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PROGRAMMA

Macrogiovani 2018

14 Giugno 2018

14:00 **Apertura Lavori**

14:15 Elkid Cobani

Sepiolite fibers in rubber nanocomposite: the self-assembly effect

14:30 Marco Contino

Environmental stress cracking of hdpe packages for household detergents

14:45 Maria Elena Gino

Osteoinductive multiscale composite biomaterials for orthopedic applications

15:00 Marta Zaccone

Influence of the variation of injection moulding parameters on the electrical properties and morphology of pp/mwcnt nanocomposites

15:15 Martina Salzano De Luna

Chitosan/graphene oxide aerogels with reinforced 3d architecture as broad-spectrum adsorbents for dye removal

15:30 Daniele Rigotti

Plane-stress fracture toughness of thin ethylene-fluoroethylene films

15:40 Giacomo Foli

Solvent Free Preparation Of A Poly([R]-3-Hydroxybutyric Acid) Derivative

15:50 Massimo Tawfilas

Compatibilization Of Inorganic Nanoparticles In Polymer Matrix For Novel Nanocomposite Materials

16:00 **Coffee Break**

16:30 Alberto Marcolongo

Melt Stereocomplexation Of PLLA And PDLA Under Different Shear

16:40 Alessandro Sinisi

Synthesis of novel biobased ketal-diester derivatives of levulinic acid and use as PVC plasticizers

16:50 Martina Ussia

Multifunctional Materials Based On GO-Phema Zno For Pollutants Adsorption And Photodegradation

17:00 Annarita De Meo

Influence of the process on the morphology of semi-crystalline polymers

17:10 Lorenza Maddalena
Layer-By-Layer Coatings Based On Graphene Oxide For Non Flammable Flexible Polyurethane Foams

17:20 Martina Marinelli
A Regioregular Double-Cable Copolymer For Organic Solar Cells

15 giugno 2018

09:00 Massimo Christian D'Alterio
Mechanistic insights in lactide polymerization

09:10 Francesco De Bon
A Stainless Steel reactor for electrochemically mediated ATRP: toward the scale-up

09:20 Giulia Fredi
Study of the synergistic effect of metal hydroxides and fumed silica as flame retardants in polyethylene-based single-polymer composites

09:30 Giuseppe Cesarelli
Micromolding of biocompatible and biodegradable polymers to engineer modular scaffolds with precise microarchitecture and spatiotemporal release capability

09:40 Cristiano Aliberti
Phosphorous-Terminated PMMA As Deterministic Dopants For Microelectronic Applications

09:50 Riccardo Chiarcos
Synthesis of multiblock copolymers via micellar polymerization

10:00 Coffee Break

10:30 Andrea Doderò
Rheological characterization of sodium alginate solutions

10:40 Maria Giulia Longo
Analysis of the mechanical properties of polymeric membranes by afm and tensile tests

10:50 Angelo Nicosia
Correlation Between Building Blocks Structure And Effects On Symmetry Breaking Phenomenon In Supramolecular Aggregates Made Of Porphyrin Based Polymers

- 11:00 Denise Besghini
Polyoxazolines-PLA Nanostructures For Drug Delivery
- 11:10 Giovanni Nicola Vitticano
Applicazioni di polimeri riciclati in guaine bituminose: opportunità per un'economia circolare
- 11:20 Gabriella Munzi
Polymer nanocomposites based on ultrathin silicon nanowires
- 11:45 **Premiazione E Closing Remarks**
- 12:00 **Pranzo**

ABSTRACTS

Phosphorous-Terminated PMMA as Deterministic Dopants for Microelectronic Applications

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ABSTRACT

The control of the dopant dose is one of the crucial steps for supporting the evolution of the semiconductor industry. Conventional doping technology, by ion implantation process, provides the capability to precisely control the dopant dose but induces severe crystal damages. Contrarily, diffusion approaches, using solid- and gas-phase sources, represent a gentle doping solution but lack of the desired uniformity and control over the areal dose of dopant. Recently, a technology based on self-assembled monolayers of dopant-containing molecules, was proposed as a promising solution to overcome the limitations of conventional doping approaches. This non-destructive technique, usually referred to as monolayer doping (MLD), guarantees uniform and conformal coverage of semiconductor surfaces. However, optimization of the grafting process is required for each specific dopant-containing molecule to account for its thermal stability and specific chemical interaction with the target substrate. Spin-on organic dopants for silicon have been proposed as an hybrid solution between monolayer doping technique and traditional inorganic spin-on dopants. This approach provides a simple and low-cost methodology to control the doping by properly adjusting the thickness of the polymeric layer and tuning the polymer chemistry. However, this approach is far from ideal, since accuracy in the dopant surface concentration is limited and consistent residues of the polymeric film are present on the silicon surface after the thermally promoted drive-in process. To overcome this limitation, in this work we proposed an alternative strategy for precisely controlling the amount of dopant atoms tethered on silicon, based on the "*grafting to*" reaction of dopant containing end-functional polymer chains. As the "*grafting to*" is a self-limiting reaction, it is straightforward to produce a grafted layer featuring homogeneous thickness on a large area. In addition, the limiting thickness, the grafting density and consequently the phosphorous surface density, are controlled by the molar mass of the employed end-functional polymer.

In this frame, a series of hydroxyl-terminated poly(methyl methacrylate) samples with different molar masses and narrow molar mass distribution were prepared by ARGET-ATRP and then reacted with diethyl chlorophosphate to obtain diethyl phosphate end-capped PMMAs. Samples were characterized by SEC, ¹H-NMR and ¹³C-NMR to assess the polymer structure. These polymers were grafted onto silica-coated silicon substrates by thermal annealing in a Rapid Thermal Processing apparatus. Subsequent removal of the organic layer by oxygen plasma and capping with SiO₂ leads to the formation of a P δ-layer embedded in a SiO₂ matrix and spatially separated from the Si substrate. The amount of phosphorous bounded to the surface was determined by means of Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Repeated cycles of polymer grafting followed by plasma hashing allowed progressive stepwise increase in the dose of P atoms grafted to the silica surface. P injection in the silicon substrate was promoted and precisely controlled by high temperature thermal treatments.

Keywords: *Doping; Phosphorous; ARGET-ATRP; RTP*

Polyoxazolines-PLA Nanostructures for Drug Delivery

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ABSTRACT

Lately the interest for innovative Drug Delivery Systems (DDS) has been focused on polymeric nanoparticles made up of amphiphilic block copolymers with a prevalent hydrophobic block, that can self-assemble in water into a great deal of "crew-cut" structures. Their properties vary depending on the blocks and the assembly parameters, although the influence of each parameter on the resulting particles is not yet fully understood. This work is part of a wider project on the synthesis and characterization of potential substitutes to polyethylene glycol (PEG). PEG is currently the most employed hydrophilic component, but recent research showed possible negative side effects of repeated injections.

Poly(2-R-2-oxazoline)s are possible alternatives since they are "pseudo-polypeptides" and possess PEG-similar hydrophilicity, stealth properties and biocompatibility. We carried out Poly(2-ethyl-2-oxazoline) synthesis by Living Cationic Ring Opening Polymerization (CROP). The OH end groups were then exploited as initiators for the growth of PLA chains with a higher polymerization degree than the PetOx block, by DBU-organocatalysed ROP of lactide which had, to our knowledge, never been applied to polyoxazolines. The resulting copolymers were self-assembled through water nanoprecipitation in 3 non-selective solvents, i.e. acetone, dioxane and DMF.

AFM analysis in liquid were conducted to study the shape of nanoparticles, an unusual approach for non-ionic, soft systems. They are particularly challenging, requiring to identify a surface able to firmly adsorb the particles. Most of the samples were spherical, except one sample where rods were simultaneously present, highlighting the cooperative effect of solvent and composition on the morphology of this system.

This rods-spheres mix was hypothesized to derive from a gradual transition from rods to spherical micelles. We therefore studied the effect on shape of increasing water content during nanoprecipitation. AFM pictures showed a progressive transition from membrane-like to intertwined worm-like to mixed rods and spherical structures. The gradual shortening of the worm-like micelles in a broad range of added water volume makes these systems very appealing for the production of rods with controlled length. In fact, it was demonstrated that rods circulation time *in vivo* and number of drug molecules hosted increases with their length, with eventually increased efficacy of the treatment.

Keywords: *Nanoparticles; Copolymers; Poly(2-ethyl-2-oxazoline); Filomicelles*

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Micromolding of biocompatible and biodegradable polymers to engineer modular scaffolds with precise microarchitecture and spatiotemporal release capability

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ABSTRACT

Tissue engineering (TE) is an interdisciplinary field whose aim is to restore, maintain or enhance damaged tissues. Scaffolds are one of the key elements to achieve TE goals.

Among traditional and non-conventional techniques, new methods based on bottom-up approaches are catching on TE experts interest for the possibility to stack different building blocks (BBs). An advantage of bottom-up approaches is also the possibility to embed, in a predefined way, different biochemical cues within the scaffolds while assembling layers. Accurate design of the entire 3D structure [1], biochemical cues spatial gradient generation [2] and temporal release mechanisms [3] have been demonstrated to be an important improvement for in vitro and in vivo tissue regeneration in many case studies.

However, it is still lacking a bottom-up complex system designed and fabricated considering all together these three principles.

In this context we show a new, bottom-up design approach capable of fabricating 3D scaffolds with controlled architecture, morphology, porosity, pore size and spatiotemporal release capability. Composite 3D release elements, made of biochemical cue-loaded microparticles enclosed by a natural polymer shell, and structural 2D synthetic polymer BBs are separately fabricated through two different soft-lithography (SL) micromoulding processes. Then, BBs and release elements are integrated with the aid of an automatic micro-positioning apparatus, considering scaffold design prerequisites, and finally BBs are stacked to create the definitive 3D system.

In this presentation we illustrate, for each fabrication phase, previous works of inspiration and the complete pathway that leads to BBs and release elements moulding, respectively.

The proposed method could be used in perspective to fabricate a 3D scaffold whose design would be optimized to promote the maximal efficacy of the spatial and temporal gradients to the restoration and/or improvement of some selected tissues regeneration processes, even without implanted cells aid.

Keywords: *bottom-up tissue engineering; micromolding; automatic micro-positioning; spatiotemporal release*

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Synthesis of multiblock copolymers *via* micellar polymerization

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ABSTRACT

Multiblock copolymers, with hydrophilic and hydrophobic alternating blocks, can be used to design materials with self-healing and shape-memory behavior i.e. materials capable to recover their original mechanical strength after fracture and their shape once subjected to various stimulations. This class of soft and smart materials is of great interest both in academia and industry due to the huge amount of applications. In particular, hydrogels capable of recovering their shape are receiving considerable attention in biomedical applications because of their similarity to biological tissues and great permeability for transport of molecules like metabolites. The specific aim of this work is the preparation of hydrogels characterized by a hyperbranched hydrophobic core that can be processable as thermoplastics. The synthetic strategy is focused on the micellar radical copolymerization of a hydrophilic monomer (acrylamide), dissolved in aqueous medium, and a hydrophobic monomer (n-octadecyl acrylate), dispersed in micelles stabilized by surfactants. The polymerization is initiated by a redox system consisting of ammonium persulfate and sodium metabisulfite. Several series of hydrogels were prepared with different ratios between the hydrophilic and hydrophobic monomers. In addition a small amount of multifunctional monomer was added to the reaction mixture. The conversion of monomers was determined by HPLC. All materials were characterized by Differential Scanning Calorimetry (DSC) and thermomechanical analysis to evaluate the mechanical properties of the hydrogels. Self-healing and shape-memory were tested to assess the peculiar behavior of the hydrogels.

Keywords: Micellar Polymerization; Multiblock Copolymer; Hyperbranched Core, Hydrogels; Shape-memory

Sepiolite Fibers in Rubber Nanocomposite the Self-assembly effect

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The incorporation of nanoparticles (NPs) into the elastomer matrix is a growing area of interest of rubber research in order to produce high-performance polymer nanocomposites (PNCs). Due to their unique structure and physical properties associated with two-dimensional confinement, clay fillers are of great interest because environmental friendly, naturally occurring and readily available in large quantities at lower cost compared to the other fillers. Nevertheless, the clay dispersion in the polymer matrix to the point where particles are coated by the polymer, is still extremely critical. For this, it is necessary to chemically modify a natural clay in order to favor: i) good clay compatibilization in polymer matrix, ii) effective chemical filler-rubber interaction and iii) well-defined NPs distribution that influence reinforcing and hysteretic properties in rubber NCs for tire application.

In this context, we explored a new approach to prepare PNCs based on nano-sized sepiolite (NS-Sep) fibres [1]. Pristine Sep was structurally modified by an acid treatment, which provides NS-Sep fibers with reduced particle size and increased silanol groups on the surface layer. NS-Sep fibers were used to prepare styrene-butadiene rubber (SBR) NCs with enhanced mechanical properties. Dynamic-mechanical analysis of Sep NCs demonstrated that the modified Sep fibers provided an excellent balance between reinforcing and hysteretic behavior compared with large-sized pristine Sep (Fig.1) and isotropic silica.

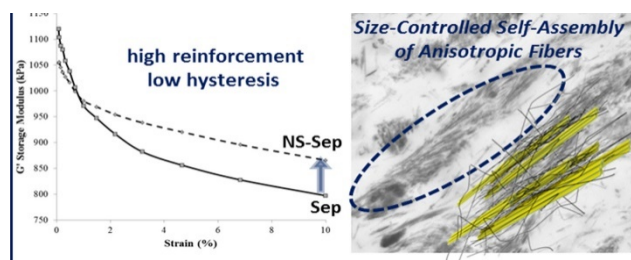


Fig.1 Storage modulus G' vs Strain of NS-Sep/SBR and schematic representation of NS-Sep self-Assembly

This was related to the enhanced interfacial chemical interaction between NS-Sep/NS-SilSep and rubber, as well as to the size and self-assembly of anisotropic nanofibers. In detail, transmission electron microscopy analyses (TEM) analysis shows that inside elastomeric matrix, the Sep smaller size allows the self-assembly of fibers in Sep network structures, while the low field 1H Nuclear Magnetic Resonance analysis (NMR) reveals the presence of surface-immobilized rubber only in the presence of both modified NS-Sep and NS-SilSep fillers. Thus, the preparation of NCs, based on Sep nanofibers obtained by a versatile acid treatment, is a simple and effective method to prepare Sep NCs suitable for advanced technological applications.

Keywords: (Sepiolite; rubber; nanocomposite; Self-assembly; Filler networking)

References:

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Environmental stress cracking of HDPE packages for household detergents

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ABSTRACT

High-density polyethylene (HDPE) is a polymer widely used for many packaging applications. During its service life a container can be exposed to substances which can alter its mechanical properties and can lead to a premature failure of the container itself.

This work concerns the effects of commercial bleach. Due to the fact that it contains a large number of ingredients, the determination of the effect of the single ingredients on the mechanical properties of the polymer and the identification of the nature of their interaction is of particular interest to properly describe the occurring phenomena. In fact, it has been reported that, in principle, substances like sodium hypochlorite can cause an oxidation of the polyethylene [1], while surfactants can be absorbed by the material in proximity of a defect favouring the phenomenon called Environmental Stress Cracking (ESC) which can lead to a premature failure of polymeric materials [2]. However, due to the different nature of the two interactions and to the different amount of time required for their occurrence, it is not straightforward to predict which mechanism would be active.

Therefore, the two phenomena were studied separately and during the first part of this research the extent of the chemical interaction between the commercial bleach and two commercial grades of HDPE was evaluated via ageing experiments. After six month only a small increase of the sample mass, related to the absorption of the solution, was measured while no effect on different mechanical properties was found indicating that, if present, the chemical degradation of the materials is practically negligible.

Concerning ESC, instead, a fracture mechanics approach was adopted to study the fracture initiation and propagation behaviour of the two materials in air and in presence of two solutions, both containing sodium hydroxide, sodium carbonate perfume and surfactant, one with and one without sodium hypochlorite (i.e. the bleaching agent). It was observed that in presence of either of the solutions, after a critical interaction time, crack initiation occurs earlier and it propagates faster with respect to what observed in air. Moreover, since the two solutions had the same effect on the material behaviour it was concluded that, in the considered case, sodium hypochlorite did not affect the fracture resistance of HDPE.

The effect of the temperature on ESC was also investigated: as expected, increasing temperature the phenomena occurring during fracture are accelerated leading to a lower initiation time and a higher crack propagation rate. It was found that the temperature effect observed during the tests in air and in the presence of the solutions was the same indicating that only the viscoelasticity of the material and not the interaction with the solutions is influenced by the temperature. Finally, a time-temperature superposition reduction scheme allowed the evaluation of the long term fracture and ESC resistance of the considered materials.

Keywords: *HDPE; Detergents; Environmental Stress Cracking; Fracture mechanics*

References

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Echanistic insights in lactide polymerization

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ABSTRACT

Poly(lactide) (PLA), is one of the most important synthetic biodegradable polymers used for a wide range of biomedical and pharmaceutical applications [1]. Moreover, recent concerns with our environment call for the development of eco-friendly materials derived from renewable resources such as corn and sugar beets.

The most efficient method for the generation of PLA is the ring-opening polymerization (ROP) of the six-membered cyclic ester lactide (LA). The presence of two stereogenic centers in the LA monomer may give rise to different polymer stereoregularities which affect physical and mechanical properties of the material.

Several aluminum complexes, including tetradentate-dianionic sequential [ONNO]-type ligands (Al-Salan, Al-Salen and Al-Salalen) producing stereoregular PLAs, have been recently synthesized [2]. Even if this plethora of catalytic systems exists, little is known about the mechanism(s) of stereocontrol in the PLA synthesis obtained by ROP.

We used quantomechanical calculations based on density functional theory (DFT) to unveil the reasons which lead to a stereoselective ROP for the PLA synthesis promoted by a chiral Al-Salen system, SALBinapAl-OCH₃, which is supposed to perform an enantiomeric-site (ES) control mechanism [3,4] (Figure 1).

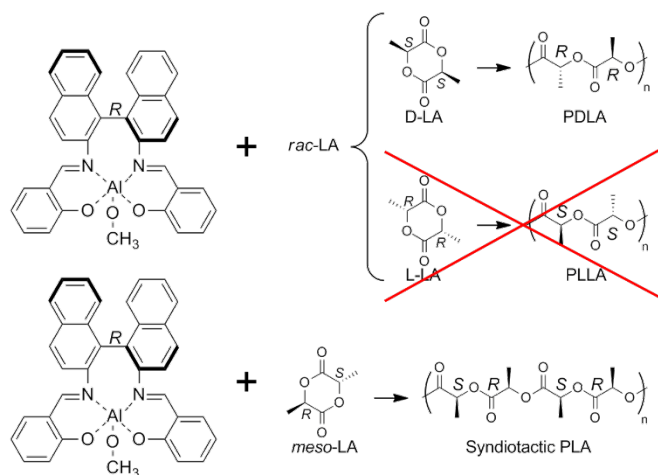


Figure 1: *R*-SALBinapAl-OCH₃ acts on *rac*-LA producing PDLA [3], and acts on *meso*-LA producing Syndiotactic-PLA [4].

The model of stereocontrol we proposed for chiral Al-Salen system may lead to a rational catalyst tuning for targeted material properties.

Keywords: Computational Model; Homogeneous catalysis; Site control; Biodegradable Polymers; Renewable Feedstock.

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A Stainless Steel reactor for electrochemically mediated ATRP: toward the scale-up

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ABSTRACT

Atom Transfer Radical Polymerization (ATRP) is a powerful and versatile polymerization technique for the synthesis of well-defined polymers and copolymers. The polymerization exploits a reversible transfer of a halogen atom from a dormant species P_n-X to a metal catalyst Mt^zL_m (often a copper-amine complex) in a low oxidation state to produce the propagating radical $P_n\cdot$ and the oxidized metal complex $X-Mt^{z+1}L_m$. The equilibrium is strongly shifted toward the dormant state ($K_{ATRP} \ll 1$), thus the concentration of $P_n\cdot$ is very low and bimolecular terminations become negligible¹. Electrochemically mediated ATRP (eATRP) is the electricity-driven variant of ATRP. It allows fast (re)generation of Cu^I from Cu^{II} , easy control of the distribution of Cu^I and Cu^{II} species in solution and the possibility of switching the process from active to dormant state and vice versa, by varying the electrochemical parameters applied to the system. eATRP provides a concrete possibility for deeply controlling the process.^{2,3}

Despite its very wide use in academia, there are only few industrial applications, none of which involving electrochemical ATRP. We designed, built and successfully tested an electrochemical reactor with the dual function of cathode and vessel. It represents an all-in-one solution, specifically designed for non-experts of electrochemistry. The reactor operates in a galvanostatic mode (eATRP is triggered by an applied current) with a sacrificial aluminum anode with the possibility to work also under pressure (up to 10 bar). For one monomer, methyl acrylate, the effect of several electrolysis programs was studied. With one appropriate electrolysis program, the catalyst concentration and the solvent were varied to understand how the reaction is affected by the external stimulus. The chain extension of macroinitiator of poly(methyl acrylate)-Br with methyl acrylate confirmed that the process proceeds as a controlled polymerization with high chain-end fidelity.

Two other monomers, butyl acrylate and acrylamide, were successfully polymerized inside the reactor with appropriate catalysts and initiators. eATRP triggered inside the reactor overall afforded well defined polymers, with $\bar{D} = 1.10-1.20$ and $M_n > 30000$. The SS304 reactor represents a significant and crucial step for scale-up and commercialization.

Keywords: ATRP, scale-up, electrochemistry

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Influence of the process on the morphology of semi-crystalline polymers

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ABSTRACT

In common polymer processing operations such as injection molding, film blowing, and fiber spinning, semicrystalline polymers are largely adopted. In most of cases, the crystallization process takes place while the polymer is still flowing and this induces a dramatic change of rheological properties and sometimes an anticipated and unpredicted solidification. The description of the effects of crystallinity on flow is still challenging, mainly because of the difficulties in measuring simultaneously rheological properties and crystallinity evolution. Furthermore, the problem is complicated by the fact that crystallinity increases by effect of flow, and thus the test itself modifies the material behavior. This is the other side of the phenomenon, which by itself is of great practical interest and is equally challenging: the so-called "flow-induced crystallization". In this work, by using a new generation rheometer, the Haake Mars II, rheological experiments during crystallization of an isotactic polypropylene are conducted. By adopting a parallel plates geometry, in which one of the plates is transparent, simultaneous measurements of rheology and observations of the morphology are performed. In this way, a better understanding of the relationship between rheology and morphology can be achieved compared to a test that combines parallel measurements of rheology and evolution of morphology. During the isothermal crystallization of a polypropylene, rheological tests are carried out to measure the viscosity of the material. Images of the sample showing the evolution of the morphology along the entire thickness are simultaneously acquired. By analysing the images, the evolution of the density of crystal nuclei and the growth rate of the spherulites are observed. Furthermore, also the crystallinity evolution of the material during each rheological test is evaluated. The measured viscosity and the corresponding morphological parameters are correlated and discussed.

Keywords: Crystallinity, Rheo-optical Measurements, Morphology, Solidification, Polypropylene

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Rheological characterization of sodium alginate solutions

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ABSTRACT

Sodium alginate (SA) is an anionic polysaccharide consisting of 1,4-linked β -D-mannuronic acid (M) and 1,4 α -L-guluronic acid (G) residues arranged in homogeneous (MM, GG) or heterogeneous (MG) block-like patterns. SA is commercially available in various grades of molecular weight, composition, and distribution pattern of M-block and G-block, which influence its physical and chemical properties.

The aim of the present work was to investigate the behaviour of three different alginates in water and their rheological properties. Firstly, the molecular weight of the examined polymers was calculated using the Mark-Houwink relation, after that the intrinsic viscosity $[\eta]$ was measured through rheological experiments. Subsequently, steady state flow sweeps were performed to evaluate the critical concentrations separating the dilute, the semi-dilute unentangled, the semi-dilute entangled, and the concentrated regime, (i.e. the overlap concentration c^* , the entanglement concentration c_e , and c^{**}). The dependence of the specific viscosity η_{sp} upon the polymer concentration was carefully investigated and correlated both to alginate molecular weight and composition, which was determined testing alginate powders with FTIR spectroscopy.

In order to obtain electrospinnable systems, alginate solutions were mixed with poly (ethylene oxide) solution and Triton X-100 (i.e. a non-ionic surfactant); the viscosity, the viscoelastic properties (i.e. storage modulus G' and loss modulus G''), and the thixotropy of such solutions were investigated.

The polyelectrolyte behaviour of alginate solutions is more evident when the number of G-blocks is higher. Furthermore, PEO decreases the viscosity of alginate solutions and the effect is greater for alginates with a high number of M-blocks.

Keywords: Sodium Alginate; Polyelectrolyte; Rheology; Critical Concentrations.

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Solvent free preparation of a Poly([R]-3-hydroxybutyric acid) derivative

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ABSTRACT

Polyhydroxyalkanoates (PHAs) are a group of bacterially synthesized polyesters totally biodegradable, biocompatible and bioresorbable¹ representing to be interesting candidates for realization of biomedical devices.² More than 150 types of PHAs are known and, among them, poly([R]-3-hydroxybutyric acid) (PHB) is one of the most representative members. In particular, PHB is a hydrophobic polymer and, due to its side chain methyl groups, is highly rigid and brittle, which limit its potential application.³ For these reasons chemical modifications are required, in order to tune PHB mechanical properties and make such material a valuable alternative to the synthetic polymers. A simple possibility is the modification of the neat biopolymer with polyethylene oxide (PEO), as a hydrophilic and biocompatible segment, to obtain PHB-based block copolymers.⁴ Typically, in the first step of the process, PHB depolymerizes by reacting with diols, leading to a di-hydroxyl-terminated lower molecular weight derivative, PHB-diols.⁵ Copolymers are finally prepared via a diisocyanate chain extension reaction between PEO and PHB-diol segments. In the last decades, basically two synthetic approaches for PHB-diol preparation have been reported.^{6,7} Both of them are performed in solution, using dichloroethane or diglyme as solvent, with a reaction time between 4 and 6 h and using high excess of diol, depending on the desired molecular weight of the final PHB-diol.⁸

In this work, we present a rapid solvent free and low diol consuming preparation of PHB-diol. Acid catalyzed reaction between high molecular weight PHB and 1,4-butanediol is performed in molten state at 190°C. The well know thermal degradation of PHB⁹ is deeply suppressed thanks to the extremely low reaction time of about 5 minutes. Furthermore, ¹H-NMR spectroscopy, DSC analyses and Hydroxyl Value (OHV) determination show that, after a careful reaction conditions optimization, the yielded PHB-diol has the same characteristics of the product prepared by the previously proposed wet-chemistry expensive procedures. The obtained PHB-diols, characterized by various molecular weight, can be considered building blocks for the realization of biodegradable polymers with better properties with respect to biosynthesized neat PHB, opening the possibility to employ this material in different technological fields of application.

Keywords: (PHB, PHB-diol, biopolymers, biodegradable polymers, polyesters alcoholysis)

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Study of the synergistic effect of metal hydroxides and fumed silica as flame retardants in polyethylene-based single-polymer composites

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ABSTRACT

Polymers and polymer composites are widely used due to their remarkable combination of mechanical and physical properties, low density and high processability, but one of their main drawbacks is the low fire resistance [1]. Metal hydroxide flame retardants (FRs) are diffused as they are highly effective and do not release dangerous compounds. However, they are quite expensive and need to be present in high weight fractions, and thus they are often combined with other FRs [2]. The aim of this work was to study the synergistic effect of aluminum/magnesium hydroxides (Al(OH)₃, Mg(OH)₂) and fumed nanosilica as FRs in a linear low-density PE (LLDPE) matrix, to produce flame-resistant PE-based single polymer composites. The fillers were added to LLDPE in different amounts, to investigate the separate and combined effect of the FRs on the microstructural, mechanical, thermal and fire resistance properties. Melt flow index (MFI) tests showed that the fluidity was not noticeably degraded upon metal hydroxide introduction, while a dramatic MFI reduction was detected for silica contents higher than 5 wt%. Thermogravimetric analysis and onset oxidation temperature tests highlighted that FR introduction considerably improved the thermo-oxidative stability, and a synergistic effect could be appreciated after the measurement of better thermal properties on the samples combining the two FR types at the same total filler amount. Tensile tests revealed that a high metal hydroxide weight fraction caused a stiffening and an embrittlement of the material, while nanosilica introduction at low concentrations helped to preserve the failure properties of the neat LLDPE. Limiting oxygen index (LOI) and cone calorimetry tests highlighted that the fire performance of the samples with optimized compositions were strongly enhanced with respect to those of the neat LLDPE, and also these tests evidenced the synergistic effect between micro- and nanofillers. The outcome of this work allowed the choice of the most suitable composition to fabricate fire resistant PE-based single-polymer composites with the introduction of UHMWPE fibers, which is the subject of current and future work.

Keywords: *Fire retardants; single-polymer composites; fumed silica; metal hydroxides; cone calorimetry.*

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OSTEOINDUCTIVE MULTISCALE COMPOSITE BIOMATERIALS FOR ORTHOPEDIC APPLICATIONS

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ABSTRACT

Polymer scaffolds provide a temporary matrix into which cells can migrate, proliferate and differentiate to regenerate functional tissues. The aim of this Thesis was the design and the production of a biocompatible and biomimetic composite scaffold which might be used for the regeneration of bone tissue in case of an arthrodesis surgery. The developed scaffold consisted of a fibrous polymer matrix produced by the electrospinning technology, closely mimicking the fibrous component of the ECM, inserted between two layers of gelatin crosslinked with genipin and loaded with osteoconductive and osteoinductive molecules, i.e. hydroxyapatite and Tantalum. Blends of PLGA 75:25 and PEG with different molecular weight (PEG MW 400 Da, PEG MW 1500 Da) were investigated to obtain a polymeric fibrous mat through electrospinning. The composite material was designed in order to achieve a desired gelatin degradation kinetics on the basis of the thickness and degree of cross-linking of the gelatin layers. The composite scaffolds have been characterized by means of TGA, DSC, WCA, WAXD, SEM, AFM, TEM; crosslinking degree, swelling degree and gelatin release kinetics were also evaluated. The biological response of the composite was finally studied through cytotoxicity tests performed by direct contact of the materials with osteoblasts. The obtained results demonstrated that the composite system has excellent biocompatibility. Additional biological tests are currently underway to demonstrate that the overall characteristics of the scaffold developed in the present Thesis make it an excellent candidate for biomedical applications and in particular, given its 3D structure and its functionalization, it can provide a useful support to stimulate healing and regeneration of the bone tissue.

Keywords: *composite materials; scaffolds for tissue engineering; electrospinning; gelatin;*

ANALYSIS OF THE MECHANICAL PROPERTIES OF POLYMERIC MEMBRANES BY AFM AND TENSILE TESTS

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ABSTRACT

In the last years, the development of novel materials with superior gas transport properties enhances the exploitation of polymer membrane gas separation technology in new markets or in replacement of traditional technology¹. The transition from lab-scale membrane to real industrial use requires a fully physical-chemical characterization of the materials. A promising material should couple the superior gas transport properties with a mechanical stability. The mechanical properties are commonly investigated by tensile test or rheological characterization. However, these techniques present two main drawbacks: they are destructive and require an amount of sample, which is not always available. The Atomic Force Microscopy (AFM) worked in Force Spectroscopy mode is a technique to investigate the mechanical and viscoelastic properties of materials². This technique is non-destructive, requires a small amount of material, and it makes possible the investigation of the mechanical properties at nano and micro scale. The aim of this work is to assess the comparability of the mechanical properties analysed through these two different techniques. The mechanical properties of a rubbery polymer, Pebax®1657, added with different amount of the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], and the mechanical properties of glassy polymers of intrinsic microporosity (PIMs), are investigated. The tensile test data, obtained for Pebax samples, are in agreement with the ones obtained with AFM on micro scale. On nano scale, the probe has dimensions comparable with polymer domains and it can distinguish their different rigidity. The force spectroscopy analysis on PIMs showed how the thermo-mechanical history influences the mechanical properties. and the correlation with the diffusion and permeability coefficients.

Keywords: *Atomic Force microscopy; mechanical properties; gas separation; membrane technology.*

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Layer-by-layer coatings based on graphene oxide for non flammable flexible Polyurethane foams

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ABSTRACT

Polyurethane (PU) foams represents one of the first item to be ignited in fires as they can ignite and burn very quickly releasing toxic gasses. Because polymer flammability is a typical surface property, the Layer-by-Layer (LbL) technique has been adopted for the construction of coatings capable to improve the flame retardancy of PU foams introducing Graphene Oxide(GO) as flexible high aspect ratio nanoparticle [1].

The LbL growth of the GO coupled with different natural and synthetic polyelectrolytes, was monitored with FT-IR spectroscopy. The effects on LbL growth of different deposition conditions were evaluated on the bases of ionic strength and pH. Scanning Electron Microscopies demonstrated that the LbL is a tool able to penetrate inside the foam structure and homogeneously coat each available surfaces with a dense multi-layered nanostructure. Flammability tests in horizontal configuration demonstrated the complete suppression of the melt dripping phenomenon and self-extinguishing behaviour for foams treated at high ionic strength. Surprisingly, by cone calorimetry some of the treated foams showed no ignition at all when exposed to heat flux typical of developing fires. Flame penetration tests demonstrated that GO-treated PU foams are able to withstand an impinging flame and to maintain an excellent thermal insulation, with a gradient of about 570°C/cm, comparable in performance to a commercial silica aerogel within the first 5 minutes of flame applications.

The proposed GO multilayer coatings represent a valuable and efficient alternative for the reduction of the fire threat of PU foams and open new scenery for PU application in field where flame retardancy is necessary.

Keywords: Graphene oxide; Layer by Layer; Flame retardancy; Self-extinguishment; flame penetration;

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Melt stereocomplexation of PLLA and PDLA under different shear conditions

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ABSTRACT

The structural manipulation of stereocomplex (sc) polylactic acid is the key to leverage fully its surpassing performance, such as heat resistance and mechanical properties. In this study, we investigated the evolution of crystalline morphology/structure of racemic blends under the quantitative shear field modulated by the use of a laboratory-made rheo-Raman device. The instrument couples a Raman spectrometer and optical microscope to a rotational rheometer through an optically transparent base, and the resulting simultaneous measurements are particularly advantageous in situations where the flow properties vary due to either chemical or conformational changes in molecular structure. Shear-induced crystallization proceeded above the melting point of homocrystals, allowing the exclusive formation of crystallites. The possible mechanism of stereocomplex formation was achieved in this study and the shear force and particle size play an important role during the melt mixing process.

A REGIOREGULAR DOUBLE-CABLE COPOLYMER FOR ORGANIC SOLAR CELLS

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ABSTRACT

Polymeric solar cells (PSCs), that are generally based on a bi-continuous network of an electron-donor (a conjugated polymer) and an electron-acceptor (fullerene or its derivatives), are very attractive devices, due to their light-weight, processability and suitability to further scale-up.

However, since the main parameters of this type of architecture, defined as bulk hetero-junction (BHJ), are determined by the mechanism of carrier generation and transport processes, the microstructure and morphology of the blend electron-donor/acceptor are indeed of primary importance. On these bases, with the purpose of obtaining optimal phase segregation between the donor and acceptor molecules for the charge generation, as well as maintain a continuous path in each phase for the efficient transport of electrons and holes, the synthesis of donor-acceptor double-cable polymers appears particularly intriguing.^[1]

A thiophenic monomer bearing the C₆₀-fullerene group at the end of a hexylic side chain at position 3 and the related soluble thiophenic copolymer, have been prepared with a simple and straightforward procedure based on the Grignard coupling. The copolymer was characterized using ¹H-NMR, gel permeation chromatography (GPC), thermal analyses (DSC, TGA), UV-Vis and IR spectroscopy. In addition to investigating the films of the copolymer by AFM measurements, the current density/voltage (J/V) characteristics of solar cells prepared with the above double-cable material as photoactive layer were determined in order to evaluate its photoconversion efficiency.

Keywords: *conjugated polymers; fullerenes; bulk heterojunction.*

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POLYMER NANOCOMPOSITES BASED ON ULTRATHIN SILICON NANOWIRES

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ABSTRACT

Polymer nanocomposites are an emerging class of versatile materials which are conceived for multiple applications, spanning from optical integrated circuits to sensors. The inclusion of nanofillers is frequently designed to enhance or modify various polymer matrix properties, such as barrier or electric properties [1,2]. In particular, ultra-thin Silicon Nanowires (SiNWs) have been recently proposed as attractive components for optoelectronic devices [3].

In this work, SiNWs 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. The properties of a non-conducting (ethylene-vinyl acetate) and a conducting polymer (Polyaniline) are studied as a function of the different SiNW concentration.

These nanocomposites are prepared by using the well-established ball milling process [4]. This technique presents many advantages, such the possibility of working at room temperature, the absence of a solvent phase, reduced costs and an easy scale-up to industrial level. Finally, the characterization of such phase-separated structures is studied by the combined use of Scanning and Transmission Electron Microscopy. These techniques will give details, at the nanoscale, about the uniformity of SiNWs within the matrices. Indeed, the optimal SiNW dispersion is crucial to preserve the optoelectronic properties of these hybrids.

In fact, our aim is to demonstrate that the easy processing of polymers associated with the peculiar properties of SiNWs, could give rise to a variety of novel nanocomposites which can be exploited for future applications in optoelectronics.

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Keywords: (*Nanocomposite; Silicon Nanowires; Silicon/polymer interface; Transmission Electron Microscopy*)

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Correlation between building blocks structure and effects on symmetry breaking phenomenon in supramolecular aggregates made of porphyrin based polymers

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ABSTRACT

The spontaneous symmetry breaking is a controversial natural phenomenon that happens in every scientific fields, from biology to nuclear physics. One of the most diffuse method to investigate on this phenomenon is to study the supramolecular aggregates made of achiral molecules. With this aim, were already used a particular achiral porphyrin derivative that shows spontaneous aggregation in water solution, the 5,10,15,20-tetrakis[*p*-(ω -methoxy-polyethyleneoxy)phenil]porphyrin[1] (Star350).

It was already demonstrated that the symmetry breaking phenomenon in supramolecular aggregates of Star350, can be induced and/or annulled in stagnant water solution through the interaction with asymmetrical thermoforetic forces[2]. Moreover, managing the direction and the intensity of the asymmetrical thermal gradient applied to the solution, it is possible to manage the phenomenon not only in magnitude, even in circular dichroism profile[3].

In this contribute, the attention has been focused on the effects of the structure of the building blocks. Were used some PEGylate porphyrin derivatives isobars to the Star350, but with different molecular arrangements {the 5,15-[*p*-(ω -methoxy-polyethyleneoxy)phenil]-10,20-di[*p*-hydroxyphenyl]porphyrin (Trans750), and the 5,10-[*p*-(ω -methoxy-polyethyleneoxy)phenil]-15-20-di[*p*-hydroxyphenyl]porphyrin (Cis750)}, and even a PEGylate porphyrin dimer with a molecular arrangement similar to the Star350, but with a higher hydrophobic moiety {the cicle-di-{5,10-[*p*-(ω -methoxy-polyethyleneoxy)phenil]-15,20-di[*p*-hydroxyphenyl]porphyrin}-formals (Di-Cis750)}.

For every building block, were studied the quali-quantitative differences respect to the aggregation phenomenon, using UV-visible spectroscopy. Moreover, thanks to circular dichroism experiments in thermal ramp, was founded a possible cause-effect correlation between the molecular structures of the building blocks and the symmetry breaking phenomenon in water stagnant solution, focusing on the roles of the intermolecular forces and of the mesoscopic morphology of the supramolecular aggregates.

Keywords: (Spontaneous symmetry breaking; supramolecular aggregates; porphyrin; thermoforetic force)

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PLANE-STRESS FRACTURE TOUGHNESS OF THIN ETHYLENE-FLUOROETHYLENE FILMS

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ABSTRACT

The Essential Work of Fracture (EWF) approach has become very common in the estimation of the plane-stress fracture toughness of highly ductile thin polymer sheets. The approach is based on the separation between the work spent in the fracture process zone (FPZ), the so called EWF, which is the energy per unit area dissipated locally in forming the fracture surfaces, from the other dissipative contributions to the total energy (such as plastic deformation) [1, 2]. In this work the EWF tests have been applied to determine the temperature and strain-rate dependency of the fracture toughness of ethylene-fluoroethylene (ETFE) thin films.

The essential specific work of fracture (w_e) and the non-essential specific work of fracture (β_{wp}) parameters have been measured. Moreover, the w_e value has been partitioned into two terms, one related to the specific energy contribution for yielding up to the onset of fracture ($w_{e,init}$), and another one representing the subsequent crack propagation process ($w_{e,prop}$), respectively. The same partitioning approach has been extended to the non-essential work of fracture, resulting in two terms related with the energy dissipated during the yielding of the ligament zone ($\beta_{wp,init}$) and during the propagation of the crack ($\beta_{wp,prop}$).

EWF tests were conducted at different temperatures (i.e.) and different testing speeds (i.e.). EWF showed that w_e decreases with the increasing of the strain rate apart for the test conducted at 23°C and this trend is associated with the increase of the crack propagation component ($w_{e,prop}$) while the yielding component ($w_{e,init}$) decreased with the increasing of the crosshead speed with a magnitude related to the testing temperature. Thermal observations revealed an increase of the temperature at the crack tip for the highest strain rate suggesting a competing effect of strain-embrittlement and adiabatic heating for the sample tested at the lowest temperature. For as concern the non-essential part, β_{wp} is governed by its crack propagation component ($\beta_{wp,prop}$) and it slightly increased with the increasing of the strain rate. Digital Image Correlation (DIC) analysis was also performed on different samples and it revealed an oval shape of the fracture process zone prior to the start of the crack propagation and the area of the FPZ increased linearly with the square of the ligament length.

Keywords: *Essential Work of Fracture; ETFE; Fracture Mechanics; Digital Image Correlation.*

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CHITOSAN/GRAPHENE OXIDE AEROGELS WITH REINFORCED 3D ARCHITECTURE AS BROAD-SPECTRUM ADSORBENTS FOR DYE REMOVAL

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ABSTRACT

The use of synthetic dyes is common in many industrial sectors, such as textile, paper, plastics and cosmetics. Removing dyes from contaminated water represents an important challenge for the scientific community, due to the rapid increase of water pollution. Among the possible purification techniques, adsorption is considered one of the most feasible and low-cost approach. In this context, chitosan (CS) is currently studied as biocompatible and biodegradable material for adsorption of anionic dyes from contaminated water, due to the electrostatic interactions that occur between its amine and hydroxyl groups and anionic pollutant molecules [1]. On the other hand, its effectiveness towards cationic dyes is rather scarce due to adverse electrostatic interactions. Different approaches have been recently investigated for the realization of broad-spectrum adsorbent materials able to simultaneously remove anionic and cationic pollutants from wastewater [2, 3]. In particular, the use of graphene oxide (GO) in combination with chitosan is greatly promising, as GO sheets contain epoxy, hydroxyl and carboxyl groups that can bind cationic compounds via electrostatic interactions. Besides the proper selection of the main constituents of the adsorbing material, the nature of the adsorbent itself plays a crucial role in determining the final performances. Aerogels are highly porous and large surface area materials, which well suit for possible application in dyes adsorption. The present work fits in this scenario, as it addresses the optimization of the preparation procedure of highly adsorbing and mechanically resistant CS/GO aerogels for dye removal from aqueous solutions. Specifically, the aerogel performances have been tailored by tuning the mixing method, the crosslinking strategy, and the freezing conditions.

Acknowledgments

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Keywords: *Chitosan; Graphene oxide; Aerogel; Dye removal; Mechanical properties*

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Synthesis of novel biobased ketal-diester derivatives of levulinic acid and use as PVC plasticizers

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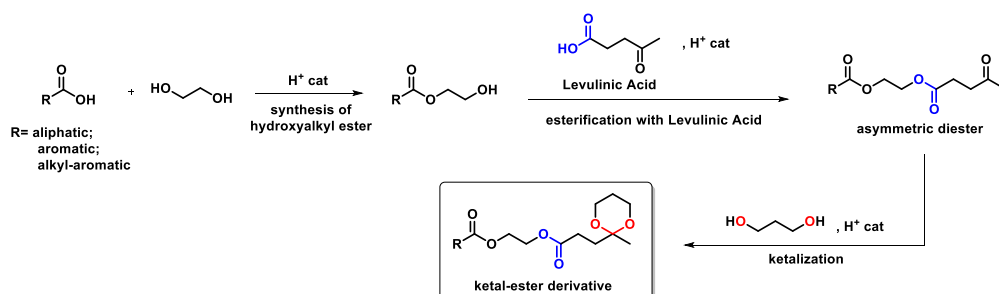
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ABSTRACT

Poly(vinyl chloride) (PVC) is one of the largest thermoplastic commodities used for a wide range of industrial, construction and domestic applications. However, as a result of the characteristic dipole located in each C-Cl bond, neat PVC is a stiff and brittle material with difficult processing. Consequently, plasticizers are usually added in order to enhance PVC flexibility by reducing the cohesive interaction forces between the polymer chains¹. Among the hundreds of commercially available PVC plasticizers, petroleum-based phthalate esters are the most commonly used due to their good performance and low price. However, these plasticizers are not chemically bonded with PVC polymer chains and therefore they can leach out during use or after disposal of the material, resulting in potential human exposure. Since some of these compounds have been identified as being toxic, their use was regulated.

In order to develop new non-toxic and biodegradable plasticizers, levulinic acid has recently attracted considerable attention as building block due to its renewable origin and chemical versatility². Exploiting the bifunctional nature of this acid (which bears both carboxylic and keto groups on its structure), a three-step protecting-group-free synthesis leading selectively to asymmetric ketal-diesters was set up (Scheme 1).



Scheme 1 Synthesis of ketal-diester derivatives of levulinic acid

With this approach, different novel biobased ketal-ester derivatives of levulinic acid were synthesized in good to high yields. Their chemical structures were confirmed by means of NMR and FT-IR spectroscopies. Different amounts of these molecules and PVC were then co-dissolved in order to prepare thin films of plasticized PVC by solvent casting. DSC analysis of these plasticized PVC samples showed a pronounced decrease in the glass transition temperature, while the improved thermal stability was evaluated by TGA. SEM analysis, DMTA measurements and leaching tests are under investigation in order to evaluate the compatibility between the phases, the viscoelastic properties and the migration stability, respectively.

Keywords: *Plasticizer; Levulinic Acid; Bio-based; PVC*

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Compatibilization of inorganic nanoparticles in polymer matrix for novel nanocomposite materials

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ABSTRACT

Nowadays, polymeric materials are used in everyday life, starting from the simple plastic bag to more sophisticated fibers or membrane. Thanks to their high processability, cheap costs and custom tailoring they have been studied and applied in different scientific fields. In order to improve some properties it is possible to act on the chemistry of the polymer chains, sometimes a limit is reached and other strategies are needed. An interesting suitable solution to improve physical and mechanical properties is the introduction of inorganic nanoparticles (NPs) into polymer matrixes[1]. In order to express the filler intrinsic properties it is necessary to work on the surface ligand engineering with the functionalization of the NPs surface. The presence of a thin polymeric layer on the surface enables a good dispersion in the polymer matrix avoiding the aggregation and precipitation phenomena. Thanks to the control over the graft density (σ) and the grafted chains molecular weight (N) it is possible to manage the morphology of the dispersions in matrix[2]. Controlling the conformation of the grafted polymer, that can be idealized in two limiting structures: brush or mushroom, it is possible to improve the solubility of the nanocomposite into polymer matrixes and give specific properties to the final material[3]. Many techniques have been developed and in our contribution we explored the NPs compatibilization through the *grafting to* and the *grafting from* approach using Reversible Addition Fragmentation Chain Transfer (RAFT). The *grafting to* approach consists in tethering a polymer chain via an anchoring group on the inorganic surface; while the *grafting from* approach is a surface-initiated polymerization that starts from an initiator attached on the NPs surface. RAFT polymerization technique, a pseudo-living radical polymerization, gives the control over the grafted polymer molecular weight, PDI and the chemistry of the polymer anchoring groups. A conformational study of grafted polymer chains has been made using a *grafting to* approach of polystyrene (PS) and polyethylene oxide (PEO) on anatase nanocrystals. NPs can be useful beyond just the mechanical improvement of a polymer matrix; it is shown how the *nano-size effect* can change the gas permeability properties of a polymer[4]. In our contribution we will show how using a *grafting from* approach on silica NPs gives a fine control over graft density and molecular weight, this provide the creation of a matrix-free nanocomposite with enhanced gas permeability.

Keywords: (*Nanocomposite; compatibilization; ligand engineering, conformation control*)

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Multifunctional materials based on GO-pHEMA ZnO for pollutants adsorption and photodegradation

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ABSTRACT

Due to rapid population growth and intensification of agricultural and industrial activities, a diverse array of hazardous pollutants is progressively entered in the aquatic system. Particularly, persistent organic contaminants such as pesticides, solvents, dyes, detergents and industrial chemicals, constitute a pressing ecological problem that poses a great threat to human health [1]. In fact, main water purification methods were applied in the last decades, but often they involve high operating costs and could generate toxic secondary pollutants into the ecosystem [2]. An eco-friendly and definitive process to eliminate contaminants from water is their complete mineralization by using photocatalytic approach [3], followed by an efficient and easily catalyst separation at the end of the process. Recently, the combination of inorganic (TiO₂ and ZnO) [4] and organic (photosensitizers and photoactive polymers) materials [5] with polymer cryogels has received more and more interest in water-purifying fields. In particular, the polymer support can be used as template for the deposition of a uniform layer of photoactive nanomaterials, as well as for the incorporation of efficient adsorbent with the aim to develop smart cryogels, able to remove contaminants from water and their rapid mineralization at the same time. Among the materials designed for both absorption and photocatalysis, a key role is reserved to graphene-based polymer composites. In this context, graphene oxide (GO) was intensively investigated, thanks its low cost preparation, the high specific surface area and the abundant functional groups that strongly enhances GO ability to bind contaminants via electrostatic interactions or to anchor chemical functionalities driving the material to one or more specific goal [32,33]. From these considerations we have formulated a novel multifunctional super-adsorbent sponge based on poly-2-hydroxyethyl methacrylate/GO composite developed by a cryo-polymerization in water. In addition, taking advantages by the hydroxyl pendant groups present on both HEMA and GO moieties, our strategy involves the use of the sponge as a support to link ZnO by using Atomic Layer Deposition (ALD), conferring to the sponge the ability to degrade pollutants *via* photocatalytic process after the adsorption step.

Keywords: *Cryogels; Graphene Oxide; ZnO; Dye removal; Atomic Layer Deposition*

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Applicazioni di polimeri riciclati in guaine bituminose: opportunità per un'economia circolare

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ABSTRACT

Lo studio condotto consiste nella realizzazione e caratterizzazione di mescole bituminose nell'ottica di una economia circolare. Sono stati quindi utilizzati polimeri di riciclo come le poliolefine o gli elastomeri, tutti provenienti da realtà che trattano e recuperano queste materie. Anche i flussanti (plastificanti), tra cui gli oli minerali, da noi inseriti per dare corpo alla mescola provengono tutti da rigenerazione di oli esausti. Anche l'additivo da noi testato per abbattere l'odore durante la produzione della mescola è un rifiuto della lavorazione degli oli vegetali (AVO, ossia Acque Vegetative Olearie). Lo stesso polverino da pneumatici fuori uso (PFU) che viene inserito nella mescola proviene da una filiera che opera in tutt'Italia per il recupero di tali materiali, creata dal consorzio Ecopneus, e cerca soluzioni per individuare sempre nuove applicazioni per il PFU come alternativa ad elastomeri vergini. In questa cornice abbiamo formulato delle mescole bituminose per cercare di ottenere un prodotto finale dalle proprietà richieste dal mercato ma con un basso impatto ambientale, ad un costo competitivo, ma soprattutto con un forte interesse all'incrementare la produzione per aumentare lo smaltimento di tutti questi rifiuti che sono un'ottima alternativa a polimeri vergini usati oggi. Quella che noi proponiamo potrebbe quindi essere un'ottima soluzione e i futuri studi di IPool saranno atti a migliorare e rendere più efficiente il settore del riciclo, valorizzare e nobilitare materiale di scarto.

Keywords: (*guaine bituminose, polverino pneumatico; acque vegetative olearie; olio minerale esausto; polimeri riciclati*)

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Influence of the variation of injection moulding parameters on the electrical properties and morphology of PP/MWCNT nanocomposites

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ABSTRACT

Nowadays, polymers have a fundamental role in everyone daily life [1]. The combination of their main features makes these materials essential in several industrial sectors. Numerous techniques are generally used to manufacture components: the most commonly adopted are melt mixing and injection moulding processes.

Nevertheless, in literature it is reported that both these techniques and their working conditions strongly affect the properties of the final components [2-6]. In fact, it is known that a tough orientation of molecular chains and fillers, which are often added to obtain specific properties in the final formulations, occurs inside the molten material during the processing phases. This phenomenon creates a marked anisotropy in the morphology and in the resulting final properties [7, 8]. The systematic study of this mechanism is important to modify correctly and to optimize the processing conditions, in order to tailor the final properties of the materials.

This work aims to investigate the electrical anisotropic behaviour of injection-moulded polymeric MWCNT-based nanocomposites, correlating the change of process conditions and the morphological structure of the PP nanocomposites. With this purpose, several formulations were prepared and manufactured using injection moulding process. Three parameters were changed, namely temperature of the melt, temperature of the mould and injection rate. Moreover, an innovative injection molding technique, i.e. the Heat & Cool, was implemented to vary quickly the mould temperature, increasing and decreasing it.

As a main result, the variation of the processing conditions plays a fundamental role in modifying the morphological structure and the electrical behaviour of the MWCNT-based nanocomposites, especially when the MWCNT content is in the range of the electrical percolation threshold. In particular, the increase of the temperature of the mould and of the injection rate act as the main responsible of the decrease of the electrical resistivity of the prepared nanocomposites.

Keywords: (*electrical resistivity; processing parameters; nanocomposites; injection moulding; multiwalled carbon nanotubes*)

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