP composite systems, containing also a commercial non-halogenated flame-retardant in the formulation, were produced and characterized.

Materials and methods: The polymer matrix was the PP Moplen EP310D (MFR at 230°C/2.16 kg = 0.95 g/10 min; LyondellBasell Industries) and the fillers were the biosafe inert (C) produced in lab from MSWI residues and the intumescent flame-retardant (FR) Exolit AP766 (Clariant). Binary and ternary systems with different composition of C (10% or 20%) and/or FR (15% or 20%) were produced by sheet extrusion after melt compounding of the constituents in a twin-screw extruder. Using the same processing conditions neat PP was also produced, for comparison. All samples were then analyzed for their rheological, thermal and mechanical behavior.

Results: The addition of C and/or FR fillers does not significantly affect the complex viscosity behavior of the host matrix, but gives a lowering of the composites ductility, a slight reduction of their overall crystallinity, an increase of the melt crystallization temperatures of ca. 10°C and a strong shift of the thermo-degradation process towards temperatures up to 50-70°C higher.

Discussion: The C filler was demonstrated effective in obtaining a marked improvement of the PP thermal stability, without worsening the matrix processability; in particular, the best results were obtained for the ternary PP/C/FR blend. Moreover, from preliminary flammability tests, it showed no charring behavior when used alone in the composites.

PHOTOCATALYTIC ACTIVITY OF COLOR PIGMENTED PLASTERS

Strini A¹, Schiavi L¹, Marras P¹, De Marco T², Bottalico L²

¹ Construction Technologies Institute (ITC), CNR, San Giuliano Milanese (Milan) - Italy

² Italcementi-HeidelbergCement Group, i-lab, Bergamo - Italy

Introduction: Recent architectural trends are pushing for the development of pigmented photocatalytic coatings for building applications. The presence of a pigment in the formulation can however be detrimental for the photocatalytic activity because of possible phenomena of photon absorption competition. In

the present study, the effects of three selected mineral color dyes (yellow, red and blue, respectively) on the activity of photocatalytic plaster were assessed by measuring the nitric oxide (NO) degradation in air.

Materials and methods: All samples for photocatalytic measurements were prepared using an experimental photocatalytic cement plaster premix based on photocatalytic white cement (i.active, Italcementi) and industrial inorganic color dyes in different concentrations from 0.05% to 2% (as dye/dry matter w/w ratio). The photocatalytic activity of the samples was assessed by measuring the degradation of NO at 75 ppb in air using a dedicated experimental system.

Optical absorbance of dyes was evaluated by measuring the reflectance spectra of dye dispersions in gypsum (calcium sulphate, reagent grade).

Results: The UV-Vis reflection spectra of gypsum-dispersed dyes demonstrate different UV absorption profile with respect to the visible optical absorbance. Particularly, a relatively high UV adsorption was measured for the yellow and red pigments, while the blue pigment demonstrated a remarkably lower absorption. The photocatalytic activity of yellow and red colored samples indicates a strong correlation between dye content and photocatalytic activity while the activity of blue samples (characterized by a low UV absorbance), appears to be slightly influenced by the presence of the dye.

Discussion: The reported evidences indicate a significant correlation between the UV pigment absorbance and the respective interference with the photocatalytic activity, with a significant-inhibition effect demonstrated by the yellow and red pigments (UV absorbing) and a negligible effect for the blue pigment (low UV absorbing). These results suggest a major role of UV absorption competition in the determination of the final performance of colored photocatalytic plasters. The selection of an appropriate pigment (with minimized UV absorbance) therefore appears to be a key factor in order to optimize the performances of photocatalytic color plasters.

FLAME SYNTHESIS OF SUPPORTED TITANIA PHOTOCATALYTIC LAYERS

Strini A¹, Schiavi L¹, Zanoni R¹, De Iulius S², Dondè R², Maffi S², Migliorini F²

¹ Construction Technologies Institute (ITC), CNR, San Giuliano Milanese (MI) - Italy

² Institute of Condensed Matter Chemistry and Technologies for Energy (ICMATE), CNR, Milan - Italy

Introduction: Flame synthesis is a widely implemented method for the industrial synthesis of nanocrystalline oxides and very reactive photocatalytic powders are currently produced using this method. However, for most applications (e.g. air and water treatment or industrial chemical transformations) the use of a powder photocatalyst poses several problems of process design and implementation, mainly because of the difficult final separation and catalyst recovery. The availability of supported photocatalyst is therefore very interesting. Several powder-supporting technologies are available but a number of associated drawbacks (e.g. process costs and activity depletion) is hindering their implementation. The present work addresses this issue, by flame synthesis of titania photocatalyst directly supported on alumina or stainless steel sheets.

Materials and methods: Titania films were produced by flame spray pyrolysis using an oxygen-assisted spray apparatus in order to inject the precursor coaxially with the pilot flame. Titanium tetraisopropoxide in ethanol (0.5 M) was used as liquid precursor. A constant 3 ml/min solution feed rate through the spray nozzle was obtained with a syringe pump. Titania nanoparticles were deposited by orthogonal impingement on a cooled substrate holder placed at 30 cm HAB (height above the burner). Cooling temperature was kept at about 100°C to avoid water condensation on the holder. Stainless steel or alumina substrates were used with an exposure area of 5.2 cm². A pneumatically operated mechanical shutter placed above the target substrate allows the control of the exposure time of the aerosol-generated powder deposition. After synthesis, titania films were properly annealed in order to improve film-substrate adhesion. The photocatalytic activity of titania films was evaluated by measuring the degradation of toluene in air at typical environment concentration.

Results: Titania films supported on stainless steel and alumina substrates exhibit good photocatalytic activity for toluene degradation in air. The experimental data also suggest that post-deposition thermal annealing is very important in order to optimize the film-substrate adhesion.

Discussion: These preliminary results demonstrate the potentials of flame synthesis in the direct production of photocatalytic titania films on solid substrates. Further studies are in progress in order to optimize the process and fully characterize the titania films obtained.

A NANOSTRUCTURED LIGHTWEIGHT CERAMIC ABLATOR (LCA) BASED ON EX-PAN CARBON FIBERS

Torre L^{1,2}, Rallini M¹, Natali M^{1,2}

¹ Department of Civil and Environmental Engineering, University of Perugia, Terni - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: The aim of our work was to produce a nanostructured PICA (n-PICA) substituting the traditional carbon fiber felt used in the standard formulation with milled ex-PAN carbon fibers (MCFs) combined with nanosized fillers such as Multi-Walled Carbon Nanotubes (MWCNTs) and nanoclays.

Materials and methods: The n-PICAs were produced using a commercial resol resin as a matrix. Milled Carbon Fibers (MCFs), MWCNTs and montmorillonite (Cloisite 30B) were used as reinforcements. Three porous n-PICA formulations were produced with the same amount of MCFs: PICA1 had a balanced 30B/MWCNT ratio, PICA2 an excess of nanoclay and PICA3 an excess of MWCNTs. The materials were tested in terms of mechanical, thermal and ablative properties.

Results: From Thermo-mechanical Analysis (TMA) tests the n-PICAs were characterized by a better dimensional stability if compared to traditional carbon/phenolic laminates. PICA2 showed the highest elastic modulus in compression tests. PICA3 exhibited the highest thermal stability and the highest final residue from Thermo-Gravimetric Analysis (TGA) in nitrogen. In air at higher temperatures PICA1 and PICA2 exhibited higher thermal stability than PICA3. From the oxy-acetylene torch test, the registered in-depth temperatures were similar for all n-PICAs whilst all the PICAs experienced a similar loss of volume.

Discussion: The porous nature of PICAs allowed to minimize the dimensional change. The best mechanical behavior of PICA2 could be due to the presence of nanoclays that stiffen the material. The better thermal stability of PICA3 in nitrogen could be related to the higher amount of carbon that does not oxidize in nitrogen and resist to high heat fluxes. On the other hand, its different behavior in air is mainly related to the oxidation of carbonaceous components. The 30B/MWCNT ratio did not influence the thermal insulation capability: the main heat conduction mechanism was mainly due to the milled carbon fibers. From the analysis of the post-burning surfaces of the samples, PICA1 and PICA3 exhibited a wider and broader eroded area as compared with PICA2. Analyzing the post burning appearance, the formulation containing an excess of nanoclays, although the higher density, resulted to be the best compromise in terms of mechanical, thermal and erosion resistance.

STRETCHABLE SILICONE RUBBER/SILK COMPOSITES

Valentini L^{1,2}, Bittolo Bon S², Mussolin L³, Pugno NM^{4,6}

¹ Department of Civil and Environmental Engineering, University of Perugia, Terni - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Physics Department and SERMS Laboratory, University of Perugia, Terni - Italy

⁴ Laboratory of Bio-Inspired and Graphene Nanomechanics, Department of Civil, Environmental and Mechanical Engineering, University of Trento, Trento - Italy

⁵ School of Engineering and Materials Science, Queen Mary University of London, London - UK

⁶ Italian Space Agency, Rome - Italy

Introduction: Biological tissues such as skin, tendons and muscles are flexible and are subjected to large deformations under mechanical loading. Silkworm silk is known to be a biocompatible material with absence of toxicity and immunogenicity in biological environments; moreover, due to its mechanical properties, it could be considered for monitoring the mechanical response of tissues. However, the realization of a silk based strain-gauge is challenging because such material is stiffer and less stretchable than biological tissues.

Here we propose the use of silicone rubber/silkworm silk composite to fabricate a strain gauge by using the fluorescent emission intensity of the silk fibers embedded in an elastomeric matrix to measure the deformation of the composite.

Materials and methods: Commercial *B. mori* organic cocoons for face cleaning were degummed to obtain silk fibers, then the degummed silk fibers were dispersed in a silicone rubber matrix cold cured by poly-addition by adding 10wt% of catalyst. The morphology and structure of the composites were characterized by optical fluorescence, FESEM and FTIR spectroscopy. The tensile properties of the prepared samples were measured using a universal tensile testing machine (Lloyd Instr. LR30K).

Results: We illustrate the preparation method used to fill the silicone rubber with the degummed silk fibers in order to get a reinforced composite with predictable mechanical properties that depend on the orientation and dispersion degree of the fibers. The results show that the resulting composite is flexible and conformable to curved surfaces. Deforming such composite strain gauge with a constant strain rate using a tensile machine, the strain measured by the machine corresponds to the fluorescence intensity variation of the composite under deformation.

Discussion: Using degummed silk derived from *B. mori* cocoons we realized a stretchable composite with the deformation that can be tuned according to the fluorescent silk pattern of the silkworm silk in the composite. Our measurements can provide a method to measure the strain in biological environment that requires a reduced interaction with the tissue while it is measured.

BIOMATERIALS FOR 3D-PRINTED BIOMIMETIC SCAFFOLDS FOR OSTEOPOROSIS TREATMENT

Vitale-Brovarone C¹, Montalbano G¹, Molino G¹, Novajra G¹, Vozzi G², Ciapett G³, Fiorilli S¹

¹ Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

² Research Centre "E. Piaggio", University of Pisa, Pisa - Italy

³ Laboratory for Orthopedic Pathophysiology and Regenerative Medicine, The Rizzoli Institute, Bologna - Italy

Introduction: Osteoporotic patients currently undergo treatments that aim to increase bone mineral density while decreasing bone fragility, without a proper focus on the restoration of the physiological coupling between osteoblasts and osteoclasts. The ERC BOOST project aims to design a smart scaffold able to reproduce the natural bone chemistry, structure and topography in order to stimulate a physiological coupling.

To mimic bone composition, type I collagen is combined with hydroxyapatite (HA) and mesoporous bioglasses (MBG) and then processed with an *ad hoc* biofabrication platform, able to reproduce bone microstructure by using CAD/CAM model of human healthy bone.

Materials and methods: Different concentrations of collagen have been combined with HA or MBG particles and analysed to define their physico-chemical properties. After the suspension gelation at 37°C, 1-ethyl-3-(3-dimethyl-aminopropyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS) have been used for the chemical crosslink of collagen. The material stability has been assessed through FESEM on samples incubated up to 7 days at 37°C.

Results: A homogeneous suspension of inorganic particles was obtained with a collagen concentration of 1.5%wt. In order to test the material printability, collagen solutions mixed with MBG or HA particles were extruded through needles up to 30 Gauge, without needle clogging. The chemical crosslink of collagen by EDC/NHS led to a sample reduction, thereby resulting in a sharp decrease of water uptake ability and increased mechanical strength. Collagen fiber reconstitution and particle embedment were observed with FESEM.

Discussion: The addition of the inorganic phase provided greater consistency and stability to the matrix of collagen fibres reconstructed in physiological conditions (37°C, pH 7.4).

A decreased water uptake has been detected in chemical crosslinked samples, due to the formation of further covalent bonds between the polymeric chains and alternative methods are currently under investigation.

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

Aversano F¹, Branz S¹, Bassani E², Fanciulli C², Ferrario A³, Boldrini S³, Castellero A^{1,4}, Baricco M^{1,4}

¹ Department of Chemistry, NIS and INSTM, University of Turin, Turin - Italy

² Institute of Condensed Matter Chemistry and Energy Technologies (ICMATE), CNR, Lecco - Italy

³ Institute of Condensed Matter Chemistry and Energy Technologies (ICMATE), CNR, Padova - Italy

⁴ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

Results: X-Ray Diffraction and Scanning Electron Microscopy evidenced that P1 and P2 are composed by CoSb_3 single phase, while in P3, CoSb_2 and Sb phases were also observed. ODP2 and ODP3 are denser than ODP1, as a consequence of a more efficient packing of the corresponding P2 and P3 starting powders, which are characterized by a larger size distribution with respect to P1. ODP2 and ODP3 showed a lattice parameter of 9.0548 Å and 9.0446 Å, respectively, suggesting a greater solubilization of Yb inside the elementary cell in ODP2 with respect to ODP3. ODP2 and ODP3 showed microhardness values around 560-580 HV. Indents showed radial and lateral cracks. The occurrence of chipping suggests that cracks propagate by cleavage.

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

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

Botta L^{1,2}, Scaffaro R^{1,2}, Sutura F¹

¹ Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

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

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

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

Cacciotti I^{1,2}, Fortunati E^{2,3}, Puglia D^{2,3}, Melino S⁴, Kenny JM^{2,3}, Nanni F^{2,5}

¹ Department of Engineering, University of Rome "Niccolò Cusano", Rome - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Department of Civil and Environmental Engineering, University of Perugia, Terni - Italy

⁴ Department of Chemical Science and Technology, University of Rome "Tor Vergata", Rome - Italy

⁵ Department of Enterprise Engineering, University of Rome "Tor Vergata", Rome - Italy

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

Materials and methods: CNCs (5%wt), both pristine (p-CNCs) and surfactant modified (s-CNCs), were disagglomerated in CHCl_3 :DMF (67:33, in volume ratio) by ultrasonication. Then PLA pellets (15%wt/v) were added to the suspensions. Prepared suspensions were electrospun under the following conditions: applied voltage 12kV, flow rate 0.5ml/h, needle-target distance 15 cm. As a reference, neat PLA mat was also produced. The silver nanoparticles were physisorbed on the PLA fibers surface, starting from a stable Ag nanoparticles suspension (0.5mg/ml). As a reference, the PLA fibers were also loaded with 1%wt of Ag NPs, to compare the antimicrobial efficiency of the nanoparticles entrapped within the fibers and exposed on their surface.

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

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

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

Cicala G^{1,2}, Latteri A^{1,2}, Pergolizzi E^{1,2}, Tosto C^{1,2}, Giordano D^{1,2}

¹ Department of Civil Engineering and Architecture, University of Catania, Catania - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

The present paper is the result of the experimental work carried out within the COMMAND project.

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

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

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

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

Colombo A^{1,2}, Dragonetti C^{1,2}, Garoni E^{1,2}, Righetto S^{1,2}, Roberto D^{1,2}

¹ Department of Chemistry, University of Milan, Milan - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

Materials and methods: We prepared variously substituted 1,3-di(2-pyridyl)benzene Pt(II) complexes, by reaction of K_2PtCl_4 with the related ligand at reflux in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ under argon for 18h. Their second-order non linear properties were determined in DMF solution with the electric-field-induced second-harmonic generation (EFISH) technique, working with a non resonant incident wavelength of 1.907 μm .

Results: We obtained new Pt(II) terdentate complexes with different p-delocalized substituents at the central 5-position of the phenyl ring of the N^AC^AN ligand and we found a strong effect of the nature of the p-delocalized moiety on the second-order NLO properties, determined by the EFISH technique. Of particular relevance is the nature of the linker between the p-delocalized donor moiety and the 1,3-di(2-pyridyl)benzene system.

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

sion some of the new Pt (II) complexes prepared in this work are particularly appealing for NLO applications.

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

Contessi N^{1,2}, Bertoldi S^{1,2}, Angeloni V³, De Marco C³, Tanzi MC², Daidone MG³, Farè S^{1,2}

¹Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³IRCCS Foundation, National Cancer Institute, Milan - Italy

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

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

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

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

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

Curcio M¹, De Bonis A^{1,2}, Rau JV³, Fosca M³, Santagata A⁴, Teghil R^{1,2}

¹Department of Science, University of Basilicata, Potenza - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Institute of Structure of Matter (ISM), CNR, Rome - Italy

⁴Institute of Structure of Matter (ISM), CNR, Potenza - Italy

Introduction: Bioactive glasses and glass-ceramics are an important class of biomaterials capable of bonding the bone, therefore they can be used to bone tissues repair.

Since the first 45S5 Bioglass[®], several other glass and glass-ceramic have been investigated for biomedical applications. In this context, RKKP is a glass-ceramic material, recently deposited by Pulsed Laser Deposition (PLD) on Ti substrate, with the aim to coat bone-related implants. Thanks to its significant role in the metabolism of both muscle and bone, manganese oxides have been added in the RKKP composition (RRKP_Mn).

In this work films of RKKP_Mn have been prepared using PLD. It presents several advantages compared to the other deposition procedures: it is possible to control the growth kinetics, thickness, roughness and the crystallinity of the coatings.

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

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

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

2.5D PATTERNING USING FOCUSED ION BEAM AND INDENTATION LITHOGRAPHY

De Felicis D^{1,2}, Bemporad E^{1,2}

¹Engineering Department, University "Roma Tre", Rome - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: The ability to prepare patterns and structures with small dimensions has been crucial for the development of many modern technologies. Over the last two decades, different lithographic techniques have been used to fabricate complex 3D structures based on electron, laser and ion irradiation.

Focused Ion Beam (FIB) technology combined with an electron column offers promising advantages such as simplification of sample preparation, small processing times enabling imaging, milling and deposition in a single instrument over a wide range of materials.

One of the main peculiarity is the "Direct-Writing" that locally enables the control of ion dose for 3D pattern production with high shape factor and reliability, without applying resist and mask.

In this work, a new methodology is proposed to generate a stream file capable of producing both micro-and-nano scale patterns with improved quality and the possibility to replicate them on large area using both ion lithography and through a master fabrication for Indentation-lithography (IndL)

Materials and methods: The instrument used for ion lithography is FEG-FIB microscope. A nano-indenter, generally employed for surface nano-hardness test was preferred for indentation-lithography.

Materials used are silicon and PMMA for different mechanical behaviour comparison under the indenter load. Furthermore, a diamond tip for nanoindentation was patterned to fabricate a master for IndL.

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

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

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

Federici S^{1,2}, Bontempi N^{1,2}, Vassalini I^{1,2}, Litvinava M¹, Gijpalaj J¹, Alessandri I^{1,2}

¹Chemistry for Technologies Laboratory, Department of Mechanical and

Industrial Engineering, University of Brescia, Brescia - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Sensitive detection and efficient removal of micropollutants are challenging tasks in environmental remediation. In the last years, we have developed photocatalytic core/shell microspheres that are able to exploit the combination of multiple light scattering and evanescent fields to enhance the sensitivity of the Raman response, allowing the detection of different analytes with unprecedented reproducibility. In parallel, the photocatalytic efficiency of these materials is crucial for the selective removal of organic pollutants. The same spheres are excellent low-background matrices for laser desorption/ionization mass spectrometry, which enabled the development of multi-modal analytical platforms for monitoring adsorption

and degradation of the pollutants. Here we extend this approach to the production of a new class of adaptive materials that can efficiently capture and remove various micropollutants, including drugs, persistent organic pollutants and inorganic species like hexavalent chromium and arsenite/arsenate ions. The micropollutants are captured by receptors obtained by either raw or waste materials and their removal efficiency was tested in real working conditions.

Materials and methods: The core/shell $\text{SiO}_2/\text{TiO}_2$ microspheres were obtained by coating monodisperse silica beads with a conformal shell layer through atomic layer deposition. The alginate/ TiO_2 macrobeads were obtained through ionotropic gelation of anatase nanoparticles, using Ca^{2+} ions for cross-linking. The functionalization of both micro- and macrospheres with organic acids was monitored by FTIR and microRaman. The analysis of micropollutants was carried out by combining UV-Vis, x-ray fluorescence, mass spectrometry and Raman microscopy.

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

Discussion: The unique combination of macro- and microspheres functionalized with different organic acids that can be obtained from raw materials enables the efficient capture, analysis and removal of both organic and inorganic micropollutants, opening exciting perspective for technology transfer.

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

Frontera P^{1,2}, Belaustegui Y³, Zorita S³, Fernández F³, García A³, Pantò F⁴, Stelitano S⁵, Patanè S⁵, Antonucci P^{1,2}, Santangelo S¹

¹Department of Civil, Energy, Environmental and Materials Engineering (DICEAM), “Mediterranean” University of Reggio Calabria, Reggio Calabria - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Tecnalia Research and Innovation, Materials for Energy and Environment Area, Derio-Bizkaia - Spain

⁴Department of Information, Engineering, Infrastructures and Sustainable Energy (DIIES), “Mediterranean” University of Reggio Calabria, Reggio Calabria - Italy

⁵Department of Physics (DF), University of Calabria, Arcavacata di Rende - Italy

⁶Department of Mathematical and Informatics Sciences (MIFT), Physical Sciences, Physical Sciences and Earth Sciences (MIFT), University di Messina, Messina - Italy

Introduction: The ever-increasing demand of fresh water has promoted the development of a variety of desalting techniques of seawater. The capacitive deionization (CDI) method, based on the formation of electrical double layers inside the pores of the electrode material, is one of the most attractive among them. CDI is an environmentally friendly technology since no secondary contaminant is released during the process. In addition, operating at low DC potential (1.0–1.2 V), CDI can be of great help in remote areas.

Different high surface area nanocarbons, such as carbon nanotubes, carbon aerogel, mesoporous carbon, graphene (G), and activated carbon, have been successfully utilised to fabricate the electrodes in CDI cells. This contribution deals with synthesis, analysis and testing, as electrode materials in CDI cells, of G-enriched C fibers (GCFs), and C fibers (CFs) as a reference.

Materials and methods: GCFs and CFs are prepared via electro-spinning (ES). ES is carried out using polyacrylonitrile and N,N-dimethylformamide respectively as polymer and solvent, and adding graphene oxide to the spinnable solution in the case of GCFs. After stabilization and carbonization, N-doped fibres with 360 nm average diameters are obtained.

The electrochemical behaviour of the as-prepared samples is evaluated by cyclic voltammetry. A three-electrode cell is used for this purpose, with graphite, standard Ag/AgCl and (CFs- or) GCFs-based electrodes acting as counter, reference and working electrodes, respectively.

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

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

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

Genova V^{1,2}, Marini D^{1,2}, Valente M^{1,2}, Marra F^{1,2}, Pulci G^{1,2}, Valente T^{1,2}

¹Department of Chemical Engineering, Materials, Environment, Sapienza University of Rome, Rome - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Electroless Nickel-Phosphorous Plating (ENP) is one of the most promising plating technique in the field of micro or nanostructured reinforcement. This is due to its versatility in terms of complex substrate-shapes (the coating is deposited without using electrical current) and homogeneity of coating. Despite of those advantages, the introduction of a reactive element in the matrix (P) can be deleterious for composite's properties (for example mechanical fracturing caused by formation of phosphorous anhydrides even at low temperature). In this work a new Electroless Nickel Pure Plating (ENP²) technique was proposed to modify the interface of a carbon reinforcement without introducing any reactive element in the coating.

Materials and methods: Electroless nickel pure plating was carried out using hydrazine monohydrate ($\text{N}_2\text{H}_4 \times \text{H}_2\text{O}$) as reducing agent. Lactic acid and disodium EDTA were used as complexing agents in different concentrations.

Micrograf HT carbon microfibers (CMFs) were produced by PROCHIMA (Italy) and used without any further purifications. First, the as-received CMFs were added in deionized water and dispersed with assistance of both ultrasonication and mechanical stirring for approximately 30 min. Then, a quantity of hot plating solution was added. Influence of temperature and plating ratio (volume solution/mass of MCF - ml/g) was studied at different temperatures.

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

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

GREEN TOOLS FOR IMPROVING PHAS EXTRACTION FROM MICROBIAL SLURRY

Giorgini L^{1,2}, Mazzocchetti L^{1,2}, Benelli T^{1,2}, Samori C³, Torri C³, Galletti P³, Tagliavini E³

¹Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Bologna - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of Industrial Chemistry “Giacomo Ciamician”, University of Bologna, Bologna - Italy

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

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

Results: We propose alternative extraction approaches, based on green components and with good efficiency, which also maintain the very high average molecular weight typical of the bacterial PHAs.

Switching anionic surfactants (SAS) were applied without any pre-treatment of the biomass before the extraction of PHB for microbial slurry.

Alternatively, dimethylcarbonate (DMC) was used, once again without any pre-treatment of the biomass before the extraction, to recover both Poly(hydroxybutyrate) or its copolymers, separating them from bacterial residues. The PHA recovery and purity were very high, and its thermophysical characteristics were excellent, thanks to the low extraction temperature necessary for achieving these good extraction performances.

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

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

Giosuè C¹, Belli A^{1,2}, Mobili A¹, Tribuiani C², Favoni O¹, Ruello ML¹, Tittarelli F^{1,3,4}

¹ Department of Materials, Environmental Sciences and Urban Planning (SIMAU), Università Politecnica delle Marche, Ancona - Italy

² DIASEN[®] Srl, Sassoferrato (Ancona) - Italy

³ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

⁴ Institute of Atmospheric Sciences and Climate (ISAC), CNR, Bologna - Italy

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

Materials and methods: Two different types of commercial paints are considered (A and B paints). A is an acrylic paint for indoor applications, B is an acrylic paint for outdoor applications.

In the case of paint B, two different types of unconventional fillers (F1, F2), characterized by high porosity and specific surface area, are added in the commercial formulations as it is or as total replacement in volume of the conventional filler.

Paints are tested and compared in terms of inhibition of mold growth (UNI EN 15457:2008), water vapour permeability (UNI EN 1015-19:2007 - UNI 7783:2013), moisture buffering capacity (NORDTEST) and depolluting properties as ability of removal a known quantity of Methyl ethyl ketone in a closed box.

Paints are applied and tested on two different substrates: real substrate where paints are applied (pre-mixed mortar commercially available), and inert substrate.

Results: There are no evidences of moulds growth for all paints.

Paint A gives the lowest value of μ both if applied on inert substrate or pre-mixed mortar. The addition of unconventional fillers in paint B is very effective in reducing μ factor, in both cases, up to 60%.

Again, regarding the moisture buffering value (MBV), with the simple addition of unconventional filler F1, the performance of paint B is increased 3 times, when applied on the inert support, and of about 30% when applied on the mortar substrate.

The addition of unconventional fillers permits to improve the depolluting capacity of paint B of about 15%.

Discussion: The application of paint A on the mortar substrate does not imply substantial changes in the substrate properties. The addition of unconventional fillers permits to enhance the ability of paints B to positively affects IAQ. The high porosity and polarity of unconventional fillers enhance

the transpirability, the MBV and depolluting ability of this paint and, consequently, of the whole system mortar + paint.

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

Giosuè C¹, Carolosi C², Marcellini M¹, Mobili A¹, Van Tan N³, Pugnaloni F², Tittarelli F^{1,4,5}

¹ Department of Materials, Environmental Sciences and Urban Planning, Università Politecnica delle Marche, Ancona - Italy

² Department of Construction, Civil Engineering and Architecture, Università Politecnica delle Marche, Ancona - Italy

³ Hue University of Sciences, Hue City - Vietnam

⁴ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

⁵ Institute of Atmospheric Sciences and Climate (ISAC), CNR, Bologna - Italy

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

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

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

Discussion: The wide differences in colours, microstructures and chemical compositions suggests that bricks with different origins have been adopted during the maintenance works carried out in different ages. Samples 9 and 11 are probably rocks; 3, 6 and 10 are manufactured with carbonate rich raw materials and firing temperatures lower than 800°C ; 4 and 5 have firing temperatures of 900°C and sample 8 of 1000°C . The aspect of sample 9 and 10 suggests that probably they are rocks rather than bricks.

By the evidences, the mortar is hydraulic but not cementitious. The presence of gehlenite confirms a firing temperature higher than 800°C but lower than 1000°C . The low content of soluble ions indicates that masonry has not been submitted to chemical degradation.

BIOCOMPATIBLE HYBRID MAGNETIC NANOPARTICLE FOR THERANOSTIC APPLICATION

Guerrini A^{1,2}, Tenci B³, Croce R^{1,2}, Innocenti C^{1,2}, Mannini M^{1,2}, Di Cesare Mannelli L³, Mello T³, Ceci P³, Falvo E⁴, Basini M^{2,5}, Lascialfari A^{2,5}, Sangregorio C^{2,6}

¹ Laboratory of Molecular Magnetism (LaMM), Department of Chemistry "U. Schiff", University of Florence, Sesto Fiorentino (Florence) - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Department NEUROFARBA, University of Florence, Florence - Italy

⁴ Institute of Molecular Biology and Pathology (IBPM), CNR, Sapienza University of Rome, Rome - Italy

⁵ Department of Physics, University of Milan, Milan - Italy

⁶ Institute of Chemistry of Organo-Metallic Compounds (ICCOM), CNR, Sesto Fiorentino (Florence) - Italy

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

18 nm with apo-HfT, thus conjugating a high MFH efficiency with the drug carrier and targeting functions of apo-HfT. Moreover we demonstrate how the same system can be used as carrier for the chemotherapeutic drug doxorubicin

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

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

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

DISTANT NANOSTRUCTURES INTERACTING UPON AN EXTERNAL STIMULUS

Gulino A^{1,2}, Maccarrone G¹, Contino A¹, Millesi S^{1,2}

¹ Department of Chemistry, University of Catania, Catania - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

Materials and methods: In a glove box under a N₂ atmosphere some SiO₂ and Si(100) freshly cleaned substrates were covalently coated with a trichloro[4-(chloromethyl)phenyl]silane monolayer. Then some monolayer were reacted with a solution of 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphyrine, H₂THPP, and some others with a solution of 4-(2-pyridylazo)resorcinol, PAR. Then the PAR_SAMs molecules were quantitatively complexed with Cu²⁺ ions in a 1:1 ratio. The covalently immobilized monolayers were characterized by XPS, AFM and UV-vis.

Results: Two H₂THPP_SAM and Cu_PAR_SAM⁺ monolayers were fixed in a particular Teflon set-up, put in a cuvette and covered with an acidic solution (starting pH = 1.88). Then successive aliquots of a NaOH solution have been added. There are UV-vis evidences that the -OH ions activated a controlled Cu²⁺ mass transfer from the Cu_PAR_SAM⁺ to the H₂THPP_SAM.

Discussion: The monolayers setup exhibits many optically active states. We have shown that these systems can communicate among themselves and exchange mass upon a precise external input. Therefore, for the first time it has been reported a guided transfer of Cu²⁺ cations between two molecular interfaces, specifically from a Cu_PAR_SAM⁺ to a H₂THPP_SAM. This transfer was carried out in an aqueous environment and driven by a fine tuning of an external trigger (-OH). It has been possible to read the physical states of the overall system that, in turn, represent the answer (output) to the chemical OH⁻ stimulus. For the first time, the protonation and complexation equilibria of monolayers have been described. Moreover, we trust that this archetypal setup may represent the platform for the development of advanced interfacial communication systems based on optically active monolayers.

POLYMERIC NANOCOMPOSITE SYSTEMS AS PROTECTIVE MATERIALS FOR CULTURAL HERITAGE

La Mantia FP^{1,2}, Scaffaro R^{1,2}, Ceraulo M^{1,2}

¹ Department of Civil, Environmental, Aerospace and Materials Engineering, University of Palermo, Palermo - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

Materials and methods: The materials used in this work were and PLA. Mechanical characterization of the materials was carried out with a universal testing machine on samples (90 × 10 × 0.5 mm). Protective films, about 200 nm thickness, were produced by compression molding. The adhesion tests were carried out by placing the protective film on the surface of the stones. The film was heated at a temperature of about 50°C so as to adhere to the surface. For the realization of these materials, EVA with a vinyl acetate content of 28% was initially used as polymer matrix. The polymer matrix was subsequently loaded with organomodified clay nanoparticles.

Protective films were also made using the solvent casting method. In this case PLA was used as matrix and chloroform and acetone as solvents.

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

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

SURFACE MODIFICATION OF DIATOMITE TAILORED FOR RUBBER COMPOUNDS

Lamastra FR^{1,2}, Mori S^{1,2}, Cherubini V^{1,2}, Scarselli M³, Nanni F^{1,2}

¹ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

² Department of Enterprise Engineering, University of Rome "Tor Vergata", Rome - Italy

³ Department of Physics, University of Rome "Tor Vergata", Rome - Italy

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

Materials and methods: Silanol groups were introduced on the surface of an hydrophobic diatomite (D) as follows: 1g of D was added to 250 ml of a solution of H₂O:NaOH (40 wt% aqueous solution): H₂O₂ (30% v/v aqueous solution) = 2:1:1 (volume ratio). The system was stirred at 85°C for 2 h. The powder was then collected by filtration, washed and dried. The modified diatomite is referred to as D-OH. Silanization was carried as follows: 1 g of D-OH was dispersed in 50 ml of ethyl alcohol by sonication, bis(triethoxysilylpropyl) disulfide (TESPD) (0.126 ml) was then added and the mixture was heated at 100°C until the complete ethyl alcohol evaporation. Finally, the powder was heated in air at 120°C for 2 h. The silanized diatomite is referred to as DS. D, D-OH and DS were characterized by SEM/EDS, FTIR and XPS.

Results: Both D and DS are constituted of micrometric frustules with pore sizes in the range 25 nm-1 μm.

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

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

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

Lavagna L^{1,2}, Rodighiero L¹, Caimotti A¹, Restuccia L³, Ferro G³, Pavese M^{1,2}

¹ Department of Applied Science and Technology, Politecnico di Torino, Turin - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Department of Structural, Geotechnical and Building Engineering, Politecnico di Torino, Turin - Italy



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

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

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

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

BIOCOMPOSITES BASED ON POLYESTERS AND NATURAL FIBRES

Lozzeri A¹, Cinelli P^{1,2}, Seggiani M¹, Righetti MC², Coltelli MB¹, Mallegni N¹, Gigante V^{1,2}, Aliotta L^{1,2}

¹ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

² Institute for Chemical and Physical Processes (IPCF), CNR, Pisa - Italy

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

Materials and methods: Bio-polyesters such as polylactic acid and polyhydroxyalkanoates (PHAs) have been addressed as polymeric matrices for the production of biobased composites with natural fibres such as wood, ramie, cellulose, wheat, potato, peas, and *Posidonia oceanica*. Materials were processed both in laboratory and in industrial scale and extensively studied for morphological, thermal and mechanical properties.

Degradation in different environment (compost, soil, marine water) was also addressed coupled with study of products environmental sustainability by Life Cycle Assessment.

Results and discussion: Composites based on PLA or PHAs and different natural fibres up to 30% by weight was achieved on industrial scale with increasing of elastic modulus and impact energy-absorbing capability related to increasing the fibres content. Several mathematical models were applied to fit the experimental trends as a function of composition. Degradability in compost, soil, and in the case of PHAs based composites also in marine wa-

ter, was promoted by natural fibres presence. Sustainability is also improved by carbon balance due to the use of biobased polymers and bio based natural fibres, as well additives introduced in the materials, such as plasticizers were selected giving preference to biodegradable and bio-based products.

ULTRALIGHT MAGNESIUM ALLOY FILLED WITH MICRO AND NANO CARBON STRUCTURE

Marini D^{1,2}, Genova V^{1,2}, Marra F^{1,2}, Pulci G^{1,2}, Valente M^{1,2}

¹ Department of Chemical Engineering, Material, Environmental, Sapienza University of Rome, Rome - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Magnesium is the lightest structural metal with a very low density (1.74 g/cm³) and low melting temperature (650°C). In recent years, it has been increasingly used in different industrial sector: automotive, aeronautic and nautical industries. However, is interesting to improve its technological properties. In this work, micro and nano fillers were added to magnesium alloy with a centrifugal casting process directly in the metal. In particular, carbon microfibers (CMFs) and carbon nanoplates (CNPs) were chosen as reinforcement. In this work it was studied the influence of the dispersion of different carbon fillers by measuring the mechanical properties of magnesium micro and nano composites.

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

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

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

TUNING THE BEHAVIOR OF CARBON/MG(OH)₂ MATERIALS FOR THERMOCHEMICAL HEAT STORAGE

Mastronardo E^{1,2}, Bonaccorsi L³, Kato Y⁴, Piperopoulos E², Lanza M⁵, Milone C^{1,2}

¹ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

² Department of Engineering, University of Messina, Messina - Italy

³ Department of Civil, Energetic, Environmental and Materials Engineering, Mediterranean University of Reggio Calabria, Reggio Calabria - Italy

⁴ Laboratory for Advanced Nuclear Energy, Institute of Innovative Research, Tokyo Institute of Technology, Tokyo - Japan

⁵ Institute for Chemical Physical Processes (IPCF), CNR, Messina - Italy

Introduction: Referring to the Energy Efficiency Directive, waste heat storage represents a key issue for helping EU to reach 20% energy efficiency target by 2020. A growing interest matured on MgO/H₂O/Mg(OH)₂ thermochemical system that stores heat (200-400°C) through the dehydration of Mg(OH)₂ and releases stored heat when required by reversible hydration of MgO in presence of water vapour. For the future development of this technology, the improvement of the active medium performances is a key issue. In this study, exfoliated graphite (EG)-Mg(OH)₂ hybrid materials are synthesized by two preparation methods: Deposition-Precipitation (DP) and Reverse Deposition-Precipitation (RDP).

Materials and methods: DP reaction consists in the gradual addition of a solution containing Mg precursor (Mg(NO₃)₂) to a NH₄OH solution (1.3M) containing a specified amount of EG. RDP reaction, contrarily, is carried out through the gradual addition of the precipitating agent (1.3 M NH₄OH solution) into the solution containing the Mg salt and the EG. The effect of the variation of

some reaction conditions (i.e. temperature, precipitating-agent feeding rate) on morphology, crystal structure and thermochemical behaviour of the developed samples have been investigated by means of Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and ThermoGravimetric (TG) analysis.

Results: It was observed that the preparation method strongly influences the $Mg(OH)_2$ coverage on EG surface. Specifically, by DP method thin $Mg(OH)_2$ layers uniformly covers EG surface, while for RDP a worsening of coverage degree is observed. Moreover, varying RDP synthesis conditions a difference in $Mg(OH)_2$ particle size was evidenced. The smaller is the particle size, the higher is the capacity of the active medium to dehydrate/hydrate.

Discussion: It can be argued that the mean $Mg(OH)_2$ particle size is strictly correlated to the achievement rate of a supersaturation degree, which depends from the synthesis conditions: the rapid achievement of the supersaturation degree during the hydroxide precipitation favors the formation of a larger number of smaller $Mg(OH)_2$ crystals. Moreover, the smaller is the $Mg(OH)_2$ particle size the better is the dispersion over the carbonaceous support and the higher are the reaction conversions in the hydration/dehydration process. A linear correlation between particle size and dehydration/hydration conversion was observed.

POLYSACCHARIDE-BASED NANOSTRUCTURED AEROGELS

Melone L^{1,2}, Fiorati A^{1,2}, Cametti M^{1,2}, Pastori N^{1,2}, Graziano A¹, Petroselli M^{1,2}, Rossi B^{1,2}, Punta C^{1,2}

¹ Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Politecnico di Milano, Milan - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

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

Discussion: The new CNF-based aerogels were successfully tested as potential sorbent units for water remediation from heavy metals (Zn^{2+} , Cd^{2+} , Pb^{2+} , Cr^{3+} and Cu^{2+}) and organic contaminants (including pesticides and drugs). Moreover, after selective functionalization, the system can be easily modified, in order to introduce additional chemical properties, such as sensing for specific targets, or to enforce the mechanical and structural performances. These polysaccharide-based aerogels have been also investigated in terms of drug-delivery efficiency. Finally, these aerogels can also operate as suitable organic templates for further organic and inorganic coating, in order to differentiate the properties of the resulting structures (hydrophobicity, antioxidant or photocatalytic activity). This work has been sponsored and financed by Regione Toscana (POR FESR 2014-2020, Call RSI2014, Project NanoBonD) and Regione Lombardia (RL-INSTM Call2016, Project NAIADI).

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

Merlonetti G¹, Donnini J¹, Corinaldesi V^{1,2}

¹ Department of Materials, Environmental Sciences and Urban Planning, Università Politecnica delle Marche, Ancona - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: A high-performance printing concrete has been developed for an innovative freeform construction concrete-printing process. The concrete

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

Materials and methods: Different mixture were studied prepared by using Portland cement type 52.5 R (650-750 kg/m³), carbonatic aggregate with maximum size of 0.6 mm (1150-1250 kg/m³), silica fume (120-150 kg/m³), superplasticizer (3.5-4 kg/m³), shrinkage reducing admixture (3-5 kg/m³), water (265-275 kg/m³), expansive agent (either 0 or 30 kg/m³), polypropylene fibers (1 kg/m³). Mechanical properties have been evaluated after 1, 7, 28 days of air curing by three-point bending tests and compressive tests.

Results: Compressive strength was in the range 26-28 MPa after 1 day of curing, in the range 55-58 MPa after 7 days, and in the range 60-63 MPa after 28 days. Flexural strength ranged from 5 MPa after 1 day of curing up to 9.5 MPa after 28 days of curing. Density ranged from 2050 to 2150 kg/m³, indicating that a degree of compaction of about 0.89-0.93 was achieved in absence of any vibration.

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

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

Meroni D^{1,2}, Taroni T¹, Rimoldi L^{1,2}, Fidecka K¹, Cauteruccio S¹, Vago R³, Licanaro E¹, Ardizzone S^{1,2}

¹ Department of Chemistry University of Milan, Milan - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Urological Research Institute, San Raffaele Hospital, Milan - Italy

Introduction: Nanocarriers represent an emerging platform for the diagnosis and treatment of diseases such as cancer. Among them, oxide nanomaterials like halloysite nanotubes (HNTs) have recently emerged as promising candidates for drug delivery. HNTs are low-toxic and low-cost aluminosilicate clays with nanotubular structure, presenting a positively-charged $Al(OH)_3$ inner lumen and a negatively-charged SiO_2 outer surface. While drug loading based on electrostatic interactions is generally adopted in the literature, this strategy leads to poor control over the release process. Stronger interactions can be used to improve the hybrid stability and to induce the site-specific delivery of bioactive molecules using a physicochemical trigger.

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

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

Discussion: HNTs represents promising nanocarrier systems as shown by the limited toxicity in in vitro cell toxicity tests. Silane derivatives show high affinity

for both silica and alumina surfaces and are thus not suitable for the selective loading of a single HNT surface. Phosphonic acids proved the most interesting moiety for the selective functionalization of the inner lumen of HNTs, due to the lability of their interactions with silica. Surface functionalization with isocyanates was instead hindered by competition with physisorbed water. Possible mechanisms of controlled release using physicochemical triggers (light, pH) were determined.

PHOTOOXIDATION BEHAVIOR OF POLYPROPYLENE NANOCOMPOSITES WITH MODIFIED HALLOYSITE

Mistretta MC^{1,2}, La Mantia FP^{1,2}, Koci E¹, Di Maio L⁴, Legocka P³, Wierzbicka E³

¹Department of Civil, Environment, Aerospace and Materials Engineering, University of Palermo, Palermo - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Industrial Chemistry Research Institute, Warsaw - Poland

⁴Department of Industrial Engineering, University of Salerno, Salerno - Italy

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

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

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

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

AB-INITIO MODELLING OF THE ARRANGMENT OF OXYGEN VACANCIES AND THEIR EVOLUTION UNDER HEATING AND ELECTRIC FIELD IN HfO₂-RRAM

Montorsi M^{1,2}, Sementa L³, Mugoni C⁴, Siligardi C^{2,3}, Manfredini T^{2,3}

¹Department of Science and Methods for Engineering, University of Modena and Reggio Emilia, Reggio Emilia - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Institute for Chemical Physical Processes (IPCF), CNR, Pisa - Italy

⁴Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Reggio Emilia - Italy

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

Materials and methods: We performed Ab-Initio Molecular Dynamics (AIMD) on a 5 × 5 × 5 supercell of monoclinic m-HfO₂ in which oxygen atoms were extracted to design Oxygen Vacancies (OV) based filaments. Tempera-

tures from 1000 to 4000 K were considered to estimate the oxygen diffusion barrier heights, and their dependence on the charge state and electric field.

Results: The evolution of the filament shape and composition due to the re-organization of the OV during the switching operation were studied to unravel the role of the temperature and external electric fields in modulating the electrical properties, endurance and data retention of sub-stoichiometric HfO₂ based RRAM.

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

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

Moscatelli R^{1,2}, Sebastiani M^{1,2}, Bemporad E^{1,2}

¹Engineering Department, University "Roma Tre", Rome - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Instrumented Indentation Testing represents a well-established and widely used standard technique for the characterization of mechanical properties (elastic modulus and hardness). Nevertheless, new nanoindentation methods were recently introduced, opening the way to a new not-standard application. The introduction of the High-Speed nanoindentation technique, which allows to realize one complete indentation cycle per second, dramatically reduced the time needed for high time-consuming tests.

Two High-Speed nanoindentation applications are presented: an innovative tool for the mechanical characterization and high resolution mapping of high heterogeneous materials and a new technique for the surface patterning (N.I.H.L., Nanoindentation High-Speed Lithography).

Materials and methods: In the first one, two different and very high heterogeneous materials (LiMn₂O₄ polymer battery cathodes and cement pastes) were characterized combining Standard CSM and High-Speed Nanoindentation tests with FIB microscopy and SEM-EDS maps. In the second application, two different nanoindenter tips, realized by F.I.B. nanomachining, were used to nano-print surface patterns on two different substrates.

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

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

CONTROLLED CRYSTALLIZATION IN CuO-V₂O₅-TeO₂ GLASSES: CORRELATION BETWEEN STRUCTURE AND ELECTRONIC CONDUCTIVITY

Mugoni C^{1,2}, Montorsi M^{2,3}, Barbi S^{1,2}, Manfredini T^{1,2}, Siligardi C^{1,2}

¹Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Modena - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Department of Science and Methods for Engineering, University of Modena and Reggio Emilia, Reggio Emilia - Italy

Introduction: Transition metals (TMs) containing glasses represent very promising materials in the design of new-generation solid-state batteries. In particular, the addition of V_2O_5 to a tellurite glass matrix has attracted significant attention due to the relatively higher electronic conductivity reached by these systems with respect to other vanadium containing oxide glasses such as phosphates, borates, and silicates ones. In order to guarantee electronic conduction, the TM ion should exist in more than one valence state thus promoting electron transfer from ions in a lower valence state to those in a higher one. Moreover, the electronic conduction can be further enhanced through nano-crystallization of the material as a consequence of the creation of defective regions. The aim of this work is the development and characterization of vanadium tellurite glasses containing vanadium oxide crystalline grains of nano-or submicrometer sizes with the goal of enhancing the electrical conductivity of the starting glasses.

Materials and methods: Glasses belonging to $CuO-V_2O_5-TeO_2$ system were synthesized by melt-quenching method and thermally treated at different temperatures and times, in order to promote a controlled crystallization. The as synthesized glasses were characterized by means of thermal analysis, physical and electrical properties, X-Ray diffraction, Raman spectroscopy and FEG-scanning electron microscopy in order to correlate the structure with the conductivity results.

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

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

CERAMIC NANO-PARTICLES INFLUENCE ON PROPERTIES OF PHENOLIC RESIN COMPOSITES

Paglia L^{1,2}, Genova V^{1,2}, Tirillò J^{1,2}, Marra F^{1,2}, Pulci G^{1,2}

¹Department of Chemical Materials and Environmental Engineering, Sapienza University of Rome, Rome - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

Materials and methods: Nano-composite materials were obtained by mixing different nano-fillers with a commercial phenolic resin (Durite SC1008). Two different manufacturing processes were carried out in order to obtain samples suitable for bending tests (according to ASTM Standards D7265/D7264M-07) and for thermogravimetric analysis (from RT to 1000°C in inert atmosphere). In particular, in the first case 1-propanol was selected as resin solvent in order to minimize the porosity of the samples, in the second case ethylene-glycole was selected to obtain a gel phase and cured porous samples which can be easily reduced to powder. The samples were manufactured with different ceramic nano-fillers (ZrO₂, MgO, SiC) with the same granulometry (~50 nm). An ultrasonic bath and a sonicator probe were employed to optimize the dispersion of nano-particles in the solvent. After the manufacturing all samples were cured in an oven at the higher temperature of 180°C. The microstructure of the samples were evaluated by SEM analysis.

Results: Nano-composites with a phenolic resin matrix and ceramic nano-fillers show enhanced mechanical properties compared with pure

phenolic resin. For example, with addition of nano-ZrO₂ the mechanical resistance is incremented of about 50%. The thermogravimetric data enlighten some difference in the pyrolysis reaction depending on the nano-filler addition.

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

ELECTROCATALYTIC BEHAVIOR OF SUB-NANO Cu CLUSTERS IN THE CO₂ REDUCTION REACTION

Passalacqua R^{1,4}, Parathoner S^{1,4}, Centi G^{1,4}, Halder A⁵, Tyo EC⁵, Yang B⁵, Seifert S⁵, Vajda S⁵

¹Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (CHIBIOFARAM), University of Messina, Messina - Italy

²Department of Mathematical and Informatics Sciences, Physical Sciences and Earth Sciences (MIFT), University of Messina, Messina - Italy

³National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

⁴European Research Institute of Catalysis A.I.S.B.L. (ERIC), Bruxelles - Belgium

⁵Argonne National Laboratory, Argonne, IL - USA

Introduction: Copper is a peculiar element in the electrocatalytic reduction of CO₂, an area of growing relevance. Sub-nano Cu clusters have been suggested by computational studies to be good candidate for CO₂ reduction, being able to lower the overpotential in the reaction. However, there is no clear evidence on how these sub-nano copper particles behave during electrocatalytic conditions.

Here, we report an electrochemical investigation of two size-controlled Cu nanoclusters, prepared by a deposition method developed at the Argonne National Laboratory (ANL). The absence of organic ligands or capping agents in the resulting clusters, even at the level of contamination (which cannot be avoided in conventional wet techniques) makes these materials very interesting for electrocatalytic studies.

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

Results: The electrochemical investigations evidence that the coordination of CO₂ influences the electrocatalytic behavior of sub-nano Cu clusters.

Discussion: Cu₅ and Cu₂₀ clusters were chosen being representative of a planar-type cluster configuration and of a 3D-type (double icosahedron) structure, respectively. Grazing-incidence X-ray absorption near edge structure measurements were used to determine the valence state and chemical composition of Cu in the as fabricated samples. The electrochemical study of naked Cu₅ and Cu₂₀ nanoclusters evidences some relevant results regarding the redox behavior of these sub-nanometre size copper particles and the effect of CO₂. Cu₂₀ nanoclusters show anodic redox processes occurring at much lower potential with respect to Cu₅ nanoclusters, which behave relatively similar to much larger Cu particles.

However, Cu₅ nanoclusters coordinate effectively CO₂ (hydrogen carbonate) in solution differently from Cu₂₀ nanoclusters and larger Cu particles. This effect, rather than the redox behavior, is connected to the ability of Cu₅ nanoclusters to reduce CO₂ under cathodic conditions at low overpotential.

ACTIVATED CARBON CLOTH AS AGGREGATE FOR SPECIAL MORTARS

Pierpaoli M¹, Forconi D¹, Monosi S^{1,2}, Ruello ML^{1,2}

¹Department of Materials, Environmental Sciences and Urban Planning, Università Politecnica delle Marche - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: Activated Carbon Cloth (ACC) is an adsorbent for the removal of micropollutants from the gaseous and aqueous phase, characterized by its woven fabric structure. Once exhausted, these materials are disposed as CER 150203 or as CER 150202* depending the presence of hazardous substances.

In our study a non-hazardous ACC waste was used as a partial replacement of the aggregate in special mortars, both to meet the EU priority in waste management, both to obtain lighter mortars with special characteristics.

Materials and methods: For this purpose, mortars with water/cement equal to 0.45 by weight and aggregate/cement equal to 2.5 by volume were considered. The cement used was a CEM II/A-LL 42,5R. Different mixes with different percentages of ACC substituted (50%, 75%, 90%, 100%) to the fine sand (passing through a sieve with 850 μm openings) were prepared.

Compressive strength was evaluated up to 7 days of curing according to UNI EN 1015-11:2007. Additional tests as the measurement of shrinkage (UNI EN 6687:1973), the water vapour permeability (UNI EN 1015-19:2008) and the Volatile Organic Compound (VOC) adsorption were evaluated for the specimens.

Results: Replacing part of the aggregate with the ACC, the compressive strength is negatively affected and the specific weight is also reduced, while the shrinkage is not very influenced by it.

By replacing the sand with 75% of ACC, a good compromise between the reduction of mechanical strength (from 39.0 to 15.4 N/mm²) and the decrease of specific weight (from 2.07 to 1.58 kg/l) was achieved. Moreover, the obtained mortar, shows a higher water vapor and VOC adsorbent capacity.

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

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

Quitadamo A^{1,2}, Valente M^{1,2}, Santonicola MG^{1,2}

¹ Department of Chemical Materials and Environmental Engineering Sapienza University of Rome, Rome - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

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

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

EFFECT OF INJECTABLE CALCIUM PHOSPHATES ON MACROPHAGE/ OSTEOBLAST COCULTURE MODEL

Rauci MG¹, Bo Y², Xiao Y², Santin M³, Zhang X², Ambrosio L^{1,4}

¹ Institute of Polymers, Composites and Biomaterials (IPCB), CNR, Naples - Italy

² Engineering Research Center in Biomaterials, Sichuan University, Chengdu - China

³ Centre for Biomedical and Health Science Research, School of Pharmacy and Biomolecular Sciences, University of Brighton - UK

⁴ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

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

Discussion: We have demonstrated that CaP-G3KPS and Sr-CaP/G3KPS can upregulate the early and later marker of osteogenesis and may further enhance bone forming functions of the cells.

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WATER BASED POLYURETHANE ADHESIVES FOR FLEXOGRAPHIC PRINTING

Sabatini V^{1,2,5}, Farina H^{1,2,5}, Ortenzi MA^{1,2,5}, Ardizzone S^{1,2,5}, Benelli T^{3,5}, D'Angelo E^{3,5}, Mazzocchetti L^{3,5}, Giorgini L^{3,5}

¹ Department of Chemistry, University of Milan, Milan - Italy

² CRC Laboratory of Materials and Polymers (CRC LaMPo), Milan - Italy

³ Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna - Italy

⁴ Interdepartmental Center for Industrial Research on Advanced Applications in Mechanical Engineering and Materials Technology (CIRI-MAM), University of Bologna, Bologna - Italy

⁵ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

Results: Different waterborne polyurethane formulations were successfully synthesized via the pre-polymer mixing process; adhesive films were prepared via solvent casting deposition using polyethylene terephthalate films as carrier substrates. Polyurethanes macromolecular structure were

determined via ^1H NMR spectra and their thermal features were assessed via DSC measurements. DMTA analyses were performed on industrial polyurethane adhesives in order to determine reference adhesion and rheological parameters.

Discussion: A preliminary study on polyurethane water-based adhesive formulations for metal flexographic printing bars was performed. The prepolymer mixing process allows permits a good control over the soft and hard phases of prepared polyurethane samples, modulating the adhesive and the rheological behavior of the resulting polymer films obtained via solvent casting deposition. The work is continuing with an emphasis placed on the study of adhesive and rheological features, related to the microstructural properties, compared with the ones measured for industrial solvent-based samples. Sticker prototypes based on waterborne polyurethane emulsions will be prepared via Mayer bar deposition technique.

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INNOVATIVE COMPOSITES FOR ADDITIVE MANUFACTURING

Santi R¹, Dastoli C¹, Del Curto B^{1,2}, Cicala G^{2,3}, Cigada A^{1,2}, Farè S^{1,2}

¹ Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Milan - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³ Department of Civil Engineering and Architecture, University of Catania, Catania - Italy

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

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

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

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

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

Scaffaro R^{1,2}, Maio A^{1,2}, Botta L^{1,2}, Lopresti F^{1,2}

¹ Department of Civil, Environmental, Aerospace, Materials Engineering, University of Palermo, Palermo - Italy

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

Introduction: For the first time, solid-state exfoliant agents were used to hinder the re-aggregation of graphene oxide (GO) during melt processing with polyamide 6 (PA6).

This technique drastically reduces the time and difficulty related to solvent (removal, disposal, etc.), and avoids water consumption, since in this case

150 mL of water under mild operative conditions are enough to prepare the amount of GOS necessary for the realization of almost 100 grams of PA6-GOS nanocomposites with outstanding ultimate properties.

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

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

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

DREAM: DRIVING UP RELIABILITY AND EFFICIENCY OF ADDITIVE MANUFACTURING

Sciancalepore C¹, Gatto A^{1,2}, Defanti S^{1,2}, Denti L^{1,2}, Bassoli E^{1,2}, Ferrari AM^{1,3}, Barucca G^{1,4}, Mengucci P^{1,4}, Bondioli F^{1,5}

¹ National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

² Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Modena - Italy

³ Department of Sciences and Methods for Engineering, University of Modena and Reggio Emilia, Modena - Italy

⁴ Department of Materials, Environmental Sciences and Urban Planning, Università Politecnica delle Marche, Ancona - Italy

⁵ Department of Engineering and Architecture, University of Parma, Parma - Italy

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

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

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

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

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

Sciancalepore C¹, Taormina G^{1,2}, Messori M^{1,3}, Bondioli F^{1,2}

¹National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

²Department of Engineering and Architecture, University of Parma, Parma - Italy

³Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Modena - Italy

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

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

A commercial inverted SLA 3D Form 1+ printer (Formlabs Inc., USA) was used to print filled and pure resin samples.

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

Discussion: When the photoinitiator is irradiated, the homolytic photocleavage of the C-P bond in the Irgacure 819 molecules generates benzoyl and phosphonyl primary radicals, able to initiate both the photochemical synthesis of metal nanoparticles and the radical photopolymerization of acrylate monomers. During the layer-by-layer printing process, the focused UV laser beam of the printer was used to locally photo-induce the reduction of Ag⁺ to Ag⁰, generating AgNPs, and at the same time photo-polymerize the acrylate monomers to solid resin, without any spurious reactions. The so obtained Ag nanocomposites showed improved functional and structural properties compared to the pristine resin, providing further rapid prototyping option to research and development of new products.

ZNO NANOPARTICLES ANCHORED TO SILICA FILLER AS CURING ACCELERATOR FOR RUBBER COMPOSITES

Scotti R^{1,2}, D'Arienzo M^{1,2}, Di Credico B^{1,2}, Morazzoni F^{1,2}, Mostoni S^{1,2}, Susanna A³

¹Department of Material Science, University of Milano-Bicocca, Milan - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

³Pirelli Tyre SpA, Milan - Italy

Introduction: Sulfur vulcanization is a consolidated process in tire industry to improve the rubber mechanical properties. ZnO is the most efficient activator currently worldwide employed in this process, in spite of its poor dispersion in rubber and partial reaction with the other curatives. Moreover, ZnO undergoes leaching during production, use and recycling of tires. Thus, the reduction of ZnO level in rubber is becoming an urgent issue. In this context, the present work aims at improving the efficiency of the curing process and, simultaneously, at reducing the amount of employed ZnO, by replacing it with a novel activator ZnO-NP@SiO₂-NP, constituted by ZnO nanoparticles (NPs) anchored to silica, a common filler used in rubber composites for tires. ZnO-NP@SiO₂-NP behaves at the same time as curing agent and reinforcing filler.

Materials and methods: ZnO-NP@SiO₂-NP was prepared by a sol-gel synthesis to anchor ZnO NPs (3-5 nm) on the silica surface and characterized by X-Ray Diffraction, TEM Microscopy, Solid State NMR, IR and XPS spectroscopies.

ZnO-NP@SiO₂-NP were used to prepare cured polyisoprene (IR) nanocomposites with silica, by blending and compression molding. Curing rate was evaluated by the calculating the apparent activation energy in non-isothermal conditions using Differential Scanning Calorimetric measurements. The cross-linking products were investigated by a Model Compound Vulcanization approach. The composite dynamic-mechanical properties were assessed by Rubber Process Analyzer in a shear stress mode.

Results: ZnO-NP@SiO₂-NP showed higher curing efficiency in sulfur cross-linking of IR composites and the final cured materials presents improved dynamic-mechanical properties compared to those conventionally obtained by using higher amount of microcrystalline ZnO. This is due to the immobilization of ZnO NPs on silica surface, through covalent Si-O-Zn bonds, which minimizes the Zn leaching, provides a homogeneous dispersion of zinc in the rubber matrix and increases the accessibility of the curative reactants to Zn²⁺ ions.

Discussion: The higher curing efficiency of ZnO-NP@SiO₂-NP was explained by its capability to accelerate two stages of the process: the formation of the sulfurating complexes at the beginning of reaction and of the mono- and disulfide cross-linking chains which account for the higher cross-linking density and mechanical properties of the final cured material.

MECHANICAL PROPERTIES OF THERMALLY-TREATED BASALT FIBRES

Seghini MC^{1,2}, Tirillò J^{1,2}, Sarasini F^{1,2}, Valente T^{1,2}

¹Department of Chemical Materials and Environmental Engineering, Sapienza University of Rome, Rome - Italy

²National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

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

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

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

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

Toto E¹, Laurenzi S², Santonicola MG^{1,3}

¹Department of Chemical Materials and Environmental Engineering, Sapienza University of Rome, Rome - Italy

²Department of Astronautical Electrical and Energy Engineering, Sapienza University of Rome, Rome - Italy

³National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence - Italy

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

Materials and methods: Graphene nanoplatelets (thickness about 60 nm and lateral size 3-7 μm) were dispersed in aqueous solutions of double-stranded DNA (ratio of 1: 1 by weight) using sonication. PEDOT:PSS was added to the GNP/DNA solutions at different percentages. The sensing films were prepared by drop cast deposition followed by drying in oven overnight. Space-grade advanced laminates made of carbon fiber fabric and RTM6 ep-

oxy resin were used as substrates for the nanocomposite films. Electrical properties of the films before and after UV-C irradiation were analyzed by electrical impedance spectroscopy (EIS) and tomography techniques. Film morphology was investigated by SEM.

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

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

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