

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

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

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

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Introduction: A high-performance printing concrete has been developed for an innovative freeform construction concrete-printing process. The concrete

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

Materials and methods: Different mixture were studied prepared by using Portland cement type 52.5 R (650-750 kg/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

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Introduction: Nanocarriers represent an emerging platform for the diagnosis and treatment of diseases such as cancer. Among them, oxide nanomaterials like halloysite nanotubes (HNTs) have recently emerged as promising candidates for drug delivery. HNTs are low-toxic and low-cost aluminosilicate clays with nanotubular structure, presenting a positively-charged $Al(OH)_3$ 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

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

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

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

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Introduction: Instrumented Indentation Testing represents a well-established and widely used standard technique for the characterization of mechanical properties (elastic modulus and hardness). Nevertheless, new nanoindentation methods were recently introduced, opening the way to a new not-standard application. The introduction of the High-Speed nanoindentation technique, which allows to realize one complete indentation cycle per second, dramatically reduced the time needed for high time-consuming tests.

Two High-Speed nanoindentation applications are presented: an innovative tool for the mechanical characterization and high resolution mapping of high heterogeneous materials and a new technique for the surface patterning (N.I.H.L., Nanoindentation High-Speed Lithography).

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

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