MACROGIOVANI 2019

Giornate di discussione
su progetti di ricerca macromolecolare

Napoli, 1-2 luglio 2019

Organizzato da: AIM

Associazione Italiana
di Scienza e Tecnologia delle Macromolecole

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MACROGIOVANI 2019

Monday - July 1, 2019

13:45-15:45	**Oral session (12 speakers)**	
	Undergraduates	
13:45	Gisella Di Mari	Development of Titania/Polymer Composites for Environmental Pollution
13:55	Fabiana Vento	Synthesis of Biodegradable Polymer-Drug Conjugates For Biomedical Applications
14:05	Heba Meghad	Optical Determination of Molecular Diffusion Coefficient In Polymer Multilayered Sensors
14:15	Federica Ferruti	Controlled Synthesis of Polyamidoamino Acids
14:25	Massimo Marcioni	Hydrophobic Polyamidoamines: a New Class of Technological Material?
14:35	Matteo Arioli	Degradation of Linear and Crosslinked Poly-Amidoamines
14:45	Alessandro Beduini	Disulphide-Based Polyamidoamines as Flame Retardants for Cotton Fabrics
14:55	Ilaria Esposito	Multifunctional Coatings for Bronze Artifacts In Cultural Heritage
15:05	Ignazio Adamiano	Self-Healing Polyurethane-Based Coatings for Corrosion Protection
	Research fellows	
15:15	Irene Conticello	Absorbent Cryopolymeric Sponges for The Adsorbtion of Emerging Pollutants in Water
15:25	Chiara Gugliuzzo	Analisi e Contenimento dei Prodotti di Degradazione Formati Durante la Lavorazione del PET
15:35	Giuseppe Iasilli	New Materials for Luminescent Solar Concentrators
15:45-16:30	**Coffee break**	

16:30-18:10	**Oral session (10 speakers)**	
16:30	Gabriella Munzi	Polymer Nanocomposites Based on Si Nanostructures Coupled with C Nanotubes
16:40	Marco Leonardi	Innovative Smart Nanocomposites of Chitosan Nanoparticles Containing Metal Oxide as Alternative Fertilizers
16:50	Ferdinando De Luca Bossa	Green Composite-Polyurethane Foams: Effect of Natural Fillers, Walnut Shell and Cellulose, on Chemico-Physical Properties of Polyurethane
17:00	Federica Santulli	Complessi Bimetallici di Alluminio come Catalizzatori per la Sintesi di Poliesteri
		PhD Students (I year)
17:10	Bruno Grandinetti	Stimuli-Responsive Polymers Towards Biological Applications
17:20	Marianna Diterlizzi	Water-Processable Blend Nanoparticles for Sustainable Organic Solar Cells
17:30	Ilaria Silvestro	Influence of Graphene Oxide Oxygen Content on Properties of Chitosan/Graphene Oxide Scaffolds
17:40	Enrico Carmeli	On the Use of Thermal Fractionation Analysis for the Characterization of Recycled Polyolefin Grades
17:50	Alessandra Longo	Biodegradable Mosquito Repellents Polymer Fibers
18:00	Urcioli Gaia	Structural Characterization of Olefin-Based Multiblock Copolymers Obtained through Chain Shuttling Technology
19:45	**Bus leaves from Hotel Cristina - Dinner**	

Tuesday - July 2, 2019

09:00-10:30 Oral session (11 speakers)

9:00	Manohar Golla	Structure and Polymorphic Behavior of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) in Axially Stretched Films
9:10	Francesco Valentini	Polyurethane Foams for Thermal Energy Storage Applications

PhD Students (II and III year)

9:20	Giuseppe Trusiano	Controlling the Environmentally Induced Rearrangements of Perfluoropolyalkylethers at Photopolymers Surfaces
9:30	Parisa Pedram	Design and Fabrication of Polymeric Micro-Scaffolds for in Vitro Modular Tissue Engineering
9:40	Valentina Strongone	Preparazione e Caratterizzazione di Coatings Funzionali Contenenti filler Carboniosi Mediante UV-Led Curing
9:50	Andrea Dodero	Nanocomposite Alginate-ZnO Membranes Prepared via Electrospinning Technique
10:00	Riccardo Chiarcos	Nitroxide Mediated Polymerization as New Tool in the Box of Polymeric Deterministic Doping
10:10	Franceso Gamardella	A New Class of Vitrimers Based on Aliphatic Poly(Thiourethane) Networks With Shape Memory and Permanent Shape Reconfiguration
10:20	Claudio Russo	Strategies to Increase Tg and Mechanical Performance of Dual-Curing Thermosets for Advanced Applications
10:30	Mattia Di Maro	Radiation-Induced Grafting of HDPE-ATZ Composites with Chitosan For Biomedical Purpose
10:40	Ulisse Montanari	Novel Polymers From Terpenes

10.50-11.20 Coffee break

11.20-12.40 Oral session (8 speakers)

Post-docs

11:20	Alessandro Emendato	Exploiting Block Copolymer Self-Assembly Processes to Obtain New Hybrid Nanocomposite Materials for Photovoltaic Applications

11:30	Elisa Guazzelli	The Temperature-Responsive Nanoassemblies of Amphiphilic Random Copolymers by Single-Chain Folding in Water
11:40	Seif Eddine Fenni	Dynamic Vulcanization of Polyester Polyols in Poly (L-Lactic Acid) as an Effective Way for PLLA Toughening
11:50	Chiara Santillo	HAVOH/MWCNT Composites with Tailored Filler Segregation for FDM 3D Printing Technology
12:00	Stefano Gazzotti	1,3-Dioxolane-4-Ones: a Path to Explore Toward Highly Functionalized Polyesters
12:10	Angela Marotta	Curing Kinetics and Mechanical Properties of Sugar-Derived Epoxy Resins
12:20	Giuseppe Cesare Lama	Foamed Inorganic Polymers Filled with Graphene
12:30	Miriam Scoti	Crystallinity, Morphology and Elastic Behavior of Copolymers of Syndiotactic Polypropilene with α-Olefins.
12:40-15:00	**Lunch, awards ceremony and greetings**	

Development of Titania/Polymer composites for environmental pollution

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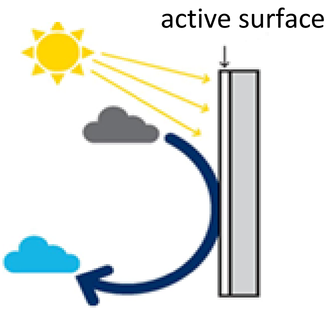
ABSTRACT:

During the years, human activity has influenced the environment in a so invasive way that caused radical changes. In general, pollutants emission is produced by various anthropogenic processes in both atmosphere and water. Many of these pollutants are extremely harmful because, in addition to global warming, some of them are carcinogenic, mutagenic and/or teratogenic. In this landscape, heterogeneous photocatalysis takes over as a method of abatement of contaminants which are present in the environment. Thanks to its photocatalytic properties, fully described in the literature, Titanium Dioxide (usually called Titania) is one of the most used photocatalysts today. Generally, heterogeneous photocatalysts are used suspended in a solution or embedded inside a matrix, which works as physical support. There are numerous attempts of supporting Titania on surfaces exposed to the atmosphere, and one of the most famous approaches consists in using concrete: it's enough to make a simple physical mixture between the two components, without other chemical/physical alteration.

However, this kind of materials shows some issues: his function as photocatalyst is exerted only by the photocatalyst present on the surface; in addition, they exhibit a natural loss of photocatalytic activity over time [1]. Instead, polymers -used as a matrix to disperse Titania- are excellent candidates, because of their advantages: chemically inertness, low production costs, low density and excellent flexibility (which make them easy to handle), easy availability and a very easy deposition on the surfaces [2]. Moreover, their use could modify the photocatalytic activity of Titania in some way.

Starting from these assumptions, in this communication there will be discussed the synthesis and the characterization of composites based on Polymethylmethacrylate (PMMA), Polystyrene (PS), and PolyVinyl Acetate (PVAc), having embedded different amount of Titania. The efficiency of these composites, used as powders or films, has been tested. The experimental data exhibit unexpected positive results, showing the capability of certain polymers, handled in a specific way, to act as active supports of photocatalytic systems.



Keywords:

Heterogeneous Photocatalysis; Titanium Dioxide; Polymers;

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Influence of Graphene Oxide Oxygen Content on properties of Chitosan/Graphene oxide scaffolds

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ABSTRACT

Tissue Engineering is a highly interdisciplinary field of medicine aiming to replace compromised tissues. The process involves the presence of reparative cells, a structural template (scaffold), transport of nutrients, and molecular and mechanical regulatory factors. The scaffold should be made of biocompatible and biodegradable material and elicit no immunological or foreign body reaction. Biopolymers, including chitosan (CS), are widely used to produce scaffolds. In recent years, CS has gained much attention in bone tissue engineering [1]. The major limitation of chitosan is its low mechanical strength. Many strategies have been pursued to improve the mechanical properties of chitosan including its combination with reinforcing materials such as hydroxyapatite, silica nanoparticles and graphene oxide [2]. Graphene oxide (GO) is obtained by oxidation of graphene sheets, causing the formation of epoxy and hydroxyl groups on the basal planes and of carboxylic groups on the edges. The hydrophilicity enhancement makes GO more compatible with CS than graphene. In addition, the content of oxygenated groups in a material can strongly affect its chemico-physical properties as well as the biological ones such as citotoxicity and interaction with cellular components like proteins [3]. In this study, in order to investigate the effects of the GO oxygen content on the mechanical and biological properties, 3D porous scaffolds based on CS/GO conjugates were prepared by employing two types of GO: a GOsigma sample at low oxygen content (commercially available) and a GOexfoliated sample at high oxygen content obtained by electrochemical exfoliation of graphite. GO was covalently bonded by a carbodiimide-mediated amidation in two concentrations (0.3% and 1%). Subsequently, the scaffolds, prepared by either the salt leaching method (SL) or freeze-drying (FD), were characterized in terms of porosity, water swelling, water retention ability, thermal properties, mechanical response in compression and in vitro cytocompatibility against primary human dermal fibroblasts. The study confirmed the ability of graphene oxide to act as a reinforcing filler for chitosan scaffolds. The results suggested that the oxygen content of GO affects the final properties of GO/CS scaffolds and the biocompatibility. In particular, the conjugation of CS with a GO sample at low oxygen content resulted in scaffolds with improved compression modulus and biocompatibility compared to pristine CS. Overall, GOsigma/CS scaffolds at 1% GO content showed good potentiality for the application in tissue engineering.

Keywords: *graphene oxide, chitosan, scaffold.*

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Optical Determination of Molecular Diffusion Coefficient in Polymer Multilayered Sensors

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ABSTRACT

Detecting vapors of volatile organic compounds is important to monitor health risks associated with their exposure in both urban and industrial settings. These risks include eye and respiratory tract irritation, headache, internal organ damage and even cancer.[1] Hence, the development of affordable, portable, reliable and fast sensors is essential for air quality control, and to properly identify any related hazard. Colorimetric sensors based on all-polymer distributed Bragg reflectors (DBRs) are promising candidates for this role owing to their low fabrication costs and to their sensitivity and selectivity without the need for chemical functionalization.[2,3] DBRs consist of an alternating sequence of polymer thin layers with refractive index contrast, forming a dielectric lattice. This ordered structure affects photons like crystals affect electrons, producing photonic band gaps (PBGs) where light of specific wavelengths cannot propagate within the lattice and is reflected.[4] As the DBRs are exposed to an analyte in the vapor phase, its intercalation within the structure swells the polymer films modifying their optical thickness. This process causes a variation in the optical properties of the multilayer and consequently sensing. The kinetic of the analyte diffusion within the multilayer allows instead to recognize different pollutants with sensitivity below 1 ppm.[5]

Notwithstanding these outstanding properties, a better comprehension of the phenomena ruling the diffusion kinetic within the multilayered structure will allow to optimize the response time for prompt detection and to further enhance the sensitivity. In this work, DBR sensors based on polystyrene and cellulose acetate made of different number of layers were fabricated through spin-coating to investigate the effect of interfaces and of the overall thickness of the structure. The evolution of DBR and single film dynamic optical response upon exposure to isopropyl-alcohol was recorded as a function of the number of layers through a simple UV-VIS set-up. This simple analysis allows to assess the analyte diffusion coefficient within the different structures and the role of thicknesses and interfaces of the layer in the diffusion process. These results will help in designing sensors with tailored response time, spectral shift and sensitivity, also providing a toolbox for customizing vapor sensors for environmental and health and safety applications.

Keywords: *colorimetric sensor; polymer photonic crystals; diffusion coefficient; distributed Bragg reflectors; volatiles sensing*

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CONTROLLED SYNTHESIS OF POLYAMIDOAMINO ACIDS

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Polyamidoamino acids (PAACs) are synthetic polymers derived from Michael-type polyaddition of natural α-amino acids, or their stereoisomers (henceforth called “A”) with a bisacrylamide (henceforth called “M”)[1] The reaction involves only the amino acid α-amine group that in the process is transformed into a *tert*-amine group without loosing its basic properties. Therefore the resultant PAAC retain both chirality and amphoteric properties of α-amino acids. Noticeably, chiral PAACs assume in water stable, pH dependent conformations [2]. However, the polyaddition process adopted so far leads to polydisperse products with *PD* ~ 2. This work presents a novel step-by-step synthetic strategy leading to PAACs with controlled structure and molecular weight, run in water and neither involving protection-deprotection steps, nor releasing by-products. It exploits the difference in reactivity between the amine hydrogen atoms of the α-amino acids towards the Michael addition [3] and, in addition, the poor solubility in organic solvents of α-amino acids and their oligomers. In the first instance, M and A in 1:2 molar ratio gave straightforwardly the nearly pure AMA trimer that treated with excess M at 45 °C for 4 days gave a mixture of MAMAM pentamer and M, removed by dissolving in wet methanol and reprecipitating in acetone; MAMAM treated with two moles of A at rt for 3 days gave the AMAMAMA heptamer, and so on. In the present work, the proof of principle of the process was achieved with A = *L*-arginine and M = N,N’-methylenebisacrylamide. It was continued with alternative A and M bis- end additions and deliberately stopped after obtaining the AMAMAMAMAMA 11-mer (*MW* 1814 Da), but it could have been continued indefinitely. It is apparent that the process is apt to give strictly monodisperse homo- and copolymeric PAACs with predetermined molecular weight and, for the latter, amino acid sequences. For instance, it was also performed with *L*-alanine (Al) and *L*-phenylalanine (Phe), obtaining AlMAl, MAlMAlM, PheMAlMAlMPhe and AMAlMAlMA oligomers. Moreover, the bis-M-terminated oligomers can be employed as building blocks capable to undergo Michael polyaddition with *prim*- or bis-*sec*-amines or even different α-amino acids, straightforwardly yielding PAAC- and PAAC/amine copolymers in which the α-amino acid- and/or amine units are regularly distributed along the polymer chain. For instance, with piperazine (P) and *L*-alanine (Al), the copolymers $[PMAM]_n$, $[PMAMAM]_n$ and $[AlMAM]_n$ were obtained. Rather surprisingly, these copolymers had very narrow PDs (1.11, 1.09, and 1.03, respectively) after a single ultrafiltration step

Keywords: *controlled synthesis; polyamidoamino acids; chirality; amino acids*

References

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HYDROPHOBIC POLYAMIDOAMINES: A NEW CLASS OF TECHNOLOGICAL MATERIAL?

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Polyamidoamines (PAAs) are synthetic polymers obtained by Michael-type stepwise polyaddition of *prim-* or *sec-* amines to bisacrylamides. PAAs, thanks also to their biocompatibility and biodegradability, have shown potential application and activity in drug and protein intracellular carriers, transfection promoters, antimalarial agents, antiviral and, in hydrogels form, as scaffold for tissue engineering [1,2]. However, the poor mechanical properties shown by PAA hydrogels don't allow their use as an implantable material. To overcome this problem, different approaches were investigated, like the preparation of composite with inorganic fillers [3] or PLLA mats [4]. A new approach was now attempted based on the development of hydrophobic, semi-crystalline PAAs with sufficient mechanical strength to be used as hydrogel support. Hydrophobic PAAs were prepared from long chain aliphatic bisacrylamides and bis-*sec*-amines or N,N-dialkyl substituted diamine. Hexamethylenbisacrylamide (HEXAMBA), octamethylenbisacrylamide (OMBA), decamethylenbisacrylamide (DMBA) and dodecamethylenbisacrylamide (DDMBA) were obtained by Schotten-Baumann reaction involving acryloyl chloride and 1,6-diaminohexane, 1,8-diaminooctane, 1,10-diaminodecano or 1,12-diaminododecano. The amine monomers used for the polymerization reactions were piperazine (PIP), N,N'-dimethyl-1,6-hexanediamine (DMHEXA), N,N'-dimethyl-1,2-ethanediamine (DMEDAs), N,N-dimethyl-1,2-ethanediamine (DMEDAp), N,N'-dibenzyl-1,2-ethanediamine (DBEDA), N,N'-diethyl-1,2-ethanediamine (DEEDA). The reactions were performed in benzyl alcohol at 60°C and the obtained PAAs were characterized by FT-IR/ATR and NMR spectroscopies. The infuence of the bisacrylamide aliphatic chain length as well as of the nature of the amine on the termal properties of the hydrophobic PAAs were investigated employing DSC and TGA techniques. The general trend showed good thermal stability, with decomposition onset ≥ 200°C and a partial crystallinity.

The amine used for the polymerization assert an important role on the final polymer, giving high melting point polymer, as DDMBA-PIP (m.p.195°C) or low melting point polymer, as DDMBA-DMEDAp (m.p.50°C). The bysacrylamide influence is less influent, but still present. For the same amine, melting point range from 80°C of HEXAMBA-DMHEXA, to 100°C of DDMBA-DMHEXA.

To investigate the mechanical properties of hydrophobic PAAs, thin films were obtained by compression molding and preliminary mechanical tests and observations were made. For the most promising polymer obtained, synthesis in the melt state was investigated, in order to achieve a more sustainable and industrially favorable process.

Keywords: *polyamidoamines; hydrophobic; materials*

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DEGRADATION OF LINEAR AND CROSSLINKED POLY-AMIDOAMINES

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Research on degradable polymers is an urgent issue, due to the pervasiveness and persistency of plastic wastes in the environment. Linear polyamidoamines (PAAs) are a family of polymers obtained by the Michael-type polyaddition of bisacrylamides with primary or bis-secondary amines. They are normally water-soluble and exhibit a wide range of applications, from biotechnology to flame retardancy, to the complexion of heavy metal ions [1]. If bis-primary amines are used, insoluble crosslinked hydrogels are obtained. In this paper, the hydrolytic degradation of both linear and cross-linked PAAs was investigated. Linear PAAs with molecular weight (MW) in the range 7-10000 were obtained from the combination of three bisacrylamides, namely N,N'-methylenebisacrylamide, 2,2-bis(acrylamido)acetic acid and N,N'-bis-acryloylpiperazine, with three different amines, namely glycine, ethylamine and 2-methylpiperazine. Hydrogel samples were obtained from N,N'-methylenebisacrylamide and glycine or 2-methylpiperazine, in which 30%, on a molar basis, of the two amines were replaced by 15%, on a molar basis, of ethylenediamine, which behaved as tetrafunctional monomer, providing a corresponding amount of cross-links. The degradation of linear PAAs was monitored by following the MW decrease by means of size exclusion chromatography run in TRIS buffer at pH 8.1. All samples were degraded down to MW≤1000 in 4-5 weeks. Hydrogel degradation was studied on both disks and particles 0.5-1 mm in size, by monitoring the variation of the swelling capacity in water and the dissolution time. Soil burial degradation tests were also performed. A multi-layer system of natural soil and inert perlite was created in closed chambers (bioflasks). A KOH solution was put inside the flasks for the monitoring of the degradation. At intervals of time, the solution was titrated for the determination of the CO_2 evolved from the samples. As regards the degradation mechanism, this was ascribed to the hydrolytic cleavage of the amide chain groups, backed by the tert-amine groups present in the γ-position along the polymer chain.

Keywords: (*Hydrolytic degradation; Soil degradation; Polyamidoamines*)

References

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DISULPHIDE-BASED POLYAMIDOAMINES AS FLAME RETARDANTS FOR COTTON FABRICS

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ABSTRACT

In previous works carboxylated polyamidoamines (PAAs) and disulphide-based polyamidoamines (SS-PAAs) proved to be efficient flame retardants (FRs) for cotton fabrics. PAAs extinguished the flame only in horizontal flame spread test (HFST) at add-ons of ~ 5% due to their intrinsic intumescence,[1] whereas SS-PAAs inhibited cotton combustion in both horizontal and vertical flame spread tests (VFST) at add-ons of ~ 16%, thanks to their intrinsic intumescent features and ability to act as scavengers for radicals.[2]

The aim of this work was to synthesize PAA/SS-PAA-based copolymers exploiting the flame retardant features of both PAA families. More specifically, PAA copolymers were synthetized by the Michael polyaddition of N,N′-methylenebisacrylamide (MBA) with different glycine (GLY)/cystine (CYSS) monomer ratios. Polymerizations were carried out in water, at rt and with no added catalysts. The resulting copolymers (70:30, 60:40, 50:50 and 30:70 GLY:CYSS) were characterized by infrared spectroscopy in attenuated total reflectance configuration (FT-IR/ATR), hydrogen nuclear magnetic resonance (^{1}HNMR) and size exclusion chromatography (SEC). Then, cotton fabrics were treated with copolymer water solutions at pH 8-9, measuring the initial and final weight in order to determine the add-on %, which was approximately 16% for all samples.

In parallel, fabrics coated with i) 50:50 blends of the MBA-GLY and MBA-CYSS homopolymers; ii) two layers of MBA-GLY and MBA-CYSS, respectively, (~ 8% add-on for each layer). All samples were characterized by FT-IR/ATR, thermogravimetry (TGA), VSFT and HFST.

The results of VFST showed that copolymers with ≥ 50% CYSS molar content were capable of inhibiting cotton combustion, whereas in HFST they extinguished the flame after few seconds. On the contrary, samples coated by the blends or with the two layers of MBA-GLY and MBA-CYSS completely burnt in vertical configuration.

This work demonstrates that, by exploiting the synthetic strategy of copolymerization, it is possible to obtain a flame retardant that, having the performances similar to those of MBA-CYSS but a significantly reduced production cost.

Keywords: *flame retardant; polyamidoamines; PAA copolymers; cotton.*

References

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MULTIFUNCTIONAL COATINGS FOR BRONZE ARTIFACTS IN CULTURAL HERITAGE

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ABSTRACT

History of art is full of bronze artifacts, which are easily damaged by atmospheric agents, even if exposed indoor. The chlorine is one of the most dangerous agents, as it binds to the copper in the bronze forming the so-called “bronze desease”, a green-blue patina composed of trihydroxy chlorides with different degrees of stability, that eventually destroys the material. In this context, the application of protective organic coatings represents one of the most widespread approaches for corrosion protection [1]. Self-healing systems are particularly intriguing since they guarantee an active protection even when the coating barrier properties fail [2]. In line with this strategy, the present work is focused on the realization of polymeric coatings with anticorrosive and self-healing properties. At the same time, the developed protective systems also had the requisites of aesthetic compatibility and reversibility required by the restoration. In particualr, the developed coatings are based on a self-healing polyurethane matrix filled with graphen oxide nanopowders properly functionalized with APTES and PDA in order to give to the final material specific features. Thermogravimetric analyses were carried out on nano-powders to establish the relative content of the various components, while to verify the successful functionalization a FTIR analysis was made. Electrochemical impedance spctroscopy was performed on bronze disks coated with the developed nanocomposite coatings to assess the coating quality in terms of resistance over the time in weakly aggressive environments. The obtained results suggest a good anticorrosion efficacy, even for the coatings realized without adding powders. Lastly, promising results have been obtained from self-healing test carried out with a NIR lamp: the scratch produced (~micron) was completely recovered after three minuts.

Keywords: *bronze; anticorrosion; self-healing; cultural heritage*

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SELF-HEALING POLYURETHANE-BASED COATINGS FOR CORROSION PROTECTION

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ABSTRACT

Bronze surfaces exposed to outdoor environment naturally form a layer called patina, which may be able to protect the metallic substrate. However, with the appearance of acid rains, a strong change in the nature of copper-based patinas occurred [1]. Studies and general observations have established that bronze corrosion patinas created by acid rain are not stable. The unstable patina is partially leached away by rainwater. Because of the instability of the patina, conservation techniques are usually required: corrosion inhibitors and functional protective coatings are typically exploited for this purpose. The present work fits in this frame, as it is focused on the optimization of a self-healing polyurethane-based coating for corrosion protection of bronze surfaces. Polyurethanes (PUs) are a class of versatile materials with great potential for use as paint and surface-coating materials [2].

Here, PU was prepared by polymerization of polytetrahydrofuran polyols with different diisocyanates: isophorone diisocyanate (IPDI), hydrogenated 4,49-diphenylmethane diisocyanate (HMDI), and 1,6-hexane diisocyanate (HDI). In such systems, the self-healing phenomenon is based on thermally reversible Diels–Alder (DA) reaction: a DA compound was indeed added in the polyurethane structure to guarantee this property. Physical and anticorrosion properties of the three different polyurethane materials were investigated. Water contact angle and water moisture absorption were measured. Electrochemical impedance spectroscopy was used to analyze the corrosion resistance of various polyurethane coatings. The results show that the polyurethane coating with HMDI diisocyante proves to be the most promising coating for corrosion protection of bronze. In addition, the preliminary results of thermally self-healing property on polyurethane-IPDI coating show that a superficial cut was completely restored in 30 seconds.

Keywords: *bronze corrosion; self-healing; polyurethane coating*

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ABSORBENT CRYOPOLYMERIC SPONGES FOR THE ADSORBTION OF EMERGING POLLUTANTS IN WATER

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ABSTRACT

Emerging pollutants are becoming a new threat for water quality and human health due to their toxicity and permanence in the ecosystem. Among these contaminants, pesticides represent one of the most important environmental problems of this century for surface and groundwater [1]. Atrazine, as a chloro-N-dialkyl-substituted triazine herbicide, was one of the most extensively used compounds for weed control in agriculture during the past few decades [2]. Even if Atrazine in Italy was withdrawn from the market by the late 90', it is still possible to reveal it, as well its metabolite in groundwater. Recently, the interest in the development of new materials capable of reducing the impact of emerging pollutants has been increased. In this work, we presented new hybrid materials based on poly (2-hydroxyethyl methacrylate) (pHEMA), graphene oxide (GO) and polymethacrylic acid (pMAA) as promising adsorbents cryo-sponges for mitigation of pesticides in water [3]. The morphology, as well as the chemical composition of the cryopolymers, have been investigated by thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). The swelling properties and mechanical performance have been also evaluated. Furthermore, the adsorption capability versus Atrazine-desethyl as contaminant-target has been tested by UV-vis spectroscopy measurements. Among the adsorbents, the pMAA sponges revealed promising results in terms of Atrazine-desethyl water removal.

Keywords: (*Emerging pollutants; atrazine-desethyl; water remediation; absorbent cryopolymeric sponges)*

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Analisi e Contenimento dei prodotti di degradazione formati durante la lavorazione del PET

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ABSTRACT

Il polietilentereftalato (PET) è un materiale molto versatile che, grazie alla sua inerzia chimica unita alle sue proprietà fisiche (trasparenza e bassa permeabilità ai gas), sta trovando sempre un maggior numero di applicazioni nel campo del packaging alimentare. Il PET, quando viene portato allo stato fuso per la lavorazione a temperature tra 270 e 280°C, nonostante le ottime caratteristiche chimico-fisiche, tende a degradarsi formando dei sottoprodotti non desiderati, i cosiddetti NIAS (sostanze non intenzionalmente aggiunte) fra cui aldeidi, chetoni, oligomeri vari e più in particolare, l'acetaldeide. Inoltre, la presenza di lubrificanti, utilizzati per evitare l'adesione del materiale fuso sulle pareti degli estrusori, può portare alla formazioni di ulteriori prodotti di degradazione che rimangono intrappolati nella matrice polimerica.
Scopo di questo lavoro è la determinazione dei prodotti di degradazione intrappolati nel PET delle bottiglie utilizzate per il confezionamento di acque minerali e lo studio di metodologie che ne possano limitare il fenomeno. I risultati sono stati ottenuti utilizzando la gas-cromatografia a spazio di testa su parti di bottiglie in PET e sono state individuate diverse molecole oltre all'acetaldeide, come esanale, ottanale, decanale, etc). La concentrazione di questi prodotti cresce quando le bottiglie sono esposte a più alte temperature (60°C) per esposizione in camere climatiche. Cresce pure la quantità di questi prodotti che vengono di conseguenza rilasciati nell'acqua contenuta nelle bottiglie. Per capire, le cause della formazione delle molecole riscontrate nell'analisi, sono state eseguite delle miscelazioni alla temperatura di 280°C di granuli di PET, grado bottiglia, tal quale e in presenza di alcuni lubrificanti utilizzati in processi industriali con lubrificanti come l'ESBO (olio di soia epossidato) e l'erucammide. Son stati identificati alcuni prodotti di degradazione simili a quelli ottenuti dall'anisi delle bottiglie di PET in commercio. Per limitare la presenza di acetaldeide e delle altre aldeidi, sono stati utilizzati degli additivi già conosciuti come "acetaldehyde scavenging agents" [2] come l'antranilamide e il polimero MXD6 [3] non ancora utilizzato per questo scopo. Sono state effettuate delle miscelazioni allo stato fuso del PET grado bottiglia con diverse concentrazioni dei due additivi (non superiore all'1%), sia singolarmente che in miscela. I risultati hanno evidenziato un abbattimento significativo della concentrazione di acetaldeide e delle altre aldeidi quando sono utilizzati singolarmente, con un effetto sinergico quando i due additivi sono in miscela.

Keywords: (*PET; NIAS; degradazione; additivi*)

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New materials for luminescent solar concentrators

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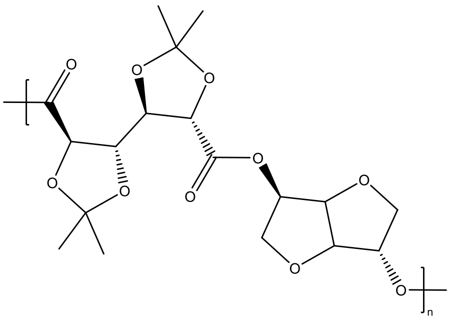
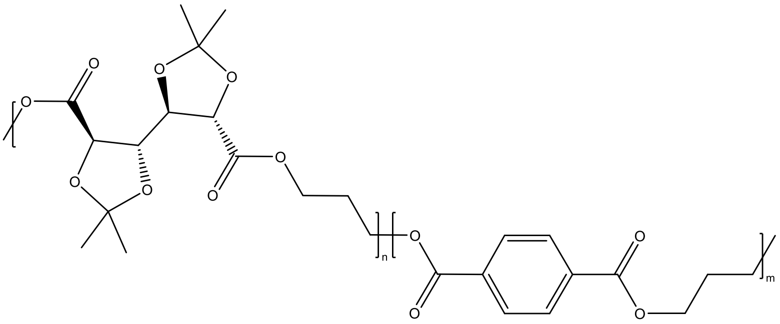
The concept of Net Zero-Energy Buildings (NZEBs) is receiving an increasing amount of attention by the scientific community and policy organizations, such as the European Committee [1]. NZEBs are technically feasible for individual houses and small buildings thanks to rooftop photovoltaic (PV) cells and efficient insulation. However, being ~7 m2 the area required per kW of peak power in NZEBs, the use of PVs is not worthwhile for larger buildings, where the rooftop space is insufficient to accommodate the PV modules necessary for meeting the electrical requirements [2]. An accessible solution to this problem is represented by luminescent solar concentrators (LSCs). LSCs are optical devices that absorb sunlight and re-emit the light via fluorescence concentrated at their edges, where it can be converted into electricity by coupled photovoltaic (PV) cells. LSCs are semi-transparent so that they leave the aesthetics of buildings mostly intact. To date, host polymers are commercially available polymethylmethacrylates (PMMA) that also show good compatibility with a wide variety of high quantum yield fluorophores [3]. Nevertheless, the oil-based nature of this polymer is a critical drawback for modern urban areas, being the use of solar harvesting systems and renewable materials-based devices highly desirable.

Hereby, we report the utilization of new bio-based host matrices, that is a GxMe and isosorbide derived homo-polyester and a copolymer of GxMe with 1,3-propanediol and dimethyl terephthalate, as thin film in the preparation of LSC [4] aiming at favouring the diffusion of the LSC/PV technology in urban areas.





Keywords: *Luminescent Solar Concentrators; LSC; Net Zero-Energy Buildings; NZEBs.*

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Polymer nanocomposites based on si nanostructures coupled with c nanotubes

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ABSTRACT

Polymer matrix nanocomposites are a class of versatile materials where the inclusion of appropriate nanofillers is intended to enhance or modify the polymer matrix properties. Such materials can be designed for multiple applications, spanning from agile mechanical materials or devices to drug delivery systems to sensors [1,2,3]. In this work, composite films are prepared using polyEthilene-co-Vinyl Acetate (EVA) as the polymer matrix, and both core/shell Silicon NanoStructures (SiNSs) and Multi Walled Carbon Nanotubes (MWCNTs) as nanofillers. The SiNSs are used as nanofillers owing to the possibility of tuning their optoelectronic properties through the control of their size via the occurrence of QC effects [4]. The MWCNTs are incorporated to improve the electrical conductivity of the composite. A two-step process is used for the film preparation, namely ball milling of the powders, followed by their film casting via hot-pressing. The structural, electrical and optical properties of the different nanocomposite films were systematically investigated as a function of the different SiNWs and MWCNTs loadings. In particular, the loading of 15% w/w MWCNTs improved the nanocomposite electrical conductivity of several orders of magnitude, making it highly conductive. The aim of our study is to demonstrate that the easy processing of polymers associated with the peculiar properties of Si based nanostructures and MWCNTs, could give rise to a variety of novel nanocomposites which can be exploited for future applications in optoelectronics.

Keywords: *(Nanocomposite; Nanostructures; Silicon nanostructures; Carbon Nanotubes; Optoelectronics)*

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Innovative smart nanocomposites of chitosan nanoparticles containing metal oxide as alternative fertilizers

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The estimated exponential rise of the global population for the future years and the consequent increasing food demand have nowadays promoted an uncontrolled use of large amounts of fertilizers with consequent big problems related to the water and soil waste. Indeed it is known that only about 30% of fertilizers are absorbed by the plants and the major quantity is lost in soil, water and atmosphere. In order to best the efficacy of fertilization, scientific efforts are recently devoted to developing alternative nanofertilizers[1]. Since their highly reactive surface nanoscaled fertilizers can allow an enhanced and prolonged delivery to or uptake by plants, with the consequent reduction of nutrient losses in the environment. In our work, we propose innovative smart nanocomposites of chitosan (CS) nanoparticles containing metal oxide (MOx). As MOx we have chosen Copper Oxide and Cerium Oxide nanoparticles because they are known to be efficient as growth stimulator and for the production of important metabolites of many plants. Chitosan has been selected for its well-known antimicrobial, antimycotic and biostimulant activities in plants[2]. Furthermore, the use of CS, as carrier of MOx nanoparticles, allows a smart release of its filler, the MOx fertilizer, that will be triggered in response to the environmental and plant stimuli, such as pH and chelating agent[3]. The nanocomposites have been prepared by polyelectrolite complexation, an environmentally friendly chemical preparation[4]. By strategical adjustments of synthesis conditions, i.e. pH and polymer / cross-linker ratio, we obtained an accurate control of the density and size of the nanocomposites. Their morphology and size distribution has been accurately studied by Scanning Electron Microscopy images and also compared with the hydrodinamic radii obtained by Dynamic Light Scattering. Moreover we demonstrate clearly the effective metal distribution inside the nanocomposite with nanometric spatial resolution by Energy Dispersive X-Ray Spectrometry (EDX) maps. UV-vis absorption have been also performed. Preliminary studies of nanofertilizers release on plants will be showed. All these results demonstrate that the proposed nanocomposite has great potentiality for applications in developing agrochemical carrier and pesticides delivery.

Keywords: (*Chitosan, Nanoparticles, Agriculture, Fertilization, Metal Oxide*)

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Green composite-polyurethane foams: effect of natural fillers, walnut shell and cellulose, on chemico-physical properties of polyurethane

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ABSTRACT

Polyurethane foams (PUs) are one of the most versatile classes of polymers, they are used in different sectors such as building, biomedical, transport etc. PUs are obtained through a combination of a polyaddition reaction (occurring between a polyol and poly-isocyanate) and expansion process, both occur simultaneously in presence of suitable catalysts and surfactant [1]. However, in the last decade the research in the polyurethane field is addressing the attention towards the “environment and sustainability concern” through two different directions: (a) the production of polyurethanes from renewable sources, that has become a need of time and (b) the enhancement of insulation properties and fire resistance of conventional PUs (by reducing thermal conductivity) due to the necessity of better insulation of buildings or appliances [2].

In the first case to synthesize greener polyurethane a good strategy is to use as sustainable precursor (such as bio-based polyols) derived, for example, from not edible by-product of food industry, such as the Cardanol (CNSL). In the second case to improve the functional properties of PUs, in terms of thermal insulation properties and fire resistance, the addition of nanofillers able to affect the morphology could be evaluated.

Here, base-Mannich polyol derived from cardanol was used as polyhydroxyl and Methylen diphenyl isocyanate (MDI) as isocyanate source, to synthesise rigid polyurethane foam in presence of suitable amount of catalysts and surfactant. H_2O was used as sustainable blowing agent. Furthermore, the effect of natural nanofillers, as ultramilled walnut shell and nanocellulose from biomass (at 5wt% with respect to the total amount of polyurethane) on the mechanical, thermo-degradation and thermal insulation properties were studied.

Keywords: *Polyurethane foam, sustainability, cardanol, walnut shell, cellulose*

Acknowledgement: *The work was supported by the European project H2020-BBI-JTI-2017(BIO BASED INDUSTRIES PP); REINVENT, Grant Agreement Number: 792049.*

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Complessi bimetallici di alluminio come catalizzatori per la sintesi di poliesteri

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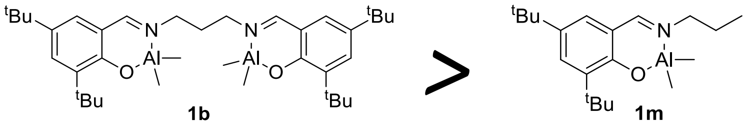
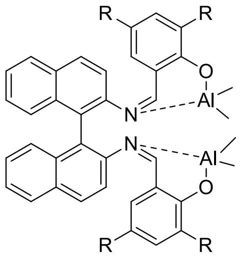
ABSTRACT

Recenti studi di letteratura hanno evidenziato come catalizzatori bimetallici presentino migliori proprietà rispetto agli analoghi monometallici in specifiche polimerizzazioni[1]. Queste osservazioni suggeriscono l’ipotesi che la combinazione di più siti catalitici in un'unica struttura di ligando può indurre percorsi di reazione cooperativi, migliorando le attività e/o le selettività[2,3,4].

Nel nostro gruppo di ricerca si è osservato che i complessi bimetallici di alluminio (**1b**) risultano estremamente attivi nella omopolimerizzazione degli epossidi, diversamente dagli analoghi monometallici (**1m**) che non mostrato alcuna attività. Inoltre, tali complessi mostrano eccellenti attività, anche di 50 volte maggiore ai rispettivi monometallici, nella polimerizzazione per apertura d’anello (ROP) degli esteri ciclici di lattide (LA) e ε-caprolattone (ε -CL)[5].



Ruolo cruciale, al fine di ottenere cooperazione, è la distanza tra le due tasche coordinative. Sono stati sintetizzati due leganti di tipo Salen recanti un ponte binaftilico rigido e dotato di chiralità assiale tra le due funzionalità imminiche. I leganti sintetizzati presentano gruppi tert-butilici o atomi di bromo come sostituenti nelle posizioni orto e para degli anelli fenossidici e quindi differiscono per ingombro sterico e per caratteristiche elettroniche. I leganti ottenuti, sintetizzati nella forma racemica e chirale, sono stati impiegati come leganti binucleanti per la sintesi di complessi bimetallici di alluminio.



rac-2: R=^{t}Bu
(R)-2: R=^{t}Bu
rac-3: R=Br

Tali catalizzatori sono stati utilizzati nelle polimerizzazioni per apertura d’anello (ROP) degli esteri ciclici e nelle copolimerizzazioni per apertura d’anello (ROCOP) di epossidi/anidridi.

Keywords: (poliesteri; complessi bimetallici d’alluminio; ROP; ROCOP)

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STIMULI-RESPONSIVE POLYMERS TOWARDS BIOLOGICAL APPLICATIONS

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ABSTRACT

Loss of myocardial motility due to genetic cardiomyopathies or valve malfunctions is the cause of an impaired ability for the heart to generate force and to pump the blood efficiently. Current treatments are extremely invasive, since they rely on heavyweight, power-demanding electromechanical contraction-assist devices.

In this context, smart biocompatible polymers, able to contract in response to an external stimulus and to allow adhesion and proliferation of cells on their surface, could be used to design artificial biomimetic muscles to restore the impaired heart contraction. Liquid Crystalline Elastomers (LCEs) meets these requirements, thanks to their peculiar structure and properties.[1] These polymers are able to change shape in response to a wide range of external trigger stimuli (heat, application of electric or magnetic fields, light) and to generate force. Moreover, they result resilient and capable to bear long-term repetitive work cycles.[1] Recently, also their biocompatibility has been demonstrated, and flat LCE films bearing homogeneous alignment showed to be suitable as scaffolds for different cell lines and to be able to direct cell alignment in myoblasts.[2]

In this communication, we will show our recent studies on LCEs in a biomedical context, to explore their use as scaffolds for cardiomyocytes, but also to design contraction-assist devices. In particular, we demonstrate how it is possible to modulate their mechanical properties by varying material composition, in terms of active and passive tension (respectively, the amount of force generated in response to light irradiation and the rigidity of the polymer), to obtain a biomimetic material with the properties of a natural muscle.[3]

Our research is currently pursuing two main objectives: the preparation of less power-demanding materials and the design of a multilayer laboratory-scale contraction-assist device. To lower the amount of operating power needed by our LCE-based materials, different modifications in polymer architecture are being explored, and will be discussed in the course of this presentation. The fabrication of a contraction-assist device, instead, is being carried out by studying the effect of the presence of multiple strips of a LCE material on the functionality of a rat heart trabecula, with the goal to use the least dye concentration to operate the device; the advances of this research line will be also presented.

The research leading to these results has received funding from Ente Cassa di Risparmio di Firenze (2017/0713), which is kindly acknowledged by the authors.

Keywords: *Regenerative medicine; artificial muscles; stimuli-responsive materials; liquid crystalline elastomers.*

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Water-processable blend nanoparticles for sustainable organic solar cells

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ABSTRACT

Organic photovoltaic (OPV) has been intensively investigated over the last decades as it represents an intriguing alternative for electrical power generation [1].

Water-processable polymer-based nanoparticles (WPNPs) received considerable attention in the OPV field because their morphology can be modulated in order to optimize the interpenetrating electron donor/acceptor networks, and thus to improve device performance [2]. Moreover, WPNPs dispersion can be obtained through miniemulsion method using a great amount of surfactants. This approach makes it possible to replace toxic and harmful halogenated organic solvents with environmentally sustainable ones in the active layer fabrication, but surfactants display an insulating behaviour and have to be removed at the end of the process [3].

Recently, our research group developed the preparation of polymer-based colloidal suspensions through miniemulsion approach using amphiphilic rod-coil block copolymers (ABCPs), bearing a rigid block (a *p*-type semiconducting polymer) and a hydrophilic flexible segment. The ABCPs are able to self-assemble without use of surfactants generating organized nanostructures under specific conditions [4]. We synthesized an ABCP series, PCPDTBT-*b*-P4VP, constituted by a low band gap copolymer PCPDTBT as rod, and tailored segments of poly-4-vinylpyridine (P4VP) as hydrophilic coil block. Furthermore, we investigated their ability to form WPNPs dispersion in aqueous medium through miniemulsion approach, neat or in blend with fullerene derivatives, without use of surfactants avoiding purification steps. The so-obtained WPNPs were optically, morphologically and electrically characterized and were tested as active layer in sustainable polymeric solar cells, obtaining a proof of concept for this original approach [5].

On these bases, our future perspectives are to develop new series of WPNPs based on other polymeric rods in order to enhance the solar radiation absorption and consequently the efficiency of the devices. Particularly, we synthetized a new rod-coil polymer, PTB7-*b*-P4VP, and NMR, MALDI, SEC and spectroscopic analysis are being carried out. We will study their capacity to self-assemble in aqueous medium to produce WPNPs with miniemulsion approach and suitable for the preparation of active layer in efficient OPV cells.

Keywords: *organic photovoltaic; rod-coil; nanoparticles; water-processable; miniemulsion*

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Influence of Graphene Oxide Oxygen Content on properties of Chitosan/Graphene oxide scaffolds

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ABSTRACT

Tissue Engineering is a highly interdisciplinary field of medicine aiming to replace compromised tissues. The process involves the presence of reparative cells, a structural template (scaffold), transport of nutrients, and molecular and mechanical regulatory factors. The scaffold should be made of biocompatible and biodegradable material and elicit no immunological or foreign body reaction. Biopolymers, including chitosan (CS), are widely used to produce scaffolds. In recent years, CS has gained much attention in bone tissue engineering [1]. The major limitation of chitosan is its low mechanical strength. Many strategies have been pursued to improve the mechanical properties of chitosan including its combination with reinforcing materials such as hydroxyapatite, silica nanoparticles and graphene oxide [2]. Graphene oxide (GO) is obtained by oxidation of graphene sheets, causing the formation of epoxy and hydroxyl groups on the basal planes and of carboxylic groups on the edges. The hydrophilicity enhancement makes GO more compatible with CS than graphene. In addition, the content of oxygenated groups in a material can strongly affect its chemico-physical properties as well as the biological ones such as citotoxicity and interaction with cellular components like proteins [3]. In this study, in order to investigate the effects of the GO oxygen content on the mechanical and biological properties, 3D porous scaffolds based on CS/GO conjugates were prepared by employing two types of GO: a GOsigma sample at low oxygen content (commercially available) and a GOexfoliated sample at high oxygen content obtained by electrochemical exfoliation of graphite. GO was covalently bonded by a carbodiimide-mediated amidation in two concentrations (0.3% and 1%). Subsequently, the scaffolds, prepared by either the salt leaching method (SL) or freeze-drying (FD), were characterized in terms of porosity, water swelling, water retention ability, thermal properties, mechanical response in compression and in vitro cytocompatibility against primary human dermal fibroblasts. The study confirmed the ability of graphene oxide to act as a reinforcing filler for chitosan scaffolds. The results suggested that the oxygen content of GO affects the final properties of GO/CS scaffolds and the biocompatibility. In particular, the conjugation of CS with a GO sample at low oxygen content resulted in scaffolds with improved compression modulus and biocompatibility compared to pristine CS. Overall, GOsigma/CS scaffolds at 1% GO content showed good potentiality for the application in tissue engineering.

Keywords: *graphene oxide, chitosan, scaffold.*

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On the use of thermal fractionation analysis for the characterization of recycled polyolefin grades

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ABSTRACT

Polyolefins represent roughly half of the whole polymers' consumption in the European market. Recently much efforts are being spent to acquire a knowledge on the properties of polymer materials sourced from recycling, although the existence of different sourcing types of recycled polyolefins implies that very different grades are available on the market. Depending on the source, mixtures of polyethylene (PE) and isotactic-polypropylene (i-PP), where the minority component usually amounts to ca. 8-10 wt% of the product, or blends of roughly 50:50 wt% of i-PP and PE can be found. These materials are characterized by a bad balance of properties, mostly due to the immiscibility of PE and i-PP. Nevertheless, the properties optimization of these materials for high-end applications is a paramount goal for major polyolefins producers, both for the economic implications and for the aspects of social responsibility.

In general, the content and the composition of PE and iPP in a recycled grade is a valuable information difficult to obtain due to the complexity of these systems. Thus, molecular fractionation of recycled grades is an obvious approach in order to identify e.g. LDPE, MDPE, HDPE content in a complex blend. However, traditional fractionation methods, like Temperature Rising Elution Fractionation ((TREF) and crystallization analysis fractionation (CRYSTAF),[1] are time-consuming, handling toxic solvents, and requiring expensive instruments that cannot always be used to this purpose due to the presence of cross-linked particles that would plug the columns. A promising route is represented by Successive Self-nucleation and Annealing (SSA) technique,[2-3] which employs easy and inexpensive DSC methods and, thanks to the inherently fast crystallization behavior of polyolefins, can be carried out at high rates, substantially reducing the analysis time.

SSA is based on the sequential application of self-nucleation and annealing steps to a polymer sample in order to enhance the potential molecular fractionation that can occur during crystallization due to the constitutional heterogeneity of the chain structure.

In this investigation we show the thermal fractionation results that can be achieved by applying the SSA protocol to different blends of recycled polyolefins. The large difference in melting points between the two main components has required the development of a tailor-made self-nucleation protocol, in order to separately study the detailed distribution of crystallizable sequence lengths of the two polymers. Thanks to the optimized thermal protocol, the recycled sample could be efficiently fractionated, highlighting the presence of iPP and PE chains with different crystallizing capability, due to the different distribution of constitutional defects which break the regularity of the polymer repeating units.

A comparison between SSA results and solution-based fractionation techniques has allowed us to establish the limit of applicability of the former technique for these complex systems and to effectively propose the method as a valid alternative to traditional and more established characterization methods.

Keywords: (*polyolefins; crystallization; blend; fractionation; recycling*)

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BIODEGRADABLE MOSQUITO REPELLENTS POLYMER FIBERS

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ABSTRACT

The study of blends and fibers of poly(L-lactic acid) (PLLA) containing a mosquito repellent agent, N,N-diethyl-3-methylbenzamide (DEET) is discussed.

DEET is the key active ingredient in many commercial mosquito-repellent formulations, and is also an environment-friendly compound, which well matches the biodegradability and compostability of PLLA.

Recently, it was proven that PLLA can also be used as a carrier/drug-delivery reservoir for DEET [1,2]. Initial investigations focused on evaluation of the solvent-rich part of the PLLA/DEET phase diagram, information considered as prerequisite for preparation of scaffolds for controlled and retarded release of DEET to the environment.

We prepared defect-free fibers by electrospinning and polymer blends by compression moulding for morphological, crystallinity and thermal studies.

Incorporation of DEET into electrospun fibers varies the thermal properties of PLLA fibers, as it leads to a reduced glass transition with the increase of DEET content. DEET also affects crystallization kinetics, acting as a plasticizer, of PLLA, with a delayed nucleation upon melt crystallization, but faster crystal growth rate, due to the enhanced mobility of PLLA chains upon addition of the plasticizer [3]. More important, evaporation of DEET is delayed in the electrospun fibers, which may allow smooth and controlled release of the insect repellent.

Thermal, morphological and structural characterization revealed that the PLLA/DEET electrospun fibers have potential as novel material for controlled release of DEET, which, coupled with the ease of fabrication, can provide innovative tools for fighting mosquito-caused diseases [4].

Keywords: Electrospinning; Poly(L-lactic acid) (PLLA); N,N-diethyl-3-methylbenzamide (DEET); Plasticizer; Crystallization kinetics.

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Structural Characterization of Olefin-based Multiblock Copolymers Obtained through Chain Shuttling Technology

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ABSTRACT

A major breakthrough in the expansion of properties of polyolefins has been the development of single-site organometallic catalysts that allow living polymerization and synthesis of olefin-based block-copolymers,[1] in which apparently irreconcilable properties may be combined together, obtaining elastomers with high melting points and stiffness. The drawback of living polymerization consists in entailing growth of just one polymer chain/metal center. To reduce catalyst consumption, coordinative chain transfer polymerization techniques were implemented, involving the usage of a single transition metal catalyst and a main group metal alkyl acting as chain transfer agent (CTA).[1] The transfer of the growing chains from the catalyst to the CTA enables growth of multiple chains/active center, saving atom economy and allowing for the synthesis of BCP starting from the resultant polymers.[1] Recently, using high throughput tools, the chain shuttling polymerization was discovered as an alternative and efficient way to produce OBC in a single step.[2] In particular, ethylene/1-octene multi block copolymers (EOBC) were synthesized by the Dow Chemical Company (trade name INFUSE) using a couple of organometallic catalysts and a CTA via a reversible chain transfer mechanism. EOBCs are thermoplastic elastomers characterized by the alternation of crystallizable hard blocks and amorphous soft blocks with low and high octene concentration, respectively and a statistical distribution in the block number and length/chain.[2] Due to the chain microstructure, EOBCs with similar molecular characteristics show different properties. A pathway to clarify the intricate chain microstructure and its role on the EOBC properties is presented.[3,4]

Keywords: *chain shuttling; olefin-based multiblock copolymers; thermoplastic elastomers; structure/properties relationship*

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Structure and polymorphic behavior of Poly(2,6-dimethyl-1,4-phenylene oxide) in axially stretched films

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ABSTRACT:

Nanoporosity in crystalline phases has been described only for two industrial thermoplastic polymers. They are syndiotactic polystyrene (sPS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which have received attention both in scientific studies as well as in industrial applications (1,2) The crystalline structures of the nanoporous crystalline (NC) forms of sPS have been well studied (3-5). For PPO, on the contrary the crystalline structures of the NC forms are still unknown, mainly due to the absence of diffraction patterns of oriented samples (6). With this inspiration, we are exploring the structure and polymorphic behavior of PPO polymer, under uniaxial stretching at different temperatures and draw ratios. Some of the preliminary results (polarized FTIR) relative to uniaxially stretched PPO films are displayed in Figure 1.

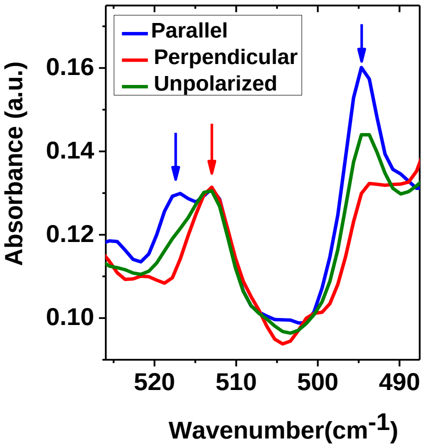

Figure 1. Polarized FTIR spectra for uniaxially stretched PPO film with a nanoporous-crystalline form.

Keywords: (*Nanoporous crystalline phases,* poly(2,6-dimethyl-1,4-phenylene oxide), *uniaxial stretching, orientation,and polymorphic behavior*)

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Polyurethane foams for thermal energy storage applications

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ABSTRACT

In recent years the environmental pollution related to the use of fossil fuels promoted the interest in sustainable resources and the development of new strategies to reduce the waste of thermal energy in building constructions. Thermal energy storage and release with phase change materials (PCM) can provide a tool for a better thermal energy management [1]. PCMs are characterized by phase transformations (solid/liquid) within a defined temperature range. During the melting process the material remains at a constant temperature absorbing energy from the environment, while during solidification the thermal energy is released [1]. Polyurethane (PU) foams are widely used for the insulation of buildings thanks to their low thermal conductivity, their high mechanical and chemical stability and low density [2]. The aim of this work is the development of novel multifunctional polymer foams for the thermal/acoustic insulation, having thermal energy/storage release capability.

Polyol and isocyanate provided from Kairos Srl (Verona, Italy) were used for the production of the PU foams. Commercial grade microencapsulated paraffin MPCM24D provided by Microtek Laboratories Inc. (Dayton, USA), having a mean size of 20 µm and a melting temperature (T_m) of 20 °C, was used as PCM. Foamed samples with PCM concentration between 10 and 50 wt% were obtained. The cryofractured surfaces of the samples were observed through a Zeiss Supra 40 scanning electron microscope (SEM). The thermal properties of the samples were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The compressive properties were assessed through an Instron 4502 testing machine. The heating/cooling profiles of the prepared panels were assessed through a Flir E4 infrared camera. The thermal conductivity of the panels was measured in different temperature intervals using a thermofluximeter LaserComp FOX 314.

SEM observations revealed a good dispersion of the microcapsules into the PU matrix, and the capsules retained their structural integrity, even at elevated PCM amount. The melting enthalpy of the paraffin inside the PU foam, evaluated through DSC analysis, was similar to the expected theoretical value, confirming thus the good dispersion of the PCM inside the matrix and the good thermal energy storage potential of the prepared materials. From thermogravimetric analysis it was clear that the degradation behavior of the matrix was not impaired by microcapsules addition. From the mechanical tests it was observed that the compressive strength of the resulting foams was not influenced by microcapsules addition. Finally, thermal characterization of panels revealed the beneficial effects due to the presence of the PCM, with the presence of a temperature plateau in correspondence of the melting temperature of the paraffin.

Keywords: (*foams; polyurethane; phase change materials; thermal energy storage*)

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Controlling the environmentally induced rearrangements of perfluoropolyalkylethers at photopolymers surfaces

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ABSTRACT

Perfluoropolyalkylethers (PFPAEs) show low polarizability, strong electronegativity, high C−F bond energy, and exceptional mobility thanks to the oxygen bridges; they represent a special class of fluoropolymers with remarkable properties (low glass transition temperature, high thermal stability, excellent chemical inertness, low surface energy, tunable mechanical properties). They, are commercially available, mostly obtained from the photooxidation of perfluoroolefins. [1]–[3] In this work, new functionalized oligomers containing a PFPAEs structure with end groups reactive in photopolymerization were synthesized by anionic polymerization of hexafluoropropoxide (HFPO), and used in very low concentration (≤2 wt.%) as efficient surface modifying agents of epoxy resins to obtain hydrophobic photocured copolymers. [4]

Thanks to the spontaneous surface segregation of the fluorinated comonomer, which migrate to the free surface due to its low surface energy, improved hydro- and oleophobicity can be imparted to the copolymer in a simple and effective way. [4] However, due to their high chain mobility, the fluorinated chains can rapidly rearrange upon contact with different surrounding environments (e.g., water, oil, polluted air), leading to a substantial reduction in material performance. With the aim of controlling the fluorinated dangling chains reorganization at the copolymer surfaces, different approaches have been investigated. Specifically, to hinder the mobility of the fluorinated segments, the length of the fluorinated comonomer chain, the epoxy matrix stiffness, and the type of functional PFPAE end-group have been tuned. We thus demonstrate that applying one of these strategies, it is possible to reduce or even inhibit the environmentally induced reorganizations of PFPAE chains, retaining the advanced surface performances of the fluorinated photocured copolymers.

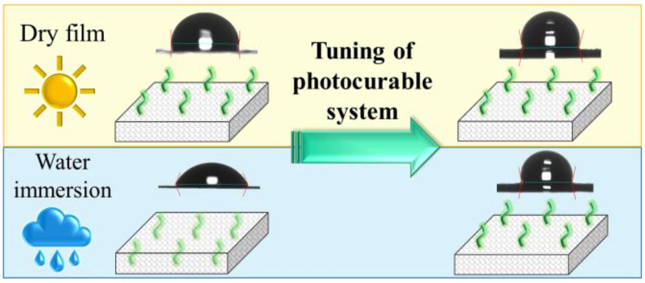

Fig. 1 Scheme illustrating the control on the environmentally induced rearrangements of PFPAE chains when one of the investigated strategies is applied.

Keywords:
(*Perfluoropolyalkylethers; Photopolymerization; Rearrangements; Hydrophobicity; Oleophobicity*)

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Desing and fabrication of polymeric micro-scaffolds for *in vitro* modular tissue engineering

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ABSTRACT

The bottom-up realization of three-dimensional (3D) hybrid structures composed of both biomaterials and cells are one of the most interesting and novel approach for in vitro and in vivo tissue regeneration [1]. Biocompatible and biodegradable polymers are essential elements of these bottom-up approaches. They serve as template structures for cells adhesion, proliferation and 3D assembly [2]. The aim of this project is the design and manufacturing of novel porous polymeric micro/particles to be used as micro-scaffolds for modular tissue engineering purposes. To this aim, we developed a fluidic emulsion/porogen leaching process for micro/scaffolds fabrication and we optimized the composition of the polymeric solution and the flow rates of the dispersion and continuous phases to control sample morphology, size distribution and shape. The micro-scaffolds are made of a biocompatible and biodegradable polymer, namely polycaprolactone (PCL), and we used polyethylene oxide as water/soluble biocompatible porogen. The morphological and structural properties of micro-scaffolds were characterized by scanning electron microscopy (SEM) and Micro-CT analysis. Then the micro-scaffolds were characterized in vitro by using human dermal fibroblasts and endothelial cells to assess their capability to promote cell adhesion, colonization, proliferation and extracellular matrix biosynthesis and blood vessels formation. The SEM and Micro-CT results of micro-scaffolds evidenced a highly porous morphology and structure with proper pores interconnectivity. The in vitro biocompatibility tests showed that micro-scaffolds are biocompatible, enabled cells adhesion and proliferation as well as promoted the formation of hybrid self-supporting structures. This study demonstrated that the proposed approach enabled the design and building cell/micro-scaffold hybrid systems with highly oriented pores suitable to promote and guide blood vessels formation in vitro and in vivo.

Keywords: *bottom-up tissue engineering; fluidic emulsion; micro-scaffolds; polycaprolactone; polyethylene oxide.*

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PREPARAZIONE E CARATTERIZZAZIONE DI COATINGS FUNZIONALI CONTENENTI FILLER CARBONIOSI MEDIANTE UV-LED CURING

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ABSTRACT

La tecnologia ultraviolet light-emitting diodes (UV-LED) curing è stata impiegata in questo studio per la realizzazione di nanocompositi a base carboniosa.
Lo scopo è di sviluppare dei film a matrice polimerica termoindurente funzionalizzati con multi walled carbon nanotubes (MWCNTs) e biochar (derivato da fondi di caffè esausto attraverso pirolisi), utilizzando un sistema di polimerizzazione radicalica estremamente vantaggioso in termini di risparmio energetico, economico e di sostenibilità ambientale. Rispetto ai processi termici convenzionali, infatti, l'UV-LED curing è condotto a temperatura ambiente, non prevede l'utilizzo di solventi, è caratterizzato da elevate velocità di reazione e da bassi consumi di energia [1].
La tecnologia UV-LED curing sfrutta una lampada che emette una radiazione monocromatica nel vicino ultravioletto con una lunghezza d'onda di 395 nm, la stessa che il fotoiniziatore deve assorbire per generare radicali che danno inizio alla reazione di reticolazione.
Il sistema da reticolare si è ottenuto aggiungendo ad una resina commerciale acrilica bifunzionale (bisfenolo A diacrilato), il fotoiniziatore (2,4,6-trimetilbenzoil-difenil-fosfinossido) e riscaldando a 80°C per facilitarne la dissoluzione. Tale miscela è stata poi usata per la preparazione di compositi che differiscono per il tipo e la percentuale in peso di filler (MWCNTs, biochar), disperso all'interno del sistema attraverso sonicazione. La dispersione liquida, così preparata, è applicata su supporto vetroso attraverso una barra stenditrice da 200 µm. Il supporto, rivestito dal sottile strato di resina, è stato quindi sottoposto a irraggiamento impiegando l'unità Heraeus Noblelight UV-LED NC1, operando in condizioni dinamiche (velocità del nastro trasportatore=1.5 m/min).
I nanocompositi sono stati sottoposti a diverse tecniche di caratterizzazione (reologica, termica, dinamico-meccanica, elettrica), per valutare l'influenza dei filler sulla morfologia, sulle proprietà termiche e sulla conducibilità termica ed elettrica. Lo scopo è di sfruttare da un lato l'elevato contenuto di carbonio del biochar [2] e l'effetto tunneling dei MWCNTs [3] per migliorare la conducibilità elettrica e dall'altro l'elevato numero di fononi dei due filler [4,5] per migliorare la conducibilità termica dei film polimerici.

Keywords: (*UV-LED curing; MWCNTs; biochar; nanocompositi*)

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Nanocomposite alginate-ZnO membranes prepared via electrospinning technique

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ABSTRACT

Sodium alginate represents a class of naturally occurring linear polysaccharides widely employed in several fields due to their unique properties. In particular, the use of alginate-based materials for biomedical applications has aroused a great interest in the last decades with particular attention to the development of wound healing patches, which however must usually be subjected to chemical crosslinking reactions to increase their stability with the disadvantage to strongly decrease their biocompatibility; moreover, the obtained structures do not considerably promote the cellular adhesion and proliferation.

In the present work, electrospinning technique was employed to prepare nanocomposite alginate-based membranes embedded with ZnO nanoparticles (ZnO-NPs) which were especially synthetized via a "green" sol-gel method to maintain the biocompatibility as high as possible. Alginate/poly(ethylene oxide)/ZnO-NPs mixed systems were prepared and rheological tests carried out to select the most suitable to be electrospun according to the viscosity results; the molecular structure of alginate was found to play an important role in the establishment of strong interactions between the polymer and the used nanoparticles, thus influencing the solution spinnability. An innovative washing-crosslinked process was developed treating the samples with a washing cycle (ethanol at T = 70 °C) and subsequently with a ionic crosslinking using Sr^{2+} ions; thermogravimetric analysis and Fourier transform infra-red spectroscopy were applied to assess the samples composition, demonstrating the total elimination of poly(ethylene oxide) and the efficiency of the used approach to obtain stable pure alginate mats. The morphological investigation, coupled with EDX spectroscopy, showed a structure with smooth and homogeneous nanofibers (diameter ~ 120 nm) and a global high porosity; moreover, no NPs aggregates could be detected, indicating their good dispersion within the mats. The mechanical behaviour of the prepared mats was assessed trough dynamic mechanical analysis and uniaxial tensile test, showing similarities with the human skin; moreover, the prepared membranes displayed high water vapor permeability and hydrophilicity. Methylene blue and congo red were then used as drug model molecules in order to study the adsorption/release kinetics and evaluate the possibility to use the mats as drug delivery systems. Finally, the biological response of the samples was investigated using a commercial collagen-based product as standard; the extremely good results indicated the actual prospect to use alginate-based mats for the regeneration of skin and soft tissues.

Keywords: *Sodium alginate; electrospinning; rheology; mechanical characterization; biological properties*.

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Nitroxide Mediated Polymerization as New Tool in the Box of Polymeric Deterministic Doping

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ABSTRACT

An extremely accurate control of the dose and the position of dopant atoms in silicon, named *Deterministic Doping*, is the necessary condition to ensure the continuous downsizing of electronic devices. Recently our group proposed an innovative technology based on polymers functionalized by a terminal group reactive with the native oxide layer on the silicon substrate and containing a phosphorus atom, the most common n-type dopant[1]. Exploiting the self-limiting nature of the *grafting to* reactions, it was demonstrated that it's possible to accurately control the grafting density, and conseguently the amount of phosphorus atoms bonded to the substrate, simply tuning the molecular weight of the polymer chains. A critical point of this technology is the synthesis of the functionalized polymers, made by *Atom Transfer Radical Polymerization (ATRP)* followed by a phosphorylation reaction. This procedure requires water free enviroment and several purification steps. An easier way to obtain polymers with the above structural features is to use the *Nitroxide Mediated Polymerization (NMP)* with *N*-*tert*-Butyl-*N*-[1-diethylphosphono(2,2-dimethylpropyl)] Nitroxide (SG1)[2] as radical controller. In this work polystyrene samples with molecular weight ranging from 2.5 to 52 kg/mol and narrow molar mass distribution were synthesized using SG1 as radical controller and were grafted onto silicon oxide substrates by *Rapid Thermal Processing (RTP)* technology[3]. The thickness of the grafted layer was observed to rapidly increase with annealing time reaching a thickness plateau value, that is significantly lower than the value obtained in the conventional *grafting to* reactions, when the pseudo-plateau thickness value approach two times the radius of gyration of the corresponding polymer chain. In addition, the plateau thickness increases as the molar mass of the grafting polymer increases for molecular weights lower than 15 kg/mol and then reaches a somewhat limiting thickness, in complete contrast to the classical grafting behavior. Despite this, the phosphorus amount linked to the surface is perfectly equal to the density of the grafted chains estimated from the thickness of the layer. Matching these data with those obtained simulating the *grafting to* reaction with direct exposure probe analysis[4], we concluded that two competing reactions are present during RTP, a grafting reaction and a degradation of the SG1 moiety. The perfect control of the phosphorus amount obtained, suggests this new system as a promising candidate in the *Deterministic Doping* scene.

Keywords: (*Doping; SG1; Grafting; Nitroxide Mediated Polymerization*)

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A NEW CLASS OF VITRIMERS BASED ON ALIPHATIC POLY(THIOURETHANE) NETWORKS WITH SHAPE MEMORY AND PERMANENT SHAPE RECONFIGURATION

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ABSTRACT

Thermosetting polymers are very useful in a broad range of industrial applications, due to their chemical, thermal and environmental resistance and because of their excellent mechanical performances. However, the existence of covalent bonding in the three dimensions of the network prevents reshaping, reprocessing, or recycling and makes difficult their reparation. To avoid these drawbacks a new family of materials, called vitrimers has been developed, they consist in three-dimensional polymeric structures with dynamic covalent bonds within an organic network, which can lead to topological changes without affecting the average crosslinking degree. [1,2] These new materials combine the excellent performance of thermosets with some of the processability advantages of thermoplastics. In recent years, different reversible exchange reactions have been explored for the preparation of vitrimers. [3] These exchange reactions are the responsible of the reformation of the network structure.

In the present study, we report a new class of vitrimeric materials based on poly(thiourethane) networks. Because the vitrimeric behaviour in poly(urethanes) was attributed to a transcarbamoylation reaction, it was hypothesized that trans-thiocarbamoylation could also lead to a rapid exchange allowing reshaping, self-welding and stress dissipation, even in a more efficient way, due to the presence of sulphur, which has an enhanced reactivity in front of its oxygen analogues. These materials can be easily prepared from readily available isocyanate and thiol monomers, respectively the hexamethylene diisocyanate (HDI) and trimethylolpropane tris(3-mercaptopropionate) (S3), in the presence of Lewis acid used as catalyst, the dibutyltin dilaurate (DBTDL). The reaction has a click nature and therefore leads to highly homogeneous networks without being accompanied by side-reactions. [4] The materials studied behave as conventional thermosets until topological rearrangement started. Freezing topological temperatures (Tv) between 132 and 95 °C were determined depending on the amount of catalyst in the material. The vitrimers prepared showed good shape memory and welding abilities and a high optical transparency and therefore they have a great potentiality in advanced engineering applications. The occurrence of the trans-thiocarbamoylation reaction, responsible of the rearrangement, has been confirmed by using model compounds. The materials remained unaltered after reprocessing, which was proved by means of FTIR and thermomechanical studies.

Keywords: (*vitrimers; poly(thiourethane); thermosets; shape-memory; click reaction).*

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Strategies to increase T_g and mechanical performance of dual-curing thermosets for advanced applications

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ABSTRACT

Sequential dual-curing processing is becoming attractive due to the possibility of being exploited in current and novel multistage technological applications and in two-stage preparation of materials with tailorable intermediate and final properties. Complex shape-memory devices can be obtained taking advantage of the intermediate thermoset processing and used in mechanically demanding applications such as thermomechanical actuators [1].

Our research group have successfully developed a novel thermally activated dual-curing system based on sequential thiol-acrylate and thiol-epoxy reactions [2]. The thermomechanical and mechanical characterization of the final thermosets revealed a wide range of properties simply varying the proportion between acrylate and thiols group. Complex-shaped thermosets were obtained, and the shape-memory behaviour was demonstrated [3]. Although the highly deformable thiol-acrylate intermediate network enables the possibility to process these materials in complex final shapes, it also leads to relatively soft final materials which are not able to perform an appreciable work output. Moreover, thermomechanical analysis evidenced broad glass transitions process which could lead to a slowdown of the recovery process [4].

In this work we investigated various strategies to improve the thermomechanical final properties of these thermosets varying the formulation components. Firstly, we analyze the effect of increasing the functionality of the epoxy component mixing the *Diglycidyl ether of bisphenol A* (DGEBA) with different amounts *tri(2,3-epoxypropyl)isocianurate* (ISO). Afterwards, the effect of the acrylate part composition is investigated mixing *Bisphenol A glycerolate (1 glycerol/phenol) diacrylate* (BAGA) and *Tricyclo[5.2.1.02,6]decanedimethanol diacrylate* at different proportions. *Pentaerythritol tetrakis(3-mercaptopropionate* is used as thiol crosslinker and the ratio between acrylate and thiol groups is fixed at 0.5. Curing processes are analysed by means of *Differential Scanning Calorimetry* dynamic analysis to demonstrate that changes in composition do not affect the sequentiality of the process. Effects of the different percentage of ISO and BAGA on final thermosets thermomechanical properties are also evaluated by means of *Dynamo Mechanical Analysis.* Finally, shape-memory devices with complex spring shape are prepared and tested demonstrating the versatility of these materials and the improvements in their shape-memory behaviour.

Keywords: *Epoxy; Acrylate; Dual-curing; Shape-memory; Actuators;*

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Radiation-induced grafting of HDPE-ATZ composites with chitosan for biomedical purpose

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In the last years, a strong effort has been devoted to fabricating bioactive composites as bone analogue replacement by reinforcing bio-inert polymers with different bioactive fillers [1], aiming at improving the mechanical properties of the polymer matrix and promoting the growth of the biological tissue after implantation. Recently, the addition of small amount of Alumina toughened Zirconia (ATZ) to Ultra High Molecular Weight Polyethylene (UHMWPE) has been proven as a promising way to enhance Young modulus, yield stress and hardness, without compromising the other mechanical parameters. Surprisingly, small amount of ATZ is able to enhance hydrophobicity and cell interaction (adhesion and viability) with respect to those of the unfilled polymer [2] extending the possible applications of UHMWPE in the biomedical field. In this light, we have dispersed ATZ in high density polyethylene (HDPE) by melt extrusion process obtaining a good dispersion of the bioactive filler in the polymer matrix and an improvement of HDPE mechanical properties. In view of preventing the disease arising from infections, chitosan, the most promising bio-polymer for tissue engineering, has been chosen as possible component of HDPE-based composites because of its proven antimicrobial properties [3]. In fact, it is well known that an important aspect to keep an eye on during orthopedic procedures dealing with prosthetic implants is the possible complication due to infections onset in the surgical site. The mean rates of infections related to surgery that involves implants are in the range of 1.5% in the case of total knee implantation and 6.8% for femur head replacement, where HDPE is widely used [4].

In this work, radiation-induced grafting of HDPE-ATZ composites with chitosan has been considered to induce a surface modification of these composites. The grafting was initiated by irradiation with a low energy electron beam system [5]. After the irradiation, the grafting process is conducted with a solution of chitosan and acetic acid at 70°C under stirring for different reaction time. As treated materials were washed with acetic acid solution, dried and stored at -80°C. Wettability measurements, SEM-EDX and ATR spectroscopy were performed to provide evidence about the feasibility of this surface modification process.

Keywords: *biomaterial; composites; chitosan; radiation process; grafting.*

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Novel polymers from terpenes

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ABSTRACT

In an age of dwindling fossil resources and increasing environmental awareness it is becoming more and more urgent to find greener alternatives to petrol-based polymers.
Recently terpenes attracted interest as a viable feedstock for bio-based polymers. Previous research showed that the most abundant terpenes could be converted to (meth)acrylates, and that these monomers could be easily polymerised via free radical polymerisation figure 1 [1].

This project focuses on one of these monomers, carvone (meth)acrylate. Its two available double bonds were selectively reacted in several ways, leaving the (meth)acrylate moiety intact. The alkene functionalisation yielded several monomers with diverse properties, from multifunctional to hydrophilic monomers. The new monomers were then homo or co polymerised in several combinations. Monomers and polymers were characterised with different analytical techniques (NMR, X-ray crystallography, GPC, DSC, TGA)

On the basis of their properties, selected polymers were electrospun to produce non woven materials composed of continuous fibres with diameters in the nm scale. By exploiting the monomer multifunctionality, the fibres surface was then functionalised with different chemical species and characterized by FT-IR, MALDI-ToF MS, and XPS. The electrospun materials are currently being tested for various applications, including filtration membranes, composite materials reinforcement and supports for enzyme immobilisation.

In parallel, hydrophilic monomers were polymerised in amphiphilic block copolymers, in order to study their phase separation and phase morphologies, and their application as surfactants or in personal care products.

Keywords: *terpenes; biopolymers; electrospinning; nanofibers; amphiphilic materials.*

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Exploiting block copolymer self-assembly processes to obtain new hybrid nanocomposite materials for photovoltaic applications

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ABSTRACT

Nanoscience is still searching for simple methods to arrange nanosized objects by means of bottom-up processes. Composite structures on the nanometer length scale are very promising candidates for next-generation materials [1]. It is well known that metal nanoparticles (NPs) possess unique, size-dependent properties associated with their large specific surface area. Those properties can be exploited through the immobilization and the assembly of nanoparticles on an appropriate substrate. Microphase separation of block copolymers (BCPs) is a phenomenon able to spontaneously produce ordered nanostructured morphologies [2]. Most importantly, BCPs domains sizes can be finely controlled, and in turn can act as hosts for sequestering nanoparticles of appropriate chemical affinity and geometry [3]. Surface decoration of NPs is a procedure often used to assure the selective inclusion in one of the BCP domains by chemical compatibility. In this way the NPs will reflect the regular organization of the BCP domain in which they are embedded. The kind of nanocomposite systems represent very promising engineering nanostructured materials endowed with unprecedented properties. In the present work a symmetric diblock copolymer, PS-b-PMMA, able to give by self-assembly a lamellar morphology, was used as host for n- and p-type semiconductor NPs in different nanodomains, with the aim of obtain a photoactive layer in bulk heterojunction solar cells devices. The inclusion of the two NPs in the BCP lamellae will create a bi-continuous interpenetrate network of charge carriers between the two electrodes, minimizing charge recombination and thus increasing the device efficiency. Morphologies characterized by the desired degree of order and orientation were obtained resorting to indium tin oxide (ITO) as transparent support, a grafting to approach, consisting in covering the ITO surface with a PS-PMMA random copolymer (RACO) [4], deposition of PS-b-PMMA on the so neutralized ITO surface, coupled to appropriate thermal annealing procedures of the final ITO/RACO/BCP systems. In the successive step, a procedure was set up for the selective removal of PMMA blocks by means of far-UV radiation treatments, with the purpose of generating nanochannels onto ITO surface. Metal NPs, ZnO and CdSe, were synthetized with appropriate surface functionalization in order to assure their selective inclusion in the PS and the nanochannel, respectively. The BCP morphology and the NPs inclusion were assessed by a transmission electron (TEM) and atomic force (AFM) microscopy analysis.

Keywords: *Block copolymers; self-assembly; metal nanoparticles; nanotechnology.*

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THE TEMPERATURE-RESPONSIVE NANOASSEMBLIES OF AMPHIPHILIC RANDOM COPOLYMERS BY SINGLE-CHAIN FOLDING IN WATER

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ABSTRACT

Special self-assembled single-chain nanostructures are generated in solution by amphiphilic copolymers, in which the hydrophilic and hydrophobic moieties interact separately and very differently with each other and with the external environment and stimuli, such as temperature (Figure 1).

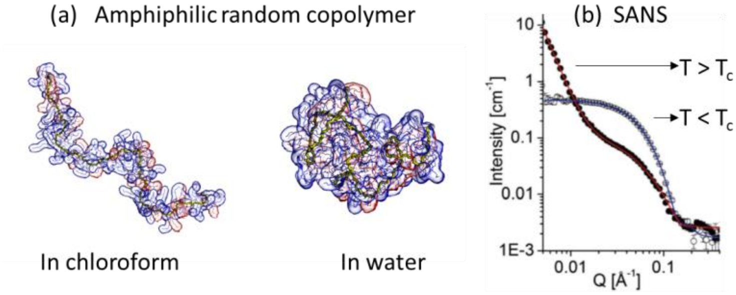

Figure 1. (a) Comparison between final structures of folding trajectories in non-selective (chloroform) and selective (water) solvents. (b) SANS profiles and the corresponding best fits to ellipsoidal model of D_2O solutions (2 mg mL^{-1}) of a typical copolymer above and below T_c

In our work, amphiphilic random copolymers composed of hydrophilic poly(ethylene glycol) methacrylate (PEGMA) and hydrophobic perfluoroalkyl acrylate (FA)[1] and siloxane[2] methacrylate (SiMA) counits could self-fold in a selective solvent into compact single-chain nanoassemblies[3] via an intramolecular self-association process. Moreover, copolymers based on PEGMA have the advantage to be soluble in both water and organic solvents and to be thermally responsive in water solution, due to the occurrence of a lower critical solution temperature-type (LCST) transition. Thus, on heating above a critical temperature T_c, multichain microassemblies are formed that revert back to nanoassemblies on cooling below T_c. This temperature-responsive transition is fully and sharply reversible.

The molecular weight, dispersity and composition of such copolymers could be tuned in a predictable way by ATRP in order to investigate the influence of macromolecular parameters on the self-assembly behaviour. Moreover, either a julolidine-based initiator or comonomer could be used to label the copolymer and to probe the aggregation state of the self-assembled confined system. Light and neutron scattering techniques revealed the distribution of these nanoassemblies in selective solvents, especially water.[1] Finally, molecular dynamics simulations showed the folding trajectories of such single-chain into prolate globular nanoassemblies with a structural variability in water solution at room temperature.[4]

Keywords: *Amphiphilic polymers; Single-chain folding; Self-assembly; Fluorescent molecular rotors; Molecular dynamics*

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Dynamic vulcanization of polyester polyols in poly (L-lactic acid) as an effective way for PLLA toughening

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Abstract

Melt blending of polymer is an effective way to achieve an attractive combination of polymer properties. Dynamic vulcanization of fatty acid based polyester polyol with glycerol and PLLA in the presence of Hexamethylene Diisocyanate (HDI) was performed with the aim of sustainably toughening PLLA [1]. The dynamic vulcanization took place in a Brabender, leading to the formation of a PLLA/PU biobased blend. Melt torque, FTIR, and gel fraction analysis demonstrated the successful formation of vulcanized PU inside the PLLA matrix. SEM analysis shows that the PLLA/PU blends exhibit sea-island morphology. Gel fraction analysis revealed the formation of a rubbery phase, insoluble in chloroform, inside the PLLA matrix. The content of PU in the blends played an important role on the mechanical properties, the thermal stability, and the crystallization behaviours of the formed PLLA/PU blends. The overall crystallization rate of PLA was noticeably decreased by the incorporation of PU while POM analysis revealed that the presence of PU network inside the PLLA resulted in a faster PLLA nucleation step. The mechanical properties were enhanced by the formation of PU network; the impact strength significantly increased while the Young's modulus decreased. However, the thermal stability of the blends was slightly reduced compared to neat PLA. With improved toughness, the PLLA/PU blends could be used as substitutes for some traditional petroleum-based polymers.

Keywords: PLLA; Polyurethane; dynamic vulcanization; toughening, crystallization

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HAVOH/MWCNT composites with tailored filler segregation for FDM 3D printing technology

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ABSTRACT

The development of nanocomposite materials for 3D printing application has recently attracted remarkable interest since the addition of nanofillers as Graphene nanoplatelets and/or Carbon nanotubes in the polymeric matrix allows the possibility to tailor the properties of 3D-printed objects. [1-2] In particular, in the preparation of nanocomposite filaments for Fused Deposition modeling (FDM), which is one of the most used 3D printing technology, the homogeneity of the dispersion of the filler into a polymeric matrix plays an essential role in the final properties of the nanocomposite material. Within this context, the Imidazole-based ionic liquids (ILs) are able to prevent the aggregation of the carbonaceous filler through Coulomb, van der Waals, hydrogen bonding, and π-π interactions [3,4] resulting in an improvement of the distribution of the filler in the polymeric matrix. Hence, the ILs allow reducing the amount of filler needed in the fabrication of polymer nanocomposites with enhanced physical properties [4] such as electrical, electromagnetic, mechanical, and thermal properties. In this study a new competitive conductive nanocomposite for FDM 3D printing, characterized by a modified polyvinyl alcohol (HAVOH) as polymeric matrix, MWCNTs as filler and Benzyl Imidazole Chloride (BenzImCl) as IL, was realized by filament extruding. In particular, nanocomposite samples were prepared by "solvent wrapping method" in which particles of the polymer are added in the MWNTs-IL dispersion and covered by the carbonaceous filler. The obtained powder was used to produce both compact samples for compression moulding and filament extrusion. The resulting distribution of the MWCNTs in the polymeric matrix was investigated by polarized optical microscopy (POM), scanning electron microscopy (SEM) and Raman Spectroscopy. Structural, thermal, mechanical and electrical properties of the samples were also analysed. Finally, HAVOH-MWCNTs nanocomposite filaments were used for printing samples which exhibited satisfying electrical properties.

Keywords: *3D printing; Graphene; polymer nanocomposites; Ionic liquid; Electrical properties.*

Acknowledgements

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1,3-Dioxolane-4-ones: a path to explore toward highly functionalized polyesters

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ABSTRACT

Within the pursue of environmentally friendly alternatives to oil-derived plastics, polylactic acid (PLA) has emerged as one of the best candidates, thanks to a winning combination of green nature and good processability properties. In addition, PLA is biocompatible and its degradation byproducts are harmless in vivo. On the other side of the coin, however, drawbacks such as poor toughness and poor thermal stability strongly limit its industrial applicability. For this reason, PLA-related research is usually aimed at improving its lacking properties, while preserving its good features. Alongside nanocomposite preparation and blending strategies, the synthesis of highly functionalized PLA-based materials, endowed with tailored properties, is scarcely investigated, due to a reduced monomer scope. Within this field, the development of O-Carboxyanhydrides (OCAs) chemistry appeared as a powerful tool, giving access to variegated structural motifs and easy polymerizations.[1] However, synthesis of OCAs relies on highly toxic reagents and their inherent instability prevents storage for prolonged time. Looking for a new monomer, able to preserve access to structural modification and reactivity while overcoming inefficient synthesis of OCAs, 1,3-dioxolan-4-ones (DOXs) appear as promising candidates. DOXs synthesis is straightforward and their high reactivity is ensured by the release of a small molecule during the polymerization, providing a strong driving force for the reaction. Given the scarce number of reported DOXs polymerizations[2] and aiming to develop a metal-free protocol, we first investigated the reactivity of the lactic acid-derived DOX monomer under protic acids catalysis conditions. The influence of different ketones and aldehydes as protecting groups on the reaction outcome was evaluated. With the aim of expanding potential DOXs applications, a new eugenol-containing DOX monomer was successfully synthesized and polymerized. Thanks to the reaction of both the hydroxy acid moiety and the eugenol allyl chain, a thermoset product was obtained, displaying self-healing and shape memory behavior, as well as remarkable tensile strength properties and complete degradability under basic conditions.[3] Finally, copolymerization studies between a DOX monomer and commercially available L-lactide have been carried out, aimed to achieve an efficient incorporation of phenol-containing, DOX-derived units into a high molecular weight polyester chain.

Keywords: *PLA; O-Carboxyanhidrydes; 1,3-dioxolan-4-ones; thermoset; copolymerization.*

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Curing kinetics and mechanical properties of sugar-derived epoxy resins

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ABSTRACT

In the field of epoxy resins the research of new monomers is becoming compelling, pushed by both the urgency to find a valuable substitute of DGEBA (which use is nowadays restricted), and the will to avoid a further consumption of the finite oil resources. Lots of work have been produced since now, where epoxy resins are obtained starting by the most various renewable feedstocks. [1]

In this frame, our research was aimed to the production of bio-based epoxy resins starting by a sugar derived molecule, namely 2,5-bishydroxymethyl furan (BHMF), epoxidated [2] and further cured with methyl nadic anhydride (MNA) in presence of an imidazole initiator. A study was performed about the effect on the curing kinetic of different epoxy/anhydride molar ratios, by means of combined chemo-rheological analysis: the degree of cure, evaluated by FTIR-ATR analysis, was correlated with rheological properties of the resin undergoing the cure process. These results were also corroborated by DSC analysis and the thermal and mechanical properties of the thermosetting resins were analyzed.

The prepared bio-based epoxy resins exhibited good thermal resistance and mechanical properties, comparable with those of DGEBA-based resin. Moreover, their mechanical properties can be tailored by varying the epoxy/anhydride ratio, moving from a rubbery to a rigid material, thus offering interesting opportunities in a wide range of application fields.

Keywords: bio-based thermosets, cure kinetic, furan-based epoxy

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Foamed inorganic polymers filled with graphene

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ABSTRACT

The development of highly performant thermal and acoustic insulators is one of the major issue in the field of high temperature processing as well as in the aerospace and building sector. In this respect, inorganic porous polymers, such as geopolymeric foam, lightweight polymer concrete as well as diatomite-based polymeric foam represent inexpensive, fire-resistant, energy-saving and environmentally insulating materials to meet these needs. [1] These materials can be categorized in the inorganic polymeric class because through a series of complex reactions (included alkali-activated binder, on silicate-, aluminate-, or sulfate- of a mixture of sand, lime, gypsum and cement), a crystalline co-continuous inorganic backbone (polymer) with high molecular weight (i.e. hydrate calcium silicate (CSH) or silico-aluminate geopolymer) is given. [2]

A growing demand of in-depth study is in the production of what is called lightweight concrete (LC), in which the components are mixed together with a foaming agent, usually aluminum or silicon powder, that produces nascent hydrogen in an alkaline environment, creating a porosity which confers a better thermal and acoustic insulation with respect to traditional concrete structures. [3]

LC materials experience a structure-directing reaction during geopolymerization, by means of water and alkali metal cations, and eventual crystal formation. [4] Despite their good insulating and chemo-structural properties, these materials are still not widely used as building materials, for example in bearing walls, due to their lower compressive strength with respect to the traditional concrete. [5]

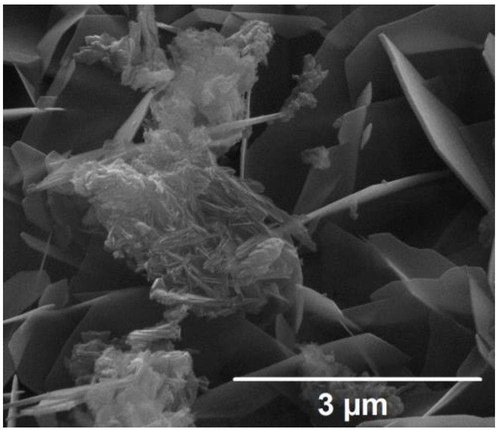

Figure 1. SEM analysis of concrete/GO system. Magnification at 50000x

With this in mind, in this work, a preliminary study of the interaction between the polymerized CSH anion structure with graphene oxide (GO) is presented (Figure 1). Graphene oxide was dispersed within the inorganic matrix in order to enhance the mechanical properties, in terms of compressive strength and strain. Moreover, each of the studied materials an improved electrical conductivity ascribed to the Thermal reduction of GO, which changes together with the applied stress. This feature can pave the way to a new kind of building sensors, thanks to which is possible to monitor the stability of a masonry. [6]

Keywords: *Graphene Oxide; Calcium Silicate Hydrate; Aerated Autoclaved Concrete; Electrical Conductivity*

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Crystallinity, morphology and elastic behavior of copolymers of syndiotactic polypropilene with α-olefins.

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ABSTRACT

We report a study of the structure and mechanical properties of copolymers of syndiotactic polypropylene (sPP) with different comonomers, as ethylene, butene, hexene, octene etc., up to long branched α-olefins. All these copolymers show elastomeric properties even though they present non negligible level of crystallinity at low comonomeric units concentration. The effect of the presence of short or long branches on the crystallization behaviour and elastomeric properties has been analyzed. Incorporation of long branched comonomers, as 1-octadecene and 1-eicosene, allows fast decrease of the glass transition temperature that, associated with the elastic properties, makes these copolymers interesting rubbers. The relationships between structure, crystal morphology and stress-induced phase transformations and mechanical properties have been clarified. In samples with low comonomer content the elastic properties are associated with a reversible polymorphic transition between different polymorphic forms of sPP characterized by chains in trans-planar and helical conformations that occurs upon stretching and releasing the tension. These phase transformations provide an enthalpic contribution to the elasticity. Samples with higher comonomer concentrations show very low crystallinity and a typical thermoplastic elastomeric behavior with a classic entropic elasticity. The study of the crystal morphology shows the presence of small bundles of rod-like lamellar crystals in all copolymers whose size decreases with increasing content and size of comonomeric units. The small needle-like crystals act as knots of an elastomeric lattice, accounting for the development of classic entropic elastic properties. Young modulus and strength of these elastomeric materials can be easily tuned by suitable modification of type and concentration of the comonomeric unit to be copolymerized with propylene that, indeed, affect the degree of crystallinity and the level of entropic and enthalpic contributions to the elasticity. These copolymers represent a new class of elastomeric materials, defined "crystalline elastomers" where the crystallinity plays a fundamental role.

Keywords: *crystallinity; morphology; elasticity; sPP copolymers*.