Macrogiovani 2023

21-23 June 2023, Catania

25 years

Workshop for Young Researchers on Macromolecular Topics

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Book of Abstract

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PLASTICA ALFA
INNOVATION & WATER TECHNOLOGIES

Wednesday, 21st June 2023

Time		
13:00-14:00	**Registration**	
14:00-14:30	**Welcome words from Organizing Committee**	
	PhD III year	
14:30-14:40	Sara Alfano	*Sustainable chemical modification of poly-hydroxy alkanoates(PHAS)*
14:40-14:50	Benedetta Brugnoli	*Tunable amphiphilicity of poly(diglycerol adipate) to improve drug encapsulation*
14:50-15:00	Clarissa Ciarlantini	*Development of antioxidant wound dressings based on functionalized and crosslinked chitosan*
14:30-15:00	Isabella Denora	*Is Mullins effecta reversible phenomenon?A study on thermal treatment effect on the fracture behaviour o fpre-stretched filled elastomers*
15:00-15:10	Valentina Dini	*Mechanoresponsive nanofibers by electrospinning of mechanochromic polymers blends*
15:10-15:20	Simone Donato	*Multi-responsive microstructures based on liquid crystalline network*
15:30-15:40	Andrea Escher	*One-step fabrication of hybrid photonic particles via the confined self-assembly of blockcopolymers*
15:40-15:50	Fred Lange	*Composite layers of polymer brushes and nanoparticles*
15:50-16:00	Viviana Ospina Guarin	*From controlled polymers to precision polymers: advances in monolayer doping using grafting to process*
16:00-16:30	**Coffee Break**	
16:30-16:40	Davide Perin	*Tuning the self-healing properties of polyamide 6 (PA6)/ cyclic olefinic copolymer(COC) polymer blends for structural composites*
16:40-16:50	Edoardo Podda	*Amphiphilic star shaped copolymers as viscosity index improvers for lubricants*
16:50-17:00	Giulia Rando	*Smart macrocycle-based blended polymers for waste water remediation: from material design to its adsorptive properties*
17:00-17:10	Matheus Saccardo	*Development of bioinspired electromechanical devices based on amphiphilic block copolymers*
17:10-17:20	Stefano Scurti	*Hybrid metal-polymer nanostructured materials for catalytic water treatment in mild conditions*
17:20-17:30	Laura Simonini	*Self-healing of functionalized interphases made of polycaprolactone coated glass fibers for composite applications*
17:30-17:40	Alessandro Sorze	*Development of super absorbent xanthan-based hydrogel composites for forestry and agricultural application*
18:00-20:00	**Poster Session + Aperitif**	

Thursday, 22nd June 2023

Time		
9:00-9:30	**Key-note Professor Francesco Picchioni (University of Groningen)**	
	PhD II year	
9:30-9:40	Nicoletta Baglieri	*Block-copolymers self-assembly via static and dynamic solvent vapour annealing*
9:40-9:50	Andrea Lanfranchi	*Polymer photonics in thermal management*
9:50-10:00	Edoardo Miravalle	*Recycling abilities of optically transparent biobased polyurethane network*
10:00-10:10	Carlos Pavon	*Tuning dispersity of polymer brushes to modulate their interfacial properties*
10:10-10:20	Mariangela Rea	*Rheological assessment of enzymatically crosslinked tyrosine-functionalized alginate hydrogel for biomedical application*
10:20-10:30	Lorenzo Rocchi	*Polymer glass/melt transformation kinetics*
10:30-10:40	Ruggero Rossi	*Liquid Crystal Elastomers by 3D printing for photo responsive actuators*
	PhD I year	
10:40-10:50	Giulia Bernagozzi	*Towards effective upcycling of polyolefines*
10:50-11:00	Niccolò Bini	*Optical and mechanical characterization of cellulose-based molded products*
11:00-11:30	**Coffee break**	
11:30-11:40	Arianna Chiappa	*Application of fused deposition mode lignin the customization of pharmaceutical dosage forms containing timapiprant*
11:40-11:50	Fulvia Cravero	*Correlation between morphology and processing parameters in polymer blends: preliminary results towards hierarchical structures*
11:50-12:00	Federica Daus	*Characterization of bacterial cellulose from kombucha tea*
12:00-12:10	Luana Di Lisa	*Development of a novel 3D bioprintable hydrogel formulation based on decellularized extracellular matrix and gelatine methacrylate*
12:10-12:20	Dario Fontana	*Conducting polymers as anticorrosion coatings*
12:20-12:30	Mattia Fornaro	*Effect of crosslinking density on the properties of reprocessable diels-alder epoxy-based thermosets*
12:30-12:40	Alberto Fracasso	*Overcoming poly(ethylene glycol) immunogenicity by developing well-defined polymer alternatives*
12:40-12:50	Luigi Gamberini	*A novel method to crosslink electrospun pullulan membranes containing carbon dots for water purification*
12:50-13:00	Gianluca Gazzola	*Oxygen tolerance during surface-initiated photo-ATRP: tips and tricks for making brushes under environmental conditions*
13:00-14:00	**Lunch**	
14:00-14:10	Andrea Giovanelli	*Solid state NMR characterization of a model anion exchange membrane*
14:10-14:20	Giorgia Giusti	*Cellulose hydrophobization for beverage packaging applications*

14:20-14:30	Valentina La Matta	*Life cycle assessment of tires: the role of the production phase*
14:30-14:40	Erica Laguzzi	*Catalyst-free vitrimer based on β-amino ester in presence of β-hydroxy functionalities*
14:40-14:50	Martina Martusciello	*All-polymer based mechanochromic Distributed Bragg Reflectors*
15:00-15:10	Monica Milani	*Adhesion enhancement in CFRP composites via topological entanglement*
15:10-15:20	Daniele Natali	*Semicrystalline polymeric networks as tailored shape-memory materials*
15:20-15:30	Rosita N. Gentile	*Design and synthesis of mechanophores for self-diagnostic vitrimers*
15:30-15:40	Gioacchino Pignatiello	*Enhancing tire performance through effective dispersion of bio-based components in rubber compounds*
15:40-15:50	Nicola Porcelli	*Synthesis of biobased monomers and polymers*
15:50-16:00	Susanna Romano	*Starch films plasticised by novel dicationic imidazolium-based ionic liquids*
16:00-16:30	**Coffee break**	
16:30-16:40	Francesco Scorcioni	*Chemical recycle of plasmix*
16:40-16:50	Giulia Scurani	*Bifunctional ATRP initiators for the synthesis of α,ω-dichloropolystyrene:new functionalities and thermal stability study*
	Student	
16:50-17:00	Alice Bianucci	*Exploring the effect of the applied thermal treatment on the fracture behaviour of a NBR/silica compound*
17:00-17:10	Luca Spagnoletti	*Viral-assisted delivery of polythiophene-based nanoparticles to rescue neurodegeneration*
From 20:30	**Social Dinner**	

Friday, 23rd June 2023

Time		
	Research fellow	
9:00-9:10	Francesco Bisio	*Synthesis of fine and conductive films of PEDOT by liquid phase and vapor phase polymerization*
9:10-9:20	Emma Contini	*Mechanochromic performaces of perylene diimide-doped polyuretanes: covalent bonding vs blending approaches*
9:20-9:30	Luca Gargiulo	*Microwave assisted extraction of hemp seeds oil and its use for food packaging systems*
9:30-9:40	Giorgia Gnoffo	*Identification of microplastics in different mixtures and blends through pyrolysis-gas chromatography/mass spectroscopy*
9:40-9:50	Elenora Lorenzi	*Development of PP-based materials with flame retardance and thermal conductivity properties for 3D printing*
9:50-10:00	Matteo Righetti	*Mixed-matrix membranes for seperation of two-component CO2-CH4 gas mixtures*
10:00-10:10	Michele Zanoni	*Two-way shape memory polymer as a platform for light-induced reversible actuation: from film to fibers*
10:10-10:20	Edoardo Zonta	*Toughening effect of 2,5-furandicaboxylate polyesters on polylactide-based compatibilized renewable fibers*
	Post doc	
10:20-10:35	Giulia Fredi	*In situ anionic polymerization of caprolactam for polyamide6-based thermoplastic composites*
10:40-11:00	**Key-note Professor Pedemonte**	
11:00-11:30	**Coffee break**	
11:30-11:45	Angelo Nicosia	*An Antibacterial agent based on Polymer-Graphene derivative decorated with Silver Nanoparticles*
11:40-12:00	Francesca Ramacciotti	*Composite electrospun mats as sustainable phototermal systems for artwork restoration*
12:00-12:15	Cecilia Velino	*Development of a novel hyaluronic acid hydrogel system for enhanced loading and controlled release of active molecules*
12:15-12:30	Stefano Zago	*Polymer based photonic sensors for the detection of toluene in water*
13:00-14:00	**Brunch**	
14:00-16:00	**Awards ceremony and greetings**	

*All talks should be about 8 minutes with 2 minute dedicate to the questions, unless for the post doc speakers that have 12 minutes with 3 minutes for the questions

SUSTAINABLE CHEMICAL MODIFICATION OF POLY-HYDROXYALKANOATES (PHAs)

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PhD student 3° year

Abstract

Polyhydroxyalkanoates (PHAs) are a group of bacterially synthesized polyesters that are very appealing in biomedicine thanks to their biodegradability in nontoxic products. However, there are many drawbacks related to their high hydrophobicity which can drastically reduce their compatibility towards living systems and therefore the spectrum of applicability.

For these reasons, chemical modifications are required to tune PHAs hydrophobicity and make such material a valuable alternative to synthetic polymers. Chemical modifications of these polyesters by acid or basic hydrolysis, or aminolysis with di- or multifunctional amines lead to the introduction of functional groups able to increase hydrophilicity and improve stability in a physiological environment. Unfortunately, the use of toxic solvents (chlorinated solvents) or reactants (di- or multifunctional amines, such as ethylene diamine or hexamethylene diamine) as well as surfactants often used for polymer functionalization and nanoparticles preparation, implies careful purification steps in the production process. In this context, the poly-3hydroxybutirate-co-3hydroxyhexanoate (PHBHHx, 11 %wt HHx) films surface was chemically modified by amynolysis. Choline taurinate (Ch-Tau), a non-cytotoxic[1] ionic liquid soluble in water and ethanol, has been used as a nucleophilic agent. The use of Ch-Tau lead to the introduction of sulfonic polar moieties on polymer surfaces and therefore to increased hydrophilicity. Aminolysis was carried out in non-toxic solvents by using ethanol and water. Functionalised films obtained at different reaction times were characterized by FTIR spectroscopy, static contact angle measurements and Scanning Electron Microscopy. Amynolized films in methanol were used as a reference.

Characterization highlighted the occurrence of functionalization and the effect of different contact times. Surprisingly, higher time does not result in a greater degree of functionalization and hydrophilicity. In fact, with a prolonged contact time, a surface etching occurs with the subsequent release of surfactant-like molecules. These kinds of structures were fractionated through selective solubilization and used for nanoparticles (NPs) production.

This preliminary work demonstrates the potential of PHAs chemical modification by using non-toxic solvents and reactants for both surface functionalization and nanostructure preparation, highlighting the possibility to broaden the range of PHAs applicability.

References

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TUNABLE AMPHIPHILICITY OF POLY (DIGLYCEROL ADIPATE) TO IMPROVE DRUG ENCAPSULATION

Philippa L. Jacob[1], Benedetta Brugnoli[2], Alessandra Del Giudice[2], Hien Phan[3], Veeren M.Chauhan[4], Laura Beckett[4], Richard B. Gillis,[4,5] Cara Moloney[6], Robert J. Cavanagh[6], Eduards Krumins[1], Morgan Reynolds-Green[1], Joachim C. Lentz[1], Claudia Conte[7], Valentina Cuzzucoli Crucitti[1], Benoit Couturaud[3], Luciano Galantini[2], Iolanda Francolini[2], Steven M. Howdle[1], Vincenzo Taresco[1]

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Role: PhD student 3° year

Abstract

The enzymatically synthesized poly (glycerol adipate) (PGA) has demonstrated all the desirable key properties required from a performing biomaterial to be considered a versatile “polymeric-tool” in the field of drug delivery. However, PGA suffers from poor amphiphilic balance, leading to weak drug-polymer interactions and subsequent low drug-loading in NPs, as well as low NPs stability.

To overcome this, we synthesised four polyadipates by changing their amphiphilicity. The effect of the variation of hydrophilic and hydrophobic polyols was investigated upon an in-depth physico-chemical characterisation and drug interactions as well as self-assembly and NPs stability. Herein, we replaced glycerol (Gly) with the more hydrophilic diglycerol (DGly), and then we adjusted the final amphiphilic balance of the polyester repetitive units by incorporating 1,6-n-hexanediol (Hex)[2].

Among the newly synthesised polymers, PDGAHex demonstrated greater stability and ability to encapsulate model dyes when compared to the other polymers thanks to the better amphiphilic balance.

Moreover, the novel materials have shown good biocompatibility in both *in vitro* and *in vivo* (whole organism) experiments.

References

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DEVELOPMENT OF ANTIOXIDANT WOUND DRESSINGS BASED ON FUNCTIONALIZED AND CROSSLINKED CHITOSAN

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Role: PhD student III° year

Abstract

Tissue engineering is an interdisciplinary field that develops new methods to enhance the regeneration of damaged tissues. Skin tissue engineering takes advantage of principles of engineering, biology and chemistry for manufacturing dressings that can promote the regeneration of injured skin. Polysaccharides such as hyaluronic acid, alginate and chitosan have appropriate biological properties to be used as wound dressings[1]. Furthermore, the presence of functional groups in their backbone makes them easily modifiable both by chemical reactions and physical interactions with different molecules, allowing the development of materials with better antibacterial and/or anti-inflammatory activity. In the present work, innovative dressings based on modified chitosan were developed using the solvent casting technique. In particular, chitosan (CS), characterized by good antimicrobial activity[2] but poor dimensional stability in physiological environment, was first modified with glycidylmethacrylate (GMA) and glycerol (GLY) and then with ethylene glycol dimethacrylate (EGDMA). GMA was introduced into the polysaccharide to have a functionality (double bond) to be exploited in the subsequent crosslinking reaction with EGDMA, while GLY was taken into consideration to provide a good degree of elasticity to polymer films, which must be able to adapt to the skin. To evaluate the effect of GLY on the mechanical properties of the developed matrices, the films were obtained by varying the glycerol concentration (10, 20 and 30% w/v). For all samples, at each concentration of GLY, an increase in the elongation at break and in the dimensional stability in aqueous environment was observed, accompanied however by a considerable decrease in the elastic modulus. The matrices were then subjected to chemical crosslinking using EGDMA to create bridges between the GMA-modified CS chains. To evaluate how the cross-linking process affected the elasticity of the films, three different concentrations of EGDMA (0.05-0.1-0.5 mM) were tested for the same reaction time (5 min). The crosslinked matrices showed a significant increase in the value of the elastic modulus, but only in the case of the lowest EDGMA concentration the matrices maintained an elongation at break suitable for the development of dressings. With the aim of avoiding possible inflammatory reactions during the healing phase, the films were functionalized with 3,4 hydroxycinnamic acid (HCAF), an antioxidant capable of limiting the phenomenon of oxidative stress[3]. The introduction of the antioxidant into the films was carried out both by covalent bonding between CS amino groups and the ortho position of the catechol ring, using laccase as catalyst, and imbibition. In both cases the introduction of HCAF molecules increased the antioxidant properties and the elastic modulus of the films. Biological tests are underway to verify the possible application of these systems in skin tissue engineering.

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Is Mullins effect a reversible phenomenon? A study on thermal treatment effect on the fracture behaviour of pre-stretched filled elastomers

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Role: PhD student XXXVI cycle

Abstract

Filler particles are usually added to rubber materials to improve their mechanical behaviour. The introduction of these particles is also responsible of the so-called Mullins effect[1,2,3]: when the material is stretched, it results to be softer and less dissipative than the virgin material. In real applications, these materials are used in products subjected to solicitations, so it is more important to study the mechanical response of softened material than of virgin one. It is known that Mullins effect is caused by a change in material microstructure induced by the stretching; however, it is still not clear what this modification actually is[2]. Mullins effect is reported to be a reversible phenomenon and a proper thermal treatment can increase the rate of the recovery of the original mechanical behaviour of the material. In literature, the effects of thermal treatments have been evaluated on the uniaxial tensile response of softened filled elastomers with different type of matrix and filler, quantity of filler, amount and type of crosslinking and pre-stretching level (some examples are [1,3,4,5]).

In this work, the effects of softening and thermal treatments have been evaluated not only on the uniaxial tensile response of the material but also on its fracture behaviour. Firstly, a thermal treatment that allows to recover the original material behaviour was defined. Secondly, the fracture toughness of the softened material before and after the thermal treatment has been compared to that of the original material. Fracture tests have been performed at room temperature and constant displacement rate on single edge notched pure shear or tension specimens. The materials investigated in this research are a carbon black filled HNBR and a silica filled NBR from Arlanxeo Germany GmbH. In both materials, as expected, the softened material resulted to be less tough than the virgin material, in correlation with a lower dissipative response. However, after a proper thermal treatment, only HNBR recovered the toughness of virgin material. The investigation about the different behaviour is still on-going.

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MECHANORESPONSIVE NANOFIBERS BY ELECTROSPINNING OF MECHANOCHROMIC POLYMERS BLENDS

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Abstract

Mechanochromic polymers have emerged as a promising class of materials that can change color or fluorescence properties in response to mechanical stimuli. One of the possible strategies to impart polymeric materials with mechanochromism is the incorporation of suitable, aggregachromic dyes. Such dyes can display a change in their optical properties in response to the nano- and microstructural changes in the surrounding polymers upon mechanical deformation.[1,2] Recently, some of us reported a macromolecular additive that carries two excimer-forming cyano-substituted oligo(*p*-phenylene vinylene) (tOPV) dyes at the termini.[3] This macromolecule, blended with commercial polyurethanes, confers mechanochromic characteristics. The fluorescence response of the resulting polymer blends turns out to be proportional to the applied strain and reversible through multiple cycles of deformation and relaxation.[4]

In this work, a semicrystalline thermoplastic polyurethane was blended with different amounts of the tOPV additive and the polymer blends were processed by electrospinning into continuous fibers with diameters in the range of 300 to 700 nm. Adapting the electrospinning collector allowed for the preparation of nonwoven mats of randomly arranged as well as parallelly aligned fibers. The fluorescence spectra of the fibers show the characteristic emission bands of monomeric tOPV at 525 nm (I_M) and for tOPV aggregates at 630 nm (I_E), mirroring results previously acquired with bulk films.[4] Fiber mats were subjected to mechanical testing in tensile mode while simultaneously acquiring emission spectra. Prior to deformation, the excimer emission band (I_E) is predominant, but sample deformation was accompanied by an increase in the intensity of the monomer emission band (I_M), indicating a disruption of tOPV aggregates. Notably, analysis of spectra recorded in situ during sample deformation showed that the ratio between the two characteristic bands (I_M/I_E) correlates with the applied strain, even at the level of individual fibers. These results demonstrate that the mechanochromic properties of the polymer blends are preserved after processing by electrospinning. Moreover, by aligning the fibers with respect to the direction of applied force, the sensitivity of the observed mechanochromic responses can be adjusted. This showcases that mechanochromic microfibers could be introduced in complex garments as deformation sensors for a range of different applications.

References

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MULTI-RESPONSIVE MICROSTRUCTURES BASED ON LIQUID CRYSTALLINE NETWORK

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The ability to fabricate materials able to perform actuation in a reliable and controlled manner is one of the primary needs for soft robotics[1]. In this field, Direct Laser Writing (DLW), a two-photon polymerization technique, is a very promising tool for the development of micrometric actuators providing novel solutions for reliably preparing of 3D micro-structures with a resolution up to of 100 nm. In recent years, our research group has focused on the development of Liquid Crystalline Networks (LCNs) capable of performing reversible shape-changing under stimuli such as light irradiation or temperature variation. Different microrobots and photonic devices printed with light responsive LCNs by DLW has been reported[2].
In this communication, we will present the use of different polymerizable LC monomers to engineer the actuation properties under stimuli. Different molecular tweaks, such as LC mesogenic core or the ratio in between monomers, it is possible to affect the responsiveness of the materials. Furthermore, we demonstrate how varying the printing conditions, free-standing microstructures can be developed with suitable shape, as shown in Figure 1A and 1B.

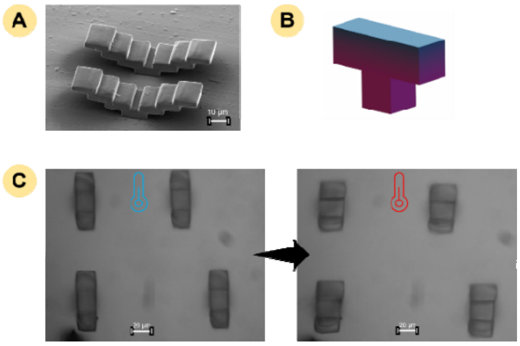

Figure 1. LCN microstructures printed by DLW. A) SEM of a 3-step stair; B) Project made for a free-standing table and C) Images of printed free-standing tables taken at low temperature (left) and high temperature (right).

An example of actuation of LCN microstructures is in Figure 1C. These multi-responsive microstructures are demonstrated useful not only in the field of micro-robotics, but also as a valuable tool in digital encryption keys.

Acknowledgments
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References

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One-step fabrication of hybrid photonic particles via the confined self-assembly of block copolymers

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Role: PhD student 3° year

Abstract

There is a growing interest for new materials that offer pure, brilliant, and long-lasting coloration. One promising approach is the use of dielectriclattices, where materials are alternated to modulate the refractive index with sub-micrometric periodicity.[1] When the this periodicity is opportunely tuned, interaction of these lattices with light generates structural colors. These systems, are called photonic crystals, as theypossess a photonic band structure that identifies spectral regions for which photons propagation is forbidden, namely the photonic bandgaps (PBGs), that are responsible for the chromatic response.

We report on the fabrication of photonic pigments using self-assembled block copolymers (BCPs) in emulsion droplets.[2] The BCP properties and emulsification conditions create ordered structures with alternating domains, resulting in vibrant structural coloration through strong light reflection. The color can be finely tuned by controlling the domain spacing. Additionally, we show that the pigment properties can be engineered with various nanomaterials like plasmonic or oxide nanoparticles and fluorescent quantum dots.[3] These hybrid structures are manufactured via a simple co-assembly procedure in emulsion droplets, with the spatial location of the inorganic nanocomponents being controlled via enthalpic and/or entropic interactions. Such an approach addresses two fundamental problems of current photonic pigments,[2] which are responsible for their limited usage.

On one hand, the low dielectric constrat between the block copolymers is enhanced by addition of high-refractive index loads , thus ensuring a more vibrant and brilliant coloring. On the other hand, introducing optically active nanomaterials enables unlocking new optical features such as fluorescence that might pave the way for developing advanced photonic devices with numerous fundamental applications.

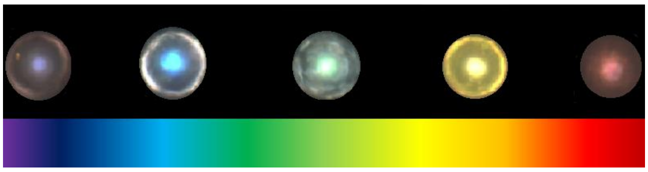

Figure 1. Optical microscopy images of photonic microparticles showing different structural coloration.

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COMPOSITE LAYERS OF POLYMER BRUSHES AND NANOPARTICLES

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Abstract

Porous layers of nanoparticles can be used for catalysis.[1] A possible way to obtain these layers is the incorporation of nanoparticles in polymeric scaffolds. Here we present a simple method to generate crack free thin layers (fig. 1) with an adjustable porosity. Therefore, cationic polymer brushes are synthesized via surface-initiated copper(0)-mediated controlled radical polymerization (SI-CuCRP).[2] In the next step, these polymeric layers are immersed in a suspension of negatively charged silica nanoparticles (NPs) to form composite layers.[3] A subsequent calcination step allows the removal of the polymeric scaffolds which results in a porous network of the beforehand embedded nanoparticles.

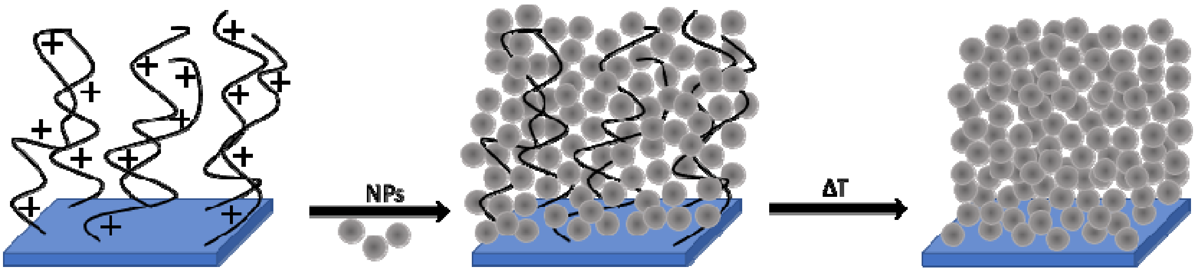

Figure 1: Cationic polymer brushes serve as scaffold for incorporation of negatively charged nanoparticles. A subsequent calcination step removes organic compounds to form porous layers.

The SI-CuCRP enables control over the grafting density and the thickness of the cationic polymer brushes.[4] This can be used to tailor the properties of the generated calcinated composite layers. For example, by implementing a grafting density gradient, a porosity gradient can be achieved.

In addition to that, the influence of the nanoparticle size was investigated as well as the concentration of the nanoparticle suspension while incorporation. Varying these parameters allows additional control over the thickness and porosity of the calcinated composites. Furthermore, the system was expanded by using gold and palladium nanoparticles instead of silica. This might allow the implementation of these porous layers in the field of catalysis.

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FROM CONTROLLED POLYMERS TO PRECISION POLYMERS: ADVANCES IN MONOLAYER DOPING USING GRAFTING TO PROCESS

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Abstract

Semiconductors materials as silicon, are commonly doped before using them in the production of transistors for the electronics industry. The precise insertion of dopant atoms is crucial to improve the size and performance of electronic devices. Therefore, phosphorus is commonly inserted into silicon crystals by atom diffusion or ion implantation. However, those strategies lack control over the number of dopant atoms. In the last years, “monolayer doping”[1] was introduced as a strategy that allows controlling the concentration of dopants. Carrier molecules containing the dopant atoms are grafted forming a monolayer on the semiconductor surface. The self-limiting nature of the grafting reaction allows controlling the available atoms for the exchange with silicon. Controlled polymers such as Polystyrene and poly-(methyl methacrylate) with narrow dispersity and containing a terminal phosphate moiety have been used to dope silicon substrates[2]. Even if they showed to be adequate for the application, they are not reproducible and lately has been reported that polydispersity has an important impact on the characteristics of the grafted polymer monolayers. Therefore, precision polymers are proposed to face the new challenges.

Monodisperse polypeptoids are synthesized by solid phase sub-monomer synthesis (SPSS). The unit-by-unit assembly mechanism is reproducible and allows to control of the monomer sequence and therefore the polymer molecular weight.

In this work, Polypeptoids containing phenyl lateral chains with different backbone lengths (5-10-14 and 19 monomer units) and containing a terminal phosphorus moiety were synthesized by SPSS. Then, they were grafted into a silicon substrate. Samples were treated by oxygen plasma ashing to eliminate the polymers and the concentration of phosphorous at the silicon surface was determined by TOF SIMS analysis. The experimental results were compared with expected values according to the theoretical grafted density.

MALDI TOF analysis confirmed the monodispersity of the synthesized polymers. *Grafting to* process conditions were optimized and determined to be 190°C and 40 s. The performance of polypeptoids for the doping of semiconductor through monolayer doping is an approach to solving problems related to polymers polydispersity. An inverse correlation was found between the phosphorus dose and the polypeptoid length. Besides the procedure is suitable for industrial integration.

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Tuning the self-healing properties of polyamide 6 (PA6)/ cyclic olefinic copolymer (COC) polymer blends for structural composites

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Abstract

The state of the art of development of composites possessing self-healing properties is primarily attempting to mimic the healing mechanisms developed by nature. However, self-healing materials are generally characterized by a limited technology readiness level (TRL). In this work, the improvement of intrinsic self-healing polymer blends, composed of a polyamide 6 (PA6) matrix and a cyclic olefinic copolymer (COC), through the tuning of a compatibilizer was performed. The produced compatibilized blends could be potentially used as matrices for multifunctional structural composites with self-healing capability.

PA6 used in this work was a Radilon S 24E 100 NAT, provided by Radici Group SpA (Gandino, Italy). The COC selected as healing agent was Topas COC 9506F-500, supplied by TOPAS (Raunheim, Germany). The selected compatibilizer was poly(ethylene-co-glycidyl methacrylate) (E-GMA) purchased from Merck (St. Louis, Missouri, Stati Uniti). PA6 and COC were melt compounded for 1 minute and then the compatibilizer was added for a total processing time of 6 minutes. This operation was performed in a Thermo Haake Rheomix 600 internal mixer, operating at 60 rpm at a temperature of 230 °C. Subsequently, the blends were grounded and compression molded in a Carver hot-plate press at 235 °C for 8 min, under an applied pressure of 1.9 MPa.

The healing efficiency of the system was determined by comparing the plane-strain fracture toughness tests in quasi-static and impact modes, before and after the healing process. The tested samples were thermally healed at three different temperatures, i.e., 140, 160, and 180 °C, applying a pressure of 0.5 MPa for 1 h. Without the compatibilizers, the healing efficiencies at 160 °C were 11.6 % in quasi-static mode and 56.9 % in impact mode. Thanks to the addition of E-GMA compatibilized COC domains homogeneously distributed within the PA6 matrix, the healing efficiencies values increased up to 37.8 % in quasi-static mode and 81.8 % in impact mode after healing at 140 °C. Hence, it can be concluded that the compatibilization performed improved significantly the overall healing efficiency. The matrix characterized by the best properties was the one with 5 wt% of compatibilizer and thus, short and long-carbon fiber composites will be produced in the future.

AMPHIPILIC STAR SHAPED COPOLYMERS AS VISCOSITY INDEX IMPROVERS FOR LUBRICANTS

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Abstract

Viscosity index improvers are polymeric additives which impart the desired viscosity to the lubricant at normal operating temperatures and reduce the viscosity-temperature relationship of the lubricants [1]. The change in viscosity of a lubricant as a function of temperature is represented by the viscosity index (VI). Another important requirement for polymeric additives is their stability over prolonged use under high mechanical shear, which can cause a permanent loss of lubricant viscosity due to chain breakage. Polymers with a star-shaped structure generally have higher shear stability than linear polymers of similar Mw, because the chain breakage due to mechanical shear has less effect on their overall rheological properties [2]. Star polymers represent a complex macromolecular architecture composed of linear polymer chains, called "arms", covalently linked to a central branching point, called "core" [3]. There are two main approaches to the synthesis of these complex structures: core-first and arm-first. In the core-first strategy, polymeric arms are grown directly from a multifunctional initiating core, and the number of arms in the star is equal to the number of initiating sites on the core. In the arm-first strategy, well-defined pre-formed linear arms are linked together by reaction with a multifunctional cross-linking agent to form the star polymers [4]. In this work, star-shaped copolymers were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization according to the arm-first technique. In particular, the RAFT polymerization was carried out using a peculiar one-pot two-steps synthetic process, called reverse micellar polymerization. Reverse micellar polymerization involves the use of a non-polar solvent containing a hydrophobic monomer, in which a hydrophilic comonomer is dispersed by means of a non-ionic surfactant. The reaction mixture is a heterogeneous system in which the hydrophilic monomer is compartmentalised within micelles stabilized by the surfactant. The initiator is hydrophobic and therefore polymerization begins in the hydrophobic phase where the growing chains react with the hydrophobic monomer. However, the compartmentalization of the hydrophilic monomer inside the micelles means that when a growing chain enters a micelle, it polymerizes the monomer contained therein and then returns to the hydrophobic phase. This process makes it possible to obtain hydrophobic polymeric arms containing hydrophilic microblocs, that exhibit an amphiphilic behaviour. In addition, it is possible to obtain amphiphilic multiblock copolymers with a star-shaped structure without any purification of the preformed polymer arms by adding a polyfunctional polar monomer to the reaction system. Star formation was confirmed by GPC analysis. The yield was always greater than 70% and increased with increasing the crossilinker amount. Rheological measurements were performed to evaluate the viscosity, and tribological tests were carried out to evaluate the mechanical stability. NMR analysis was also performed to determine the monomer conversions, which was always higher than 80%.

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SMART MACROCYCLE-BASED BLENDED POLYMERS FOR WASTEWATER REMEDIATION:
FROM MATERIAL DESIGN TO ITS ADSORPTIVE PROPERTIES

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Abstract

Clean water is essential for both economic and social growth, as well as human health. Recently, new advanced filtration techniques are increasingly being developed to purify water from the presence of emerging contaminants, such as organic dyes, which represent a serious risk to human health and ecosystems due to their chemical persistence and toxicity[1].
For example, polyethersulfone (hereafter PES) is a polymer widely used as a basis to produce nano and ultrafiltration membranes for water purification, due to its mechanical properties as well as thermal and chemical stability. New PES-based functional membranes with implemented characteristics such as hydrophilicity, porosity, surface properties and adsorption performance, can be easily produced by blending with other polymers, crosslinkers or nanofillers[2]. In particular, PDMAEMA, poly[2-(dimethylamino)ethyl methacrylate], a polymer sensitive to external stimuli such as temperature, pH and ionic strength[3], with applications ranging from the therapeutic and biomedical fields to nanotechnology, represents an excellent candidate for the preparation of these PES-based macrocyclic blend polymers.
This communication will focus on: i) the synthesis of a new smart polymer obtained by functionalization of PDMAEMA with pillararene macrocycles, already known for their ability to include organic molecules through host-guest interactions[4]; ii) its subsequent employment for the preparation of PES blends used for the development of functional membranes and beads. Furthermore, in order to determine the correlations between the structure and properties of the final obtained polymeric beads, their chemical-physical/morphological characterizations, and adsorption tests of two model organic dyes will be showed.

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DEVELOPMENT OF BIOINSPIRED ELECTROMECHANICAL DEVICES BASED ON AMPHIPHILIC BLOCK COPOLYMERS

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Abstract

Technological advances in the aerospace industry, biomedicine and robotics drive the need for innovative and more sustainable devices. An important class of advanced materials is represented by electromechanical devices, which are bioinspired materials capable of mimicking biological systems in appearance, functionality, and operation[1]. Typically, electromechanical devices present a metal/electroactive-polymer/metal sandwich-type structure, and they can change shape or bend in response to electrical stimuli, as well as generate a current upon mechanical stimulation. In addition, they generally have low density, low driven voltage, and are biocompatible[2]. Therefore, electromechanical devices are highly promising for several applications, such as actuators, sensors, and artificial muscles. On the other hand, for practical applications, electromechanical devices must possess: i) high ionic conductivity, ii) flexibility, iii) mechanical resistance, and iv) chemical, thermal, and structural stability. These requirements can be fulfilled by engineering the structure of amphiphilic block copolymers that serve as electroactive membranes in the devices[3]. These copolymers can self-assemble into well-defined morphologies with nanosized domains. Good mechanical properties and elevated ionic conductivity are simultaneously attained when a rigid, conductive phase is dispersed in a low glass transition temperature (Tg) domain. Hence, it is possible to effectively decouple the conductivity from mechanical properties, adjusting the flexibility and Young's modulus of the material by tuning the size of the blocks. Therefore, in this project, reversible addition−fragmentation chain-transfer (RAFT) polymerization was used to synthesize a library of Poly(butyl methacrylate)-b-(polystyrene-r-poly neopentyl styrene sulfonate) (PBMA-b-(PS-r-PNeoSS)) block copolymers to correlate the block size with the nanostructure. RAFT is a robust and versatile technique for preparing low-dispersity copolymers with precise composition. The appropriate selection of polymerization conditions (*i.e.*, initiator concentrations and temperature), the polymerization rate and the livingness of the systems were controlled, thus engineering block copolymers with desired properties. Subsequent thermolysis of PNeoSS segments removes the neopentyl group resulting in a polystyrene-r-polystyrene sulfonate (PS-PSS) backbone, providing the desired ionic conductivity.

Figure 1: RAFT polymerization in DMF using CPADB as chain transfer agent initiated by AIBN.

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HYBRID METAL-POLYMER NANOSTRUCTURED MATERIALS FOR CATALYTIC WATER TREATMENT IN MILD CONDITIONS

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Abstract

Water treatment represents one of the main challenges arising from climate change and a fundamental role is played by the treatment and reuse of alternative water sources. Water pollutants, especially persistent organic products (e.g. nitroaromatics compounds) (POP) are difficult to degrade by microorganisms, and many of these have carcinogenic, teratogenic, and mutagenic effects on humans and biodiversity. Scientific research has continuously developed new low-cost water purification technologies where a primary role is played by catalytic degradation/reduction which exploits the decomposition or transformation of toxic and harmful organic substances into organic ones with lower toxicity and/or a potential industrial interest, to be reinserted into the production chain as a higher value products.[1] The main issues related to catalytic processes are connected to the phase of the system, indeed development of heterogeneous catalytic systems could facilitate the recovery of the catalyst without losing efficiency, but in the other hand significant challenges inherent to the specific catalyst design to maximize liquid-solid interfaces are still presented. In this optic, the heterogenization of catalytically active colloidal metal nanoparticles (NP) through the use of a support represented a suitable strategy to produced nanostructured catalysts. However, the employment of colloidal nanostructures are strictly linked to the use of stabilizers to prevent their aggregation and therefore a loss of their catalytic properties derived from the reduced size with a direct role on catalytic mechanism in terms of active phase coverage and selectivity. From this point of view, the development of hybrid metal-polymer nanomaterials could represent a challenge to maximize the effect of polymers on the catalytic mechanism by direct supporting of the catalytic phase into polymeric matrixes (e.g hydrogel, cryogel). Among them, polymeric cryogel networks obtained under freezing condition via cryogelation methods allowing to prepare superporous materials with highly attractive network.[2,3]

Basing on this premises, in this work three different functionalized acrylic-based polymeric cryogels characterized with different acid/base properties (p-MAA, p-AEMA and p-HEMA) were prepared by cryopolymerization and employed to immobilize metal precursor ($HAuCl_4$ and K_2PdCl_6) via wet impregnation method with a low metal loading (1%). Subsequently, the active phase was reduced and the final hybrid nanocatalysts were widely characterized by spectroscopic, microscopic and thermal analysis. The as-prepared materials were catalytically tested in 4-nitrophenol reduction and the outcomes were correlated with polymeric matrix features in order to investigate structure-catalytic properties correlation.

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SELF-HEALING OF FUNCTIONALIZED INTERPHASES MADE OF POLYCAPROLACTONE COATED GLASS FIBERS FOR COMPOSITE APPLICATIONS

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Abstract

In fiber-reinforced polymer composites, the interphase between the matrix and the fibres dictates the properties of the final component. After a damage event, a self-healing interphase could restore the interaction between the two phases, if subjected to external stimuli, for example to heat. The healing process extends the service life of the composites, reducing the waste and the repairing costs, therefore improving the sustainability. This work is focused at depositing a biodegradable polymeric coating on the glass fibers surface to provide the healing of the interphase. The interphase healing was performed by heating micro composites, prepared by depositing a single micro drop of an epoxy resin on the coated fibers, at 80°C for 1h. From the micro debonding tests, the healing efficiency (HE%) was calculated as the ratio between the interfacial shear strength (IFSS) after and before the healing process. The epoxy partial melting during the heating step were also considered and subtracted from the calculated healing efficiency. From FESEM analysis, a good and homogeneous PCL nanoparticles deposition on the glass fibers surface was observed. Increasing the solutions concentration, the applied voltage and the deposition time during the EPD process, the amount of deposited coating on GF increases. Interesting results were obtained from the healing process that indicates a full recovery of the interfacial shear strength than the initial fiber/matrix interphase.

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DEVELOPMENT OF SUPERABSORBENT XANTHAN-BASED HYDROGEL COMPOSITES FOR FORESTRY AND AGRICULTURAL APPLICATION

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Abstract

The need to develop technological solutions to support planting and silviculture through appropriate forestry operations has emerged in recent years due to climate change that has brought severe damage to forest ecosystems and lack of rainfall in many areas of Europe[1]. The goal of this research is to develop innovative bio-based composites to be used as soil conditioners (SC) and topsoil covers (TSC) to support seedling growth and thus to improve water efficiency in both forestry and agricultural applications. Hydrogels based on xanthan gum[2] and cellulose pulp were prepared for the soil conditioners. Topsoil covers were produced from the previous hydrogels by forming films by crosslinking the xanthan chains using different crosslinking agents such as citric acid[3], sodium trimetaphosphate, glycerol and tannic acid. Physical, rheological, water absorption and thermal analyses were performed to fully characterize the materials and to compare their properties with respect to the type of crosslinking agent used. Tests of water absorption and water retention capacity performed on soil treated with 1.8%wt of the soil conditioner showed an increase of more than 60% in water absorption values compared to untreated soil, while also reducing the rate of water evaporation. Xanthan-based films for use as TSCs showed strong water absorption capacity (about 2100% after 30 days), which decreases by increasing the amount of crosslinking agent in the initial composition. Crosslinking the xanthan gum is a crucial step that allows the TSC to absorb water efficiently while maintaining shape and durability in the soil. Among the different crosslinking agents used, citric acid showed the best performance due to its ability to create strong bonds with xanthan chains, allowing TSCs to maintain good water absorption capacity after multiple cycles of absorption and drying. From practical experiments conducted on seedling growth, it was observed that the presence of the soil conditioners in the soil helps to retain water, which is released to plants more gradually than in untreated soil, increasing its survival rate under drought conditions. In addition, practical experiments conducted on tomato plants have shown that the use of the produced topsoil covers promotes plant growth and blocks the growth of competing weeds. The exceptional water-regulating properties of the investigated materials could allow for the development of a simple, inexpensive and scalable technology to be extensively applied in forestry and/or agricultural applications, to improve plant resilience and face the challenges related to climate change.

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BLOCK-COPOLYMERS SELF ASSEMBLY *VIA* STATIC AND DYNAMIC SOLVENT VAPOUR ANNEALING

NICOLETTA BAGLIERI[1,2], IRDI MURATAJ[2], MARGHERITA TERRAGNO[3], DIEGO ANTONIOLI[3], MICHELE LAUS[3], NATASCIA DE LEO[2], FEDERICO FERRARESE LUPI[2]

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Abstract

Block Copolymers (BCPs) have gained much interest thanks to their natural tendency to self-assemble into a variety of periodic morphologies at the nanoscale. By carefully tuning the key parameters of the fabrication process, it is possible to control the aspect of the final structures[1]. Nanometric systems and devices with intriguing properties can then be obtained as inorganic replicas of such polymeric nanopatterns.

We have been studying how to control the structural order of lamellae-forming PS-*block*-P2VP BCPs, self-assembled *via* both static (Fig.1A) and dynamic solvent vapour annealing (SVA). Indeed, the self-assembly of BCPs is strongly influenced by the conditions at which they interact with the solvent[2]. Parameters such as the evaporation rate and the flux of the solvent and the number of swelling cycles can be finely controlled through the development of an appropriate experimental setup for dynamic SVA. The results obtained so far (Fig.1B) demonstrate that the weight ratio of the constituent polymers actually is not the only parameter determining the final morphology. Patterns varying from cylinders perpendicular to the substrate to lamellae parallel to the substrate have been obtained starting from the same BCP with 1:1 weight ratio (PS : P2VP). Nonetheless, the exact control of the final morphology and its combination with the metallic infiltration process is still a matter of our research.

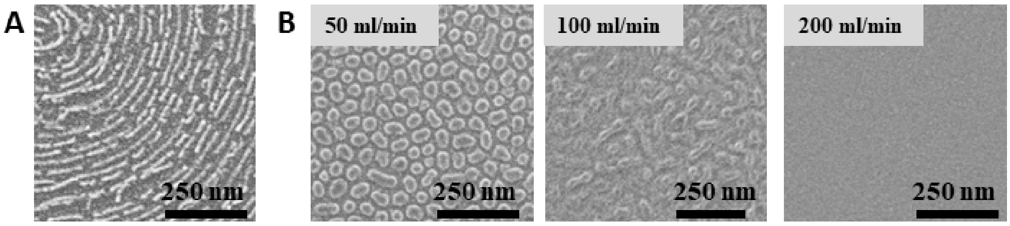

Figure 1. SEM micrographs of A) Au-infiltrated PS-*b*-P2VP (50 kg/mol) lamellae obtained *via* 1 h static SVA and B) Al_2O_3-infiltrated PS-*b*-P2VP (199 kg/mol) obtained *via* 1 h dynamic SVA with 1 swelling cycle and different solvent fluxes.

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POLYMER PHOTONICS IN THERMAL MANAGEMENT

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Abstract

Every year, global warming worsens, extreme weather phenomena increase in number and frequency, while natural biomes rapidly transform leading to a decline in biodiversity.[1] To stop the threat and keep ever-increasing warming below acceptable levels, the international community is now focused on achieving carbon neutrality, i.e., drastically reducing CO_2 emissions until a net zero level is reached.[2] Therefore, any method that offers energy savings and efficiency is of particular interest. In this regard, polymers can act either as selective reflectors for radiation or as radiative coolers.

Our research began with the former, investigating all-polymer planar photonic crystals able to reflect near-infrared radiation, which accounts for about half of the total radiant heat caused by sunlight. Planar photonic crystals are multilayer structures in which the refractive index is periodically modulated with a periodicity on the same order of magnitude of visible and NIR wavelengths. These structures exhibit high reflectance values at specific wavelength ranges and relative transparency between these ranges. The spectral position of the reflective regions can be adjusted upon changing the periodicity of the structure. The spectral width can instead be maximized via engineering both the difference in refractive index of the components and arranging them in complex manners, such as tandems or superperiodics. It is possible to design and fabricate structures that are transparent or partially transparent to visible radiation while reflecting near-infrared radiation, hindering light absorption. In our experiments, we have fabricated all-polymers near-infrared reflectors that can reduce the heating of illuminated samples by more than 20 %.[3]

Another trend in the application of polymers in passive thermal management is radiative cooling. This uses the same effect that is responsible for the formation of frost on grass or trees even when the ambient temperature is above zero. The principle of operation is that objects emit electromagnetic radiation as a mean of heat exchange. In some selected spectral ranges, mainly in the 8-13 μm range, emitted radiation is directly irradiated into the void of space, resulting in cooling of the object.[4] This happens because the atmosphere is transparent in this spectral ranges; elsewhere, bodies will exchange thermally with it, thus a sub-ambient cooling effect would not be observed.

Since not all polymers are efficient emitters of blackbody radiation, materials could be selected so that the same structures used as thermal shields might have a radiative cooling effect. In perspective, polymer photonic crystals could be processed by coextrusion over very large areas,[5] leading to their widespread application.

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RECYCLING ABILITIES OF OPTICALLY TRANSPARENT BIOBASED POLYURETHANE NETWORK

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Abstract

Polyurethanes (PU) can be thermoplastic and thermosetting counting for 8% of the globally produced plastic, putting them in sixth place as made and used polymer globally[1]. Due to its widespread commercial use, increasing quantities of PU waste are generated, including end-of-life waste, post-consumer waste, and processing scrap. It is estimated that only the customer-produced PUs waste ranges from 2.1 Mt to 3.6 Mt in Europe[2] by itself. Therefore, all processes involving the treatment of these wastes play a crucial role, particularly for thermoset PUs, which, differently from thermoplastic ones, are not compatible with direct industrial recycling. Since most current methodologies for recovering PUs are mainly ascribable as downgrading paths, new processes are being developed. Based on a particular stress-relaxation behavior first reported by Toblosky and Offenbach[3], which involves mechanisms of exchange of covalent bonds able to give rearrangement of the network defining a novel polymer class defined Dynamic Polymer Networks (DPN), a new mechanical recycling path for this type of polymer has been designed and investigated. The main characteristic of DPN is the preservation of the crosslink density during the exchange of bonds[4], which can be correlated with the retention of material properties, suitable for reworking purposes.

This work investigates the reprocessing abilities of a novel synthetized biobased PU. The pristine material has been obtained by combining a trifunctional polyol (Sovermol 780) and a difunctional isocyanate (Tolonate xflo100) in the presence of a catalyst, dibutyltin dilaurate. Both reagents are commercially available and are granted, respectively, 65% and 25% biobased. The reprocessing was done by finely grinding the initial network and then hot pressing it for 35 minutes at 170°C under 3 tons of pressure. Before and after the process, the material has been characterized via IR spectroscopy, TGA, and DSC analysis. No major differences in the IR spectra have been observed, which has been correlated to the preservation of all the pristine functional groups and the absence of any oxidative phenomena. Thermal analysis showed a slight decrease in T_g and thermal stability, in agreement with evidence already reported in the literature for this type of rework.

Subsequently, a process of post-synthetic insertion of components, polyols, and catalyst, has been proposed. A difference in the thermal properties and composition have been observed, symptomatic of successful inclusion process which, however, proved useful in improving reprocessing conditions.

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TUNING DISPERSITY OF POLYMER BRUSHES TO MODULATE THEIR INTERFACIAL PROPERTIES

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Abstract

Since the dispersity of (co)polymers and oligomers plays an important role in regulating their physicochemical properties, huge efforts have been devoted in controlling the dispersity within brushes in the last years. [1] Here we modulated the dispersity of oligomeric side chains of polymer brushes and determined its impact on technologically-relevant interfacial properties such as hydration and hydrophobic interactions in the formed polymer brushes. In this case, commercial oligo (ethylene glycol) methyl ether methacrylate, $(OEG)_mMA$, macromonomers were used for the study since they present broadly disperse OEG side chains (m = 3-15, *Figure 1*). To obtain the discrete side chains (m = constant), we performed a flash chromatography.[2] Then, P(OEG)MA brushes with either discrete or disperse side chains were prepared by atom transfer radical polymerization (ATRP) using a disulfide-functionalized initiator for the subsequent grafting of polymer ligands onto Au macroscopic surfaces. [3] The different properties were thoroughly investigated by a combination of atomic force microscopy (AFM), quartz crystal microbalance and dissipation (QCM-D), variable angle spectroscopic ellipsometry (VASE) and contact angle (CA). Monodispersity within brushes leads assemblies that are more hydrated, less adhesive and more lubricious compared to analogous films characterized by a heterogenous side chain structure. These findings open new perspectives in the design of polymer adsorbates for biomaterial functionalization, whereby the modulation of brush dispersity is exploited to achieve targeted performance.

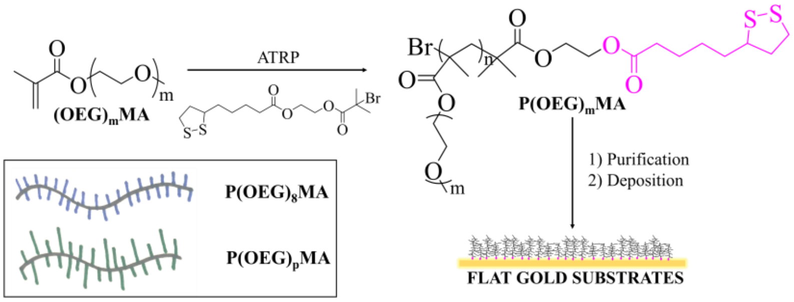

Figure 1. Process scheme for the polymer synthesis and its deposition on gold surfaces.

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RHEOLOGICAL ASSESSMENT OF ENZYMATICALLY CROSSLINKED TYROSINE-FUNCTIONALIZED ALGINATE HYDROGEL FOR BIOMEDICAL APPLICATION

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Abstract

Polymeric hydrogels are crucial materials in Tissue Engineering (TE) as they can replicate the extracellular matrix (ECM) features, including high water content, viscoelasticity, and transport of small molecules[1]. Chemical crosslinking is often used to enhance their structural stability, with UV light-catalysed crosslinking being a popular choice due to its speed, precision, and ability to define local crosslinking density and stiffness. However, limitations such as poor light penetration and potential cell damage have led to the search for safer alternatives. Enzymatic crosslinking offers a mild and biocompatible approach that can form strong covalent bonds between polymeric chains under physiological conditions without harsh organic solvents or radical species.

Among the various polymers employed in TE, alginate is particularly interesting because of its easy availability and low toxicity. It is a natural polysaccharide that can be physically crosslinked in the presence of calcium ions. Alginate must be chemically modified to conduct chemical crosslinking, for instance, methacrylate alginate (AlgMA) has been synthesized and studied for different applications[2]. However, its photochemical crosslinking is accompanied by many of the drawbacks already mentioned. To overcome these limitations, tyrosine-modified alginate was synthesized via an EDC/NHS coupling reaction to exploit enzymatic crosslinking by horseradish peroxidase (HRP) enzyme in the presence of hydrogen peroxide (H_2O_2), resulting in the formation of tyrosine dimers with either C-C or C-O linkages between alginate chains. Rheological analysis was performed to determine the optimal hydrogel concentration and HRP:H_2O_2 ratio and to monitor the enzymatic crosslinking over time. The formation of a gel-like material and an increase in storage and loss moduli (G′ and G″) were observed. The gel point and time interval of the crosslinking reaction were estimated using the 1st derivative method[3], and further rheological characterization were performed to assess material properties in static conditions. Morphological characterization confirmed crosslinking and pore formation within the hydrogel, essential for nutrient uptake and cell encapsulation. Additionally, a comparison between samples with different degrees of tyrosine substitution was carried out, and a preliminary correlation with the resulting moduli and crosslinking velocity was hypothesized. In conclusion, tyrosine-modified alginate represents a great chance to perform chemical crosslinking of alginate under cell-friendly conditions with the possibility of tuning the resulting viscoelastic moduli (G′ and G″) according to the target tissue application.

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POLYMER GLASS/MELT TRANSFORMATION KINETICS

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Abstract

The formation of a glassy phase upon cooling (vitrification) and the gradual evolution of thermodynamic state of a glassy material towards the equilibrium (physical aging) are kinetically driven processes[1]. According to Onsager regression theory, this fact suggest that they are both governed by at least one molecular mechanism, which is commonly assumed to be the main α relaxation with a super-Arrhenius temperature dependence[2]. Consequently, one could logically infer that the destruction of a glassy phase upon heating (devitrification) and the resurgence of equilibrium of a deep glass that has been heated to a temperature T_{deag} greater than the aging temperature T_{ag} (deaging) should both occur within a timescale comparable to the main α process. To obtain a deeper understanding of the underlying molecular mechanisms that govern vitrification/aging and devitrification/deaging phenomena, we employed Differential (DSC) and Flash Scanning Calorimetry (FSC) to study the time-dependent evolution of the glass enthalpic state of amorphous poly-4-chlorostyrene (Polymer Source, Mw 24.000 g/mol, PdI 1,20) across a wide temperature range.

The evolution of specific heat capacity (cp) curves with respect to aging and deaging time at 397 K is depicted in figure 1, which highlights the differences in equilibration time (τ_{eq}) of the two processes. To conclude, our study indicates that the process of eliminating thermal history in a deeply aged glass occurs at timescales that deviate from the expected values. The magnitude and direction of the deviation depend on the explored temperature range, with the timescales being either faster or slower than the alpha relaxation process.

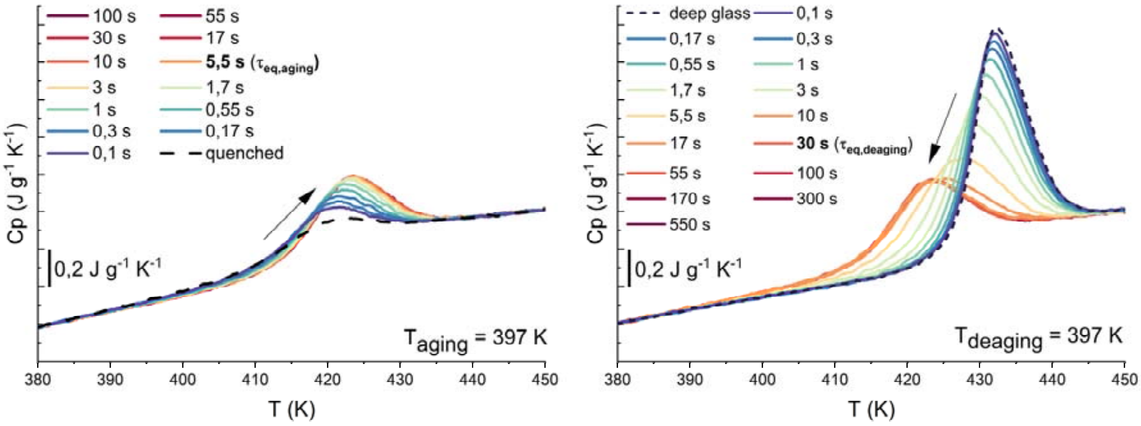

Fig.1 Specific heat capacity (c_P) curves of poly-4-chlorostyrene as function of aging and deaging time at 397 K.

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Liquid Crystal Elastomers by 3D printing for photoresponsive actuators

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Abstract

Liquid Crystalline Elastomers (LCEs) are among the best candidates for artificial muscles development, thanks to their ability to produce mechanical work in response to an external stimulus (light, temperature, etc.). However, their use for biological application inside the human body, still remains a mayor challenge. Towards this objective, we developed a series of LCEs able to work as artificial muscles under illumination with visible light[1], and we demonstrated their activation by mini-LED arrays[2] thus opening the way to prepare light responsive patches to support cardiac/muscular function in vivo. However, the obtainment of large samples and specific material shapes is limited by the preparation method used.

In this communication, we will describe the preparation and characterization of LCE-based artificial muscles prepared by a low-cost 3D printing machine[3]. Direct Ink Writing (DIW), an extrusion-based technique, has been used to shape the material and to control the liquid crystal alignment along the printing direction (Fig. 1a). A thiol-ene reaction of dyacrilate mesogens and dithiolic chain extenders was used to produce highly viscous oligomers that fit for the DIW; after the extrusion, the material has been crosslinked by UV curing.

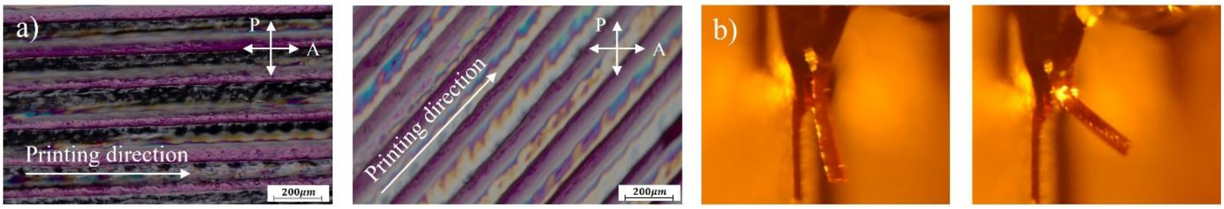

Figure 1. a) POM (Polarized Optical Microscopy) images of a 3D printed strip at different polarization angles; **b)** 3D printed strip actuation after light irradiation

Two LC-based inks showing different light actuation (under UV or visible light) have been prepared and characterized (Fig. 1b). The materials have been printed in different geometries and shapes allowing for a large-scale production of LCEs to develop custom-sized implantable patches.

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TOWARDS EFFECTIVE UPCYCLING OF POLYOLEFINES

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Abstract

The new circular economy policies developed in the recent years due to the increasing environmental awareness of society are changing the traditional way to design plastic products, in order to provide greater durability, reuse and high-quality recycle. The circular economy model suggests a rational utilization of the resources and promotes the valorization of the plastic materials already in circulation through recycling strategies. However, the market data of the last years indicate that the global economy of plastics is largely linear, with the disposition (with no recovery after their utilization) of more than half of the total amounts of plastic products produced per year. Therefore, there is an urgent need of increasing the recycling rate of plastics, to make the plastic industry more sustainable and compliant with circular economy policies. Among the different recycling technologies, mechanical recycle is the preferred option from both energetical and ecological point of view, as it ideally allows fully replacing the pristine polymers with materials recovered form wastes. Nevertheless, mechanical recycling strategies are really effective if closed-loop processes are realized. Actually, the degradation phenomena occurring during the re-processing significantly affect the polymer processability, also causing a progressive deterioration of the final properties of the secondary materials, with a consequent economic disadvantage of recycled polymers compared to their pristine counterparts. In this work, the effect of multiple re-processing cycles on the final properties of pre- and post-consumer polyolefines scraps was investigated. The materials were subjected to re-processing operations in a twin-screw extruder, and the rheological behavior, crystallinity degree and mechanical properties were evaluated as a function of the processing cycles. Furthermore, the influence of the introduction of a commercial chain extender additive was also evaluated.

OPTICAL AND MECHANICAL CHARACTERIZATION OF CELLULOSE-BASED MOLDED PRODUCTS

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Abstract

Global warming and increasing waste production put the highlight on environmental issues and made organizations, such as the European Union, act against plastic pollution, introducing restrictions on single use plastics. Moreover, packaging companies are trying to switch from oil-based (such as HDPE and PET) to bio-based starting materials, to achieve plastic-independence.

In this framework SACMI company, worldwide leader in the production of complete lines for rigid packaging, joined the task and started to work on the development of a new dry molding technology which uses a full-metal isostatic mold concept, for producing rigid packaging objects based on cellulose, the most abundant biopolymer on Earth.

Being a natural polymer, cellulose has unique features depending on its source (hardwood or softwood), on the content of other polymers, such as hemicellulose and lignin, and on treatment intensity. In fact, it is well known in the paper industry that cellulose chain length affects the final proprieties of objects made of cellulose (as for toilet paper, banknote, and others). Moreover, extraction processes of cellulose from wood can leave some residual lignin content in cellulose pulp, which affects hydrophobicity and appearance of the molded product [1]. This research project aims to characterize cellulose, both in the shape of raw material and in the shape of final molded object, so that to find a correlation between initial properties of raw cellulose material, process parameters and final properties of molded objects. Establishing this correlation is particularly helpful to foresee which kind of cellulose to be used to get the desired proprieties of the final object and set the most correct process parameters.

For this purpose, many types of cellulose raw materials were initially characterized by a staining test [2], visualizing results with an optical microscope which gave qualitative information about residual lignin content and the fiber lengths. Molding caps with two different types of cellulose having the same fiber length but different lignin content, and characterizing them by a top-load test, using a dynamometer, as expected, it was found that the residual lignin content in the raw material can significantly affect the mechanical resistance of the cap under a constant load.

It is also well known that cellulose itself is not hydrophobic and it is necessary to add additives, natural or synthetic, in order to increase its resistance to water. Another purpose of this research project is to understand if additive presence can affect the properties of the final object: if by contact angle measurement a better hydrophobic behavior was observed, by tensile tests performed on molded cellulose samples, using both raw and coated cellulose, a worse mechanical feature was noticed in coated samples. Although the research is at the beginning, the first results seem interesting in showing a correlation between starting material and molded object.

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APPLICATION OF FUSED DEPOSITION MODELING IN THE CUSTOMIZATION OF PHARMACEUTICAL DOSAGE FORMS CONTAINING TIMAPIPRANT

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Abstract

The interest in 3D printing has recently increased in the pharmaceutical field, being fused deposition modeling (FDM) among the most promising technologies, likely due to its ability to customize dosage forms, create simple and complex geometries and produce small batches with low equipment costs[1]. After evaluating feasibility of FDM in the manufacturing of immediate release (IR) dosage forms containing Timapiprant (TMP), an active molecule potentially useful in oral treatment of eosinophilic asthma proposed by Chiesi Farmaceutici S.p.A., the present work investigates the possibility of customizing the product from different points of view. First, suitable thermoplastic pharmaceutical-grade polymeric carriers, in principle capable to promote the prompt release of TMP were selected. Indeed, TMP is poorly soluble and its formulation in IR products would be particularly challenging, especially using hot-processing techniques that are well-known to provide high-density specimens characterized by slow penetration of fluids[2]. In-house-extruded (Haake™ MiniLabII) filaments were used as feeding material for the printer (Kloner3D 240® Twin). Form preliminary trials, the formulation based on poly(vinyl alcohol) was identified as the best compromise between *i)* achievable TMP load, which ranged from 5% to 40% w/w, *ii)* processability by FDM, especially in terms of number of samples produced without process interruptions setting different infill percentages (*i.e.* 100, 50 and 30%), *iii)* overall quality of the printed specimens in terms of weight and TMP content reproducibility, *iv)* prompt dissolution performance (USP apparatus II, Distek), *v)* possibility to add soluble fillers. The infill percentage turned out one of the most important printing parameters for controlling the porosity of molded products (measured by helium pycnometer, Pycnomatic ATC) and speeding up sample dissolution. After a thorough evaluation of the solid-state of TMP after processing (*via* X-ray and differential scanning calorimetry, which confirmed the stability of the formulation and the crystallinity of the TMP, prototypes containing a fixed amount of TMP (50mg) were successfully printed with attractive design from both patient-compliance and business marketing perspectives. They also resulted compliant with the set of dissolution specifications (≥ 80% of TMP dissolved within 30 min). Overall, the data collected strengthened the idea that FDM could be successfully applied to the manufacturing of dosage forms to be orally administered, which could be personalized in terms of shape, composition and performance. Overall, such aspects make this technique particularly interesting also for possible industrial implementation in the next future.

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CORRELATION BETWEEN MORPHOLOGY AND PROCESSING PARAMETERS IN POLYMER BLENDS: PRELIMINARY RESULTS TOWARDS HIERARCHICAL STRUCTURES

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Abstract

Hierarchical polymer-based materials can be defined as blend characterized by a structural order at different scale levels. The system may be made of two or more polymers and a filler can be present.

The increasing interest on these composites is due to the possibility to tune the morphology and, consequently, the properties of the overall system. In fact, several studies focus on the correlation of the morphological structure with the mechanical properties, the electrical conductivity, the permeability and the optical properties.

One of the main issues related to hierarchical polymer refers to the production techniques. Traditionally, these systems are obtained via a bottom-up chemical approach. This brings along limitations such as the production of small batches and a non-negligible environmental impact due to the use of solvents. Another approach is the top-down production from the melt, as in the case of multilayer extrusion. In this case, the main issue is the restriction on the morphological freedom correlated to the structural constraints of the production tools.

In the last years, another approach consisting in the bottom-up production from the melt has been increasingly studied. With this method, the inner morphology of the system develops during the blending or the forming step. The reciprocal arrangement is allowed by a combination of factor. Specifically, both processing parameters and materials features play an important role in the final morphology.

It is important to note that the last approach associate the freedom in tuning the morphology proper of a bottom-up method and the benefits of a solvent-free in-line process. For the above reasons, the correlation between the inner morphology and the processing parameters (e.g. temperature, strain) for different polymeric systems is investigated. In particular, blends of bimodal polyethylene also with the addition of UHMWPE, homo and copo polyamides characterized by different viscosities have been studied.

CHARACTERIZATION OF BACTERIAL CELLULOSE FROM KOMBUCHA TEA

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Abstract

Cellulose is the most abundant, inexpensive and readily available bio-polymer on Earth[1], and it is becoming increasingly popular due to its biocompatibility and its remarkable mechanical and physical properties. It is traditionally extracted from plants and plant-based materials, but it can also be produced by some bacterial strains. Bacterial cellulose (BC) is a linear homopolysaccharide of β-1,4-linked anhydro-D-glucose units with molecular formula $(C_6H_{10}O_5)_n$. It is secreted in the form of ribbons, composed of nanochains arranged in elementary fibrils further aggregated in bundles of microfibrils, interacting with each other through inter- and intra-chain hydrogen bonds and Van der Waals interactions, resulting in a highly organized structure[2]. This 3D network of microfibrils stabilized by hydrogen bonds provides BC with outstanding mechanical properties, hydrophilicity, great capacity for holding water[3] and insolubility in water and in common organic solvents. Considering its biocompatibility and non-toxicity, nowadays bacterial cellulose is mainly employed in the biomedical area as wound dressing, drug delivery systems, artificial cartilage and artificial skin. One of the many substrates from which BC can be obtained is Kombucha tea, a slightly alcoholic sugared beverage produced by the fermentation of tea leaves and sugar, during which a gelatinous cellulose-based biofilm is formed at the air-liquid interface called Scoby ("Symbiotic Culture of Bacteria and Yeasts")[4]. In this work, a preliminary characterization was carried out on the so-obtained raw material and on the purified BC membrane by means of thermogravimetric (TGA), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction, ATR-FTIR, and mechanical analyses. The obtained results showed that, after the purification process, the biofilm maintained its crystalline structure and morphology while its thermal degradation temperature slightly increased, meaning that the removal of bacteria and other impurities enhanced its thermal stability. The above-mentioned analyses suggested that bacterial cellulose obtained from Kombucha Scoby is a promising material that can be valuably used for many different applications.

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DEVELOPMENT OF A NOVEL 3D BIOPRINTABLE HYDROGEL FORMULATION BASED ON DECELLULARIZED EXTRACELLULAR MATRIX AND GELATINE METHACRYLATE

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Abstract

3D bioprinting has gained popularity in recent years as a promising solution to meet the increasing demand for organs and tissues for transplantation. This powerful technology enables the precise layer-by-layer deposition of bioinks, composed of polymeric materials (natural or synthetic hydrogels) and cellular components, to fabricate 3D constructs[1]. Decellularized extracellular matrix (dECM), a natural hydrogel, has attracted attention due to its excellent biocompatibility and preservation of functional proteins. However, challenges arise from the poor printability and weak mechanical properties of dECM[2]. Another material, widely used in bioprinting, is gelatin methacrylate (GelMa), a semi-synthetic hydrogel, which offers favourable biological properties and tunable physical characteristics[3]. This study aims to optimize a hydrogel based on dECM and GelMa (50:50 w/w), suitable for 3D bioprinting, by exploring the effect of various formulations and crosslinking procedures on the mechanical properties and printability of the final material. Pure dECM hydrogel from bovine pericardium was purchased by the Tissue Graft company, while the synthesis of GelMa was carried out by following a known gelatin methacrylation process[3]. Subsequently, different hydrogels, based on a 50:50 w/w dECM:GelMa formulation, were analysed, including (i) a blend obtained by simply mixing the two biomaterials (ii) a semi–IPN achieved through thermal crosslinking of dECM (iii) an IPN obtained using a dual crosslinking approach. Since the rheological properties are the physicochemical parameters having the largest influence on hydrogel printability, accurate rheological characterization was performed on the obtained bioinks to correlate their mechanical properties with the bioprinting process. Swelling tests and morphological analyses (SEM) were also conducted. Rheological results showed that the IPN hydrogel displays better tunable stiffness and a higher ability to recover its mechanical properties compared to the single components, especially the dECM which was not printable alone. Moreover, the morphological analysis showed that the distribution of pore sizes in the IPN hydrogel is more homogeneous compared to single biomaterials. The optimized hydrogel was then used for bioprinting, and the printing parameters were fine-tuned. The printability and shape fidelity of the fabricated constructs were evaluated under relevant conditions for 3D cell cultures. This system will be used to print a model of muscle tissue using C2C12 cells, given the promising results that we recently obtained using the same cells and a collagen-based hydrogel.

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CONDUCTING POLYMERS AS ANTICORROSION COATINGS

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Abstract

Metallic corrosion of transport facilities is an increasingly serious issue with huge loss in economy and materials. The most common approach during the last century was to add heavy metal corrosion inhibitors such as chromate to the metal alloy or to the coating. However, heavy metal elements can be released into nature over time, resulting in serious pollution.[1] Nowadays, anticorrosion coatings on a metal surface are one of the most common methods to slow down metal corrosion. Epoxy anticorrosive coatings have been widely used due to their high adhesion, excellent mechanical properties and cost efficiency.[2] However, the penetration of aggressive substances like O_2, H_2O and Cl^- into the interface of the epoxy and metallic substrate results in relatively short service life.

Therefore, it is of great significance to improve existing technology taking advantage of the synergistic effect of conductive polymers. In fact, amongst innovative solutions, conductive polymers have started to emerge as the most appealing, for their intrinsic advantages in terms of charge interactions, possibility of processing in stable thin films, redox activities.

The aim of this work is to develop conductive polymers-based coatings as anticorrosion materials. Particularly, PEDOT, poly(3,4-ethylenedioxythiophene), and PANI, polyaniline, are taken into account for their excellent conductive properties but also for their wide range of available application methods and possibility of functionalization. Our strategy is based on tuning the hydrophobicity of PEDOT and PANI polymers. In fact, hydrophobic organic functionalization of monomers can allow us to keep water away from the metal surface.

We will illustrate our approaches using both PEDOT and PANI scaffolds. As for the former, the polymerization of a novel EDOT monomers was achieved by direct heteroarylation.[3] As for the latter, approaches to polyanilines by oxidative polymerization or Buchwald-Hartwig polymerization. While the first one is a simple and quick method, easy to scale up, the Buchwald Hartwig polymerization allows us to obtain more controlled molecular weight polymers and copolymers without significant chain defects.[4] All polymers were characterized by NMR, GPC, TGA and DSC. UV spectrophotometry and spectrofluorimetry were used to study the level of conjugation, the optical band gap and fluorescence properties of these polymers. The polymers were deposited in films by drop casting and spincoating, measuring the film thickness and morphology through atomic force microscopy. Afterwards, also electrochemical impedance spectroscopy in 3.5% NaCl aqueous solution is performed to characterize the electrochemical behavior of the interface coating-metal in operative conditions.

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EFFECT OF CROSSLINKING DENSITY ON THE PROPERTIES OF REPROCESSABLE DIELS-ALDER EPOXY-BASED THERMOSETS

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Abstract

Thanks to their technological properties and versatility, epoxy-based thermosets play a key role in many application fields. However, these systems cannot be reprocessed because of their irreversible crosslinks, leading to sustainability issues. In this frame, the use of reversible covalent crosslinks represents an interesting strategy to induce reprocessability to thermosetting resins. The present work focused on the Diels-Alder (DA) thermo-reversible chemistry to produce thermosets that can be reprocessed at their end-of-life at a fixed temperature. In particular, Bisphenol A diglycidyl ether (DGEBA) was modified with both furfuryl alcohol and furfuryl amine, to obtain a bifunctional (alcoholic) and a trifunctional (aminic) Furfurylated Epoxy Resin (FER), respectively. Aminic and Alcoholic Furfurylated epoxy precursors were mixed in different ratios and then crosslinked with bismaleimide (BMI). In this way, different DA thermosets (DATs) with different crosslinking densities were produced. Characterizations and syntheses' optimizations for FERs and DATs were characterized through DSC, TGA, and FTIR [1,2].

The effect of DATs' different crosslinking densities on their technological performances was studied. Lap-shear tests were used to evaluate their adhesive properties, and thermoset resins with a higher percentage of Amine returned better adhesive performances. Furthermore, flexural tests on virgin materials showed that an increasing Amine content led to higher elastic modulus and fracture strength but lower fracture strain. Finally, the flexural properties were tested again to evaluate the effect of reprocessing. Each of the two reprocessing cycles reduced fracture stress and strain; however, the increase in brittleness was moderate enough to allow technological applications for these materials [3].

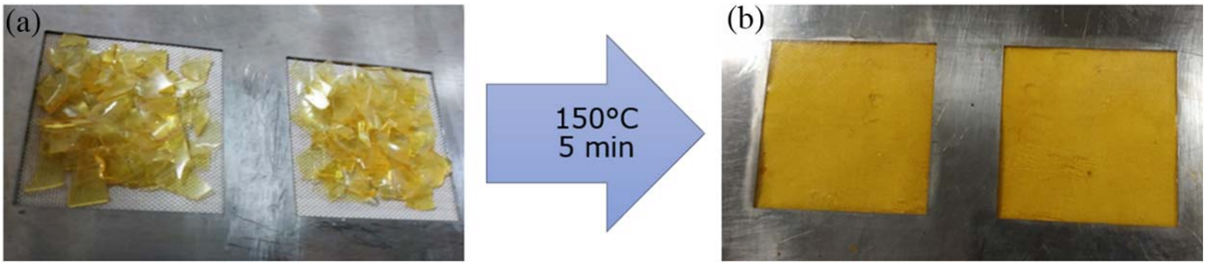

Figure 1 DAT with 100% Aminic FER: (a) virgin, broken, and (b) after reprocessing at retro-DA temperatures.

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OVERCOMING POLY(ETHYLENE GLYCOL) IMMUNOGENICITY BY DEVELOPING WELL-DEFINED POLYMER ALTERNATIVES

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Abstract

For several decades, polyethylene glycol (PEG) has been widely regarded as “golden standard” in pharmaceutical formulations. However, recent findings have indicated that a significant proportion, approximately one in four, of individuals may already possess pre-existing immunization against PEG.[1] This revelation has raised concerns regarding the safety of its utilization, as the presence of anti-PEG antibodies can elicit unwanted immune responses. Consequently, there is a growing impetus to explore alternative polymers to PEG that can offer comparable beneficial properties without triggering immunogenicity. This pursuit for novel, safe, and effective PEG alternatives aims to ensure treatment safety and mitigate the risks associated with undesirable immune reactions, while fostering the development of personalized therapeutic formulations to enhance patient well-being.

To tackle this challenge, we explored the synthesis and characterization of different biocompatible, hydrophilic polymers that have the potential to exhibit stealth behaviour. In particular, we focused our attention on poly(2-alkyl-2-oxazolines) (PAOXA) as promising candidates for PEG replacement. Various PAOXAs were synthesized by Cationic Ring Opening Polymerization (*Figure 1*), modulating key parameters such as the polymerization degree, the nature of alkyl functionality, and the topology[2]. In parallel, well-defined zwitterionic polymers were also prepared as potential alternatives to PEG. Polymerizations of 2-Methacryloyloxyethyl phosphorylcholine (MPC) were carried out using approaches such as Atom Transfer Radical Polymerization (ATRP) and Reversible Addition−Fragmentation Chain-Transfer (RAFT) polymerization. Size Exclusion Chromatography analysis revealed that the synthesized polymers had low dispersity ($M_w/M_n = 1.1$) and pre-determined molecular weight.

The ability to design PEG alternatives with precisely controlled characteristics, structures, and functionalities could enable to determine the impact of these properties on the efficacy of these polymers and their bioconjugates in polymer therapeutics.

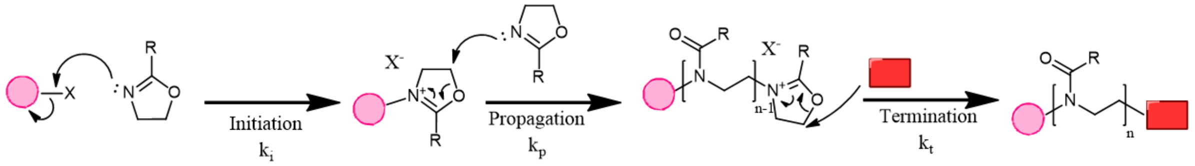

Figure 1.: Cationic Ring Opening Polymerization of 2-alkyl-2-oxazolines

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A NOVEL METHOD TO CROSSLINK ELECTROSPUN PULLULAN MEMBRANES CONTAINING CARBON DOTS FOR WATER PURIFICATION

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Abstract

Water pollution has become a major worldwide issue due to the uncontrolled release of agricultural and industrial wastewater and accidental discharges. Membrane-based technologies have shown promising results in addressing this problem due to their high separation efficiencies, low costs and easy procedure for pollution treatment. Among the many different technologies for membrane production, electrospinning is considered extremely valuable to obtain highly porous non-woven fibrous membranes. It is also possible to functionalize the nanofibers with specific compounds to improve their efficiency for tailor-made applications. For example, it is possible to load electrospun membranes with carbon quantum dots (CDs), which are a unique class of carbon-based nanomaterials that can be synthesized from carbonaceous building blocks and even from biomass, exhibiting unique features such as the absorption of light and photothermal conversion ability, so they have recently found application in energy and photocatalytic processes[1,2]. We have recently developed electrospun polylactic acid membranes loaded with hydrophobic CDs for seawater oil spill clean-up.

To extend the research to water-soluble pollutants, the possibility of using hydrophilic CDs loaded in biobased and biodegradable polymeric membranes by electrospinning was explored in this work. Pullulan was chosen as a hydrophilic biopolymer, and electrospinning was used to fabricate nanofibers containing hydrophilic CDs synthesized from biomass. A novel and green method has been optimized to crosslink the water-soluble pullulan nanofibers by blending pullulan and TEOS in an acidic aqueous solution before the electrospinning procedure, followed by thermal treatment of the obtained membrane. The crosslinked pullulan membrane exhibited excellent stability in water, and its gel content and crosslinking degree were studied. A gel content higher than 95% was obtained, and SEM analysis showed that the membrane retained its porosity and a good fiber morphology even after water immersion. The obtained results indicate that pullulan can be used as a promising biopolymer for developing a new class of CD-containing membranes for potential applications in the treatment of contaminated aqueous environments.

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OXYGEN TOLERANCE DURING SURFACE-INITIATED PHOTO-ATRP: TIPS AND TRICKS FOR MAKING BRUSHES UNDER ENVIROMENTAL CONDITIONS

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Abstract

Surface-initiated reversible deactivation radical polymerization (SI-RDRP) methods enable to tether polymer brushes to the surface of a wide variety of substrates, thus tailoring their properties and obtaining technologically relevant materials. The development of SI-RDRP techniques that are tolerant to environmental conditions is crucial for the scalability of these methods. Surface-initiated photoinduced atom transfer radical polymerization (SI-*photo*ATRP) can be performed using highly confined, small reaction volumes, without prior deoxygenation of the reaction mixture, thus presenting huge potential for translation into industrial settings[1]. However, even if the polymerization mixture is confined between the initiator-bearing substrate and a glass slide (Figure 1) oxygen can diffuse from the sides of the system, inhibiting the polymer growth on the edges of the substrate. This "edge effect" can be quantified by measuring the width of the "naked" area (d_{edge}, Figure 1), thus enabling to evaluate the role of different reaction conditions on the oxygen tolerance of the system.

SI-*photo*ATRP experiments performed with $CuBr_2/Me_6TREN$ catalytic system showed that an increment in the catalyst concentration provides faster oxygen consumption (*i.e.*, smaller d_{edge}). On the other hand, when $[CuBr_2/Me_6TREN]$ increases, the concentration of Cu^{II}-based ATRP deactivator also increases, resulting in slower polymerizations (*i.e.*, smaller dry thickness of the brushes, T_{dry}).

Furthermore, we observed that the addition of an alkyl halide (RX) sacrificial initiator, such as ethyl α-bromoisobutyrate (EBiB), in the reaction mixture has a significant effect on both d_{edge} and T_{dry}. Radicals generated in solution from the sacrificial initiator efficiently recombined with O_2, thus diminishing the "edge effect". At the same time, enhanced radical termination led to the accumulation of Cu^{II} deactivator, slowing down the polymerization, *i.e.*, decreasing T_{dry}. Importantly, in less confined systems, when polymer growth is severely hampered by O_2 diffusion, the addition of EBiB as sacrificial initiator effectively provided both oxygen tolerance and polymerization rate enhancement, enabling to expand the use of SI-ATRP to large-scale settings.

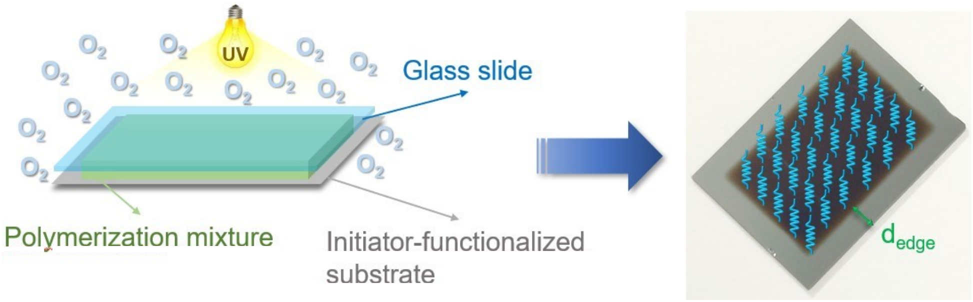

Figure 1: SI-*photo*ATRP experiment.

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SOLID STATE NMR CHARACTERIZATION OF A MODEL ANION EXCHANGE MEMBRANE

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Abstract

The urgent need of a green transition requires new strategies for the production and conservation of energy. Among different solutions, the so called green hydrogen is gaining extreme attention because of the high availability of water.

Anion Exchange Membranes (AEMs) are vital components of alkaline water electrolyzers because they allow the transfer of hydroxyl ions from cathode to anode while acting as an electric insulator.

In recent years, Fumatech GmbH developed a new class of membranes based of FAA-3, a ionomer deriving from the functionalization of Poly-Phenylene Oxide (PPO) with an undisclosed quaternary ammonium group. Because of their improved characteristics and reduced costs, these membranes are commonly used as a benchmark material to compare the properties of new AEMs. However, these materials have been characterized only in a handful of works and some aspects are still unknown[1-3].

Solid state NMR (SSNMR) could serve as a powerful tool for the characterization of these materials because it can allow to focus the attention on different aspects of membrane, such as structure, phase separation and dynamics.

In this work, we performed a multinuclear SSNMR analysis of a commercially available membrane know as FAA-3-PK-130. This membrane is based on FAA-3, which is responsible for the anion conductivity, and is reinforced with Poly-Ether-Ether-Ketone (PEEK) to improve mechanical properties and dimensional stability.

^{1}H and ^{13}C spectra and 2D maps have been used to characterize the structure of these two polymers and to try to identify the nature of the undisclosed quaternary ammonium group. Moreover, ^{19}F NMR has been used to probe the presence of fluorine in the membrane since it has previously been reported[4].

Phase separation between PPO and PEEK has been investigated by spin diffusion by measuring proton spin-lattice relaxation times at 500 MHz through an inversion recovery-cross polarization sequence (IR-CP).

Moreover, low field NMR has been used to unravel the effect of water adsorption on side-chains dynamics and on the separation of ionic channels, which has previously been reported for FAA-3 by means of atomic force microscopy[1]. In order to investigate this aspect, the membrane has been analyzed in its dry form and after hydration in a controlled environment.

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CELLULOSE HYDROPHOBIZATION FOR BEVERAGE PACKAGING APPLICATIONS

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Abstract

Plastic is used for the majority of commercially available disposable packaging, particularly beverage containers, due to its inherent benefits, including affordability, durability and simple production. To address the environmental damage brought on by the careless disposal of large amounts of non-biodegradable plastic waste, biopolymers are being closely investigated as promising alternatives to synthetic plastic. Being the most spread natural polymer worldwide, cellulose[1] is the most valuable solution. However, due to the impossibility to process it as conventional thermoplastics and its own hydrophilicity, cellulose industrial application in beverage packaging is restricted. The Italian company Sacmi accepted the first challenge and overcame it by developing a new technology to mould dry cellulose fibres, which enabled the production of complex objects e.g., bottle caps. Hydrophobizing cellulose fibres is the next challenge to be tackled. To this aim, among the many strategies suggested in the literature and with an emphasis on the process's scalability and sustainability, we will follow two different approaches: the modification of virgin cellulose fibres by Chemical Vapour Deposition (CVD) of a highly hydrophobic compound and the preliminary cellulose surface activation before carrying out the surface functionalization with a highly hydrophobic compound.

In our CVD approach, cellulose fibres are exposed to vapours of hydrophobic hexadecyltrimethoxysilane (HDTMS) by positioning the commercial cellulose substrate in a sealed glass container[2] in proximity, but not in contact, with the liquid HDTMS for different temperatures and times. Subsequently, cellulose fibres were hot-pressed and further treated at 120°C for 1 h to promote HDTMS grafting on fibre surfaces. Stable water contact angles higher than 90° are obtained by applying CVD above 20°C and after the thermal post-treatment. In light of these preliminary results, we are developing an *ad hoc* system to conduct more controlled CVD experiments. Moving on to the second method, the preliminary surface activation aims to improve cellulose reactivity towards hydrophobic compounds. In this perspective, we are applying two different approaches: (i) a wet method through reaction with tannic acid[3] and (ii) dry activation by plasma treatment[4]. Although the research is still in its early stages, preliminary tests of tannic acid adsorption over cellulose surface, as well as the application of plasma, appear promising and deserve further investigation.

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LIFE CYCLE ASSESSMENT OF TIRES: THE ROLE OF THE PRODUCTION PHASE

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Abstract

Tire industry holds significant environmental relevance due to its intensive use of natural resources, emissions associated with production, and disposal of end-of-life tires. From this perspective, Life Cycle Assessment (LCA) has become a crucial tool for evaluating the environmental impact of product throughout its entire life cycle. LCA can provide a comprehensive overview of the environmental implications of a tire production process across all stages, from raw material extraction and processing to component manufacturing, assembly, and finishing. Therefore, integrating an LCA study into decision-making processes can ensure environmental and economic benefits, allowing for the identification of "hot spot(s)" during the process and enabling companies to adopt strategies for improving efficiency and developing more eco-friendly products.

LCA studies of tires mostly focus on their end-of-life stage, investigating the advantages related to the reuse (e.g., retreading) and recycling (e.g., asphalt mixtures) of used tyres. Cradle-to-grave studies agree in identifying the use stage as most impactful, because of the fuel consumption attributed to the total kilometers performed by the tire during its life. To date, much less attention is paid on the production phase of tires[1]. When attention is focused on what happens before the "factory gate", the most impacting phase has been identified in the extraction and processing of raw materials. The extraction of natural rubber and transformation of metallic components (steel wires) are particularly critical. For this reason, the tire companies are considering the use of recycled and/or more sustainable raw materials. Unfortunately, the use of "greener" materials is not necessarily advantageous for the environment. Besides assessing the actual benefits of resorting to recycled/bioderived resources, which can bring non negligible additional burdens, the use of new materials requires substantial changes to the production chain. This implies the necessity of building a detailed model of the whole tire production phase following the LCA rules. Despite the good purpose, this is a tough challenge due to the plant complexity and the huge number of flows and production lines to deal with. A good starting point is represented by the production at the lab scale of small amounts of elastomeric compounds for tires partially based on sustainable raw materials. In the present study, we present a preliminary LCA modeling of a series of tread formulations based on styrene-butadiene rubber (SBR), polybutadiene rubber (BR), silica as filler and partially biobased chemicals. The goal is comparing the processability of the compounds to infer preliminary information of the changes to be expected in case of scale up at the industrial level. More in general, our study aims at emphasizing the utility of integrating LCA methodologies in the formulation phase of new sustainable compounds for the tire industry.

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CATALYST-FREE VITRIMER BASED ON β-AMINO ESTER IN PRESENCE OF β-HYDROXY FUNCTIONALITIES

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Abstract

Vitrimers are polymers with a crosslinked network that can be easily recovered, merging mechanical properties of thermosets with reprocessability of thermoplastics. Dynamic covalent bonds are incorporated inside the network and allow topological rearrangement when a stimulus is applied. In 2021, C. Taplan et al report the synthesis of innovative β-amino ester based vitrimers obtained using the aza-Michael addition between amine and acrylate moieties[1]. In this case, the dynamic exchange occurs *via* both retro-aza-Michael reaction and catalyst-free transesterification.

In this context, our research group has been developing - in collaboration con ELANTAS' group - a new system in which aza-Michael addition reaction occurs between sterically hindered amines and mixtures of industrial polyfunctional methacrylic monomers. As a starting point, optimization of the molar ratio between monomers has been performed and, by following the glass transition temperature (T_g, fig. 1.a) as a function of time, qualitative information on the reaction conversion has been obtained. The higher T_g value is obtained with a molar ratio between methacrylic and amine functionalities of 1:0.5 at a curing temperature of 120 °C. Rheological properties of the as-obtained samples have been evaluated by stress-relaxation measurements (Fig. 1.b) at temperatures ranging from 100 °C to 180 °C. Full stress relaxation is observed at different temperatures, thus demonstrating the effective mobility of the network crosslinking points.

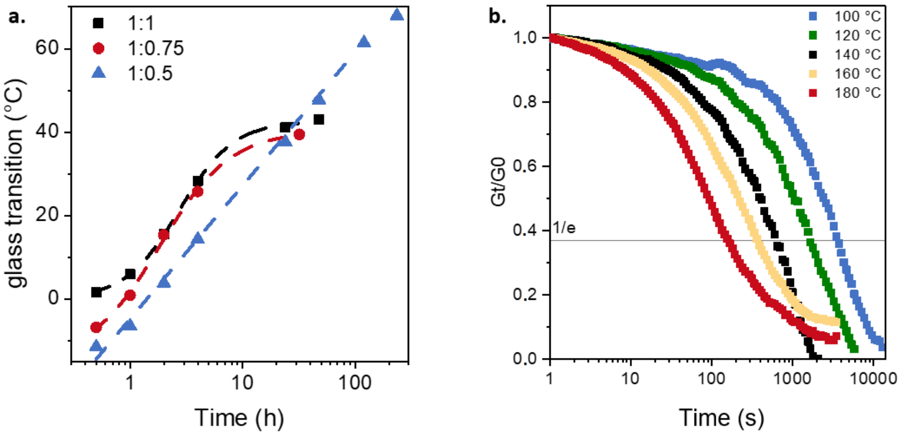

Figure 1 - a. The evolution of Tg for the molar ratios studied. b. Stress-relaxation curves at different temperatures for the molar ratio metacrylic:amine functionalities 1:0.5.

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ALL-POLYMER BASED MECHANOCHROMIC DISTRIBUTED BRAGG REFLECTORS

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Abstract

Mechanochromic materials have been used for visual strain measurement because they provide an immediate and intuitive visual response. Nowadays, flexible and stretchable strain sensors are used in applications such as personal health monitoring, electronic skin, soft robotics and structural health monitoring[1]. Strain sensors typically convert deformation stimuli into measurable electrical signals. Their major limitation is they require a power source and connection to external devices for signal processing and data acquisition. Using nature as a source of inspiration, colours enable interaction and communication between living organisms in biological and artificial environments. A famous example is the rapid change in skin colour in chameleons due to active control of the lattice spacing of guanine nanocrystal arrays in cells called iridophores[2]. Their colour is produced by the interaction of light with periodically arranged nanostructures called photonic crystals (PCs). Mechanochromic materials based on PCs have been used for visual measurement of strain because they provide an immediate and intuitive visual response. This is possible thanks to the periodic structure of PCs made of two materials with different refractive indices arranged periodically to form a dielectric lattice extending in 1, 2 or 3 dimensions. This ordered structure acts on photons as crystals do on electrons, creating photonic bandgaps (PBGs) where light of certain wavelengths cannot propagate within the lattice and is reflected or diffracted. This property gives PC a typical chromatic response[3].

In this research, we focus on 1D PC, also known as distributed Bragg reflectors (DBRs), which consist of a series of thin layers that form the dielectric lattice. We will report on a new solution-based deposition method for novel mechanochromic DBRs made from elastomeric block copolymers, which exhibit superior mechanical properties compared to those made from thermoplastic polymers. In principle, mechanical stress on these structures distorts the lattice, changing their optical response (i.e., PBG spectral position and width) and thus their colour. DBRs of different composition and cast on different substrates have been prepared. Their optical response under strain has been optomechanically characterized both in the linear and strain-hardening regimes. The comparison of such data with standard stress-strain curves allows to determine the spectral responsivity of the system for unit of applied stress/strain (mechanochromic sensitivity, MS). In addition, it was also possible to assess the potential reversibility of the mechanical properties of the entire nanostructure.

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ADHESION ENHANCEMENT IN CFRP COMPOSITES VIA TOPOLOGICAL ENTANGLEMENT

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Abstract

Carbon fiber reinforced polymers (CFRPs) are widely used for many applications due to their extraordinary properties that include lightweight, strength, and stiffness. However, these materials suffer from delamination which lead to downgrade their mechanical properties.

To enhance the interlaminar adhesion between the plies of carbon fiber composites, we selected a phenoxy resin functionalized with ODIN, a hydrogen bonding-motif. The phenoxy resin is compatible and physically miscible with the standard amine-cured epoxy resins that constitutes the major component of the matrix of CFRPs, while the ODIN moieties can dimerize forming a dynamic cross-link. The improvement of the mechanical properties of the material is achieved thanks to the topological entanglement that consist into the diffusion of the functionalized phenoxy resin into the epoxy network followed by the formation of a dynamic hydrogen-bond crosslinking.

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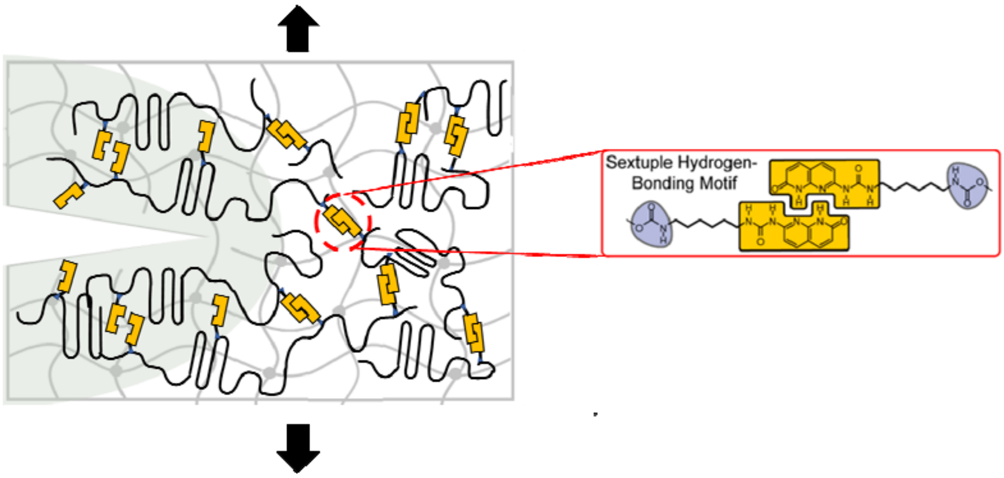

Figure: The phenoxy resin functionalized with ODIN (yellow) diffuse into the epoxy network (grey) and crosslink creating a new polymer network in situ in a topological entanglement thanks to the formation of a sextuple hydrogen-bonding motif[1].

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SEMICRYSTALLINE POLYMERIC NETWORKS AS TAILORED SHAPE-MEMORY MATERIALS

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Abstract

Shape memory polymers (SMPs) are stimuli-responsive materials that can "remember" their original shape and return to it when subjected to an external stimulus such as heat or light. According to the number of remembered forms, SMPs can be classified into three main categories: one-way SMPs that have one permanent shape and one temporary shape, multiple-way SMPs that have one permanent shape and more than one temporary shape, and two-way SMPs that are capable of a reversible transition between two different temporary shapes[1-2]. A proper material can exhibit these shape effects depending on its molecular structure and the so-called *programming cycle*. Usually, the programming step, able to fix the temporary shape, induces an orientation of chains, leaving the polymer in a high-energy unstable state; When the right stimulus is applied, the stresses are freed, and the recovery shape step starts, thanks to an entropic driving force. In the case of semicrystalline polymer networks, the trigger is represented by an increase in temperature that cause the melting of crystalline domains responsible for maintaining the temporary shape.

In this study, polybutylene succinate (PBS)/poly-ε-caprolactone (PCL) semicrystalline networks were prepared by photo-cross-linking of methacrylated prepolymers in different proportions to obtain materials capable of displaying properly designed shape memory effects (SME). Networks showed well-separated crystallization and melting regions, close to those of the two homopolymers, and exhibit suitable mechanical properties to achieve a self-standing two-way SME. Particularly, after applying a specific programming cycle, a triple-shape SME was observed, but the materials can also cyclically change their shape between two configurations upon cooling-heating cycles without any external load applied, with a two-way SME. The influence of networks' compositions and of the employed thermomechanical parameters, such as the applied strain and the actuation temperature, was investigated to shed light on the shape memory mechanism. Due to their unique properties, these materials are considered promising for applications in the biomedical field and as reversible actuators for soft robotics.

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DESIGN AND SYNTHESIS OF MECHANOPHORES FOR SELF-DIAGNOSTIC VITRIMERS

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Abstract

Vitrimers represent a peculiar class of materials that behave like thermosets at their working temperature but can be reprocessed at high temperatures like thermoplastics. This behaviour is due to their peculiar crosslinking network characterized by dynamic covalent bonds: these can be broken and restored at high temperature allowing the reprocessing and the reshaping of the material.[1] For applications where structural integrity is strongly required, the creation of self-diagnostic polymers that independently sense and indicate an early-stage damage in a non-destructive way represent a precious tool.[2] One of the most investigated approaches toward self-diagnostic polymers is focused on the introduction of meccanophores that are covalently linked to the polymer chains. Mechanophores are molecules that undergoes structural changes in response to mechanical action. Isomerization-based mechanocromophores are a particular class of mechanophores characterized by the presence of a spiro-junction. When these molecules are subjected to mechanical stress, the spiro-junction undergoes to ring opening leading to a change in colour. Under specific stimuli, such as heat, the mechanocromic behaviour can be completely reversible.[3] Here we present our last attempts to synthetize functionalized isomerization-based mechanophores to be used as crosslinkers in polymeric matrices to obtain an easily recyclable vitrimeric material preserving the self-diagnostic properties. As mechanocromophores, we focus our attention on spiropyran and naphtopyran.

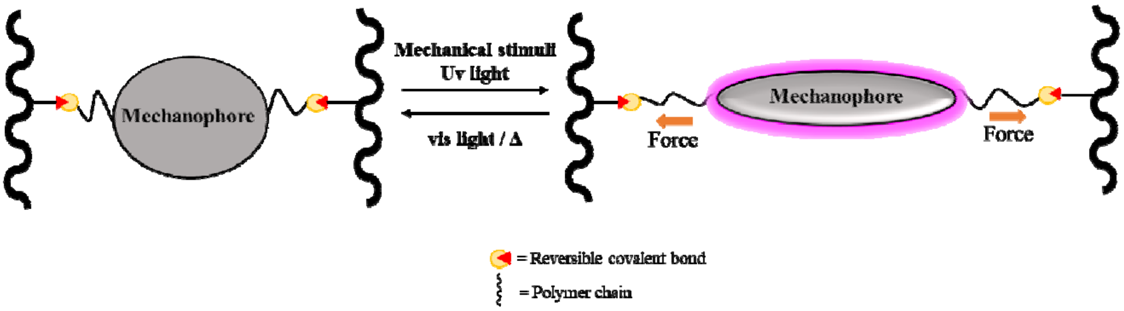

Figure: Sketch of the proposed self-diagnostic vitrimer

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ENHANCING TIRE PERFORMANCE THROUGH EFFECTIVE DISPERSION OF BIO-BASED COMPONENTS IN RUBBER COMPOUNDS

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Abstract

The performance of technical rubber items, particularly tires, strongly depends on the interaction among the components of the elastomeric compounds. These complex multiphase systems are made up of mixtures of natural and/or synthetic rubbers with reinforcing fillers, stabilizers, processing aids, and chemical agents for vulcanization. Since the last century, the tire industry has focused on developing new materials and technologies to ensure end users' safety across various tire applications, including passenger cars, trucks, buses, and motorcycles. Over the past decade, the future of tire technology has observed new horizons, looking not only at performances related to safety parameters, such as dry and wet grip, but also at environmental aspects. The introduction of parameters that consider environmental aspects has marked an important change in the approach of tire companies in developing new products.[1] To address environmental concerns and reduce reliance on fossil fuels, the incorporation of bio-based components in tire manufacturing is gaining increasing attention. Unfortunately, integrating bio-based components in an inherently complex mixture of many components is not straightforward due to the complex physical and chemical interactions that establish among the phases. A comprehensive understanding of compatibility, processing requirements, and potential interactions with other components is essential for achieving effective dispersion within rubber matrices.

In this work, a series of rubber compounds for tires containing biobased components are studied, focusing on the processability and performance of the various formulations. In particular, compounds containing different petroleum-based and bio-based resins were compared. Changing even a single component affects the processing parameters, such as torque and mixing temperature, and the rheological fingerprint of the compound. This implies complex relationships among formulation, mixing procedure, and final performance. Life Cycle Assessment methodology will support the formulation for investigating the actual sustainability of the selected green additives. Information about the system morphology and microstructure will be collected using Transmission Electron Microscopy (TEM) and dielectric analysis. The results were correlated to mechanical and viscoelastic properties analyzed with tensile tests conducted at different temperatures and Dynamic-Mechanical Analysis (DMA).

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SYNTHESIS OF BIOBASED MONOMERS AND POLYMERS

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Abstract

The project aim is to develop sustainable reaction pathways for the synthesis of monomers of biological origin and, consequently, the development of polymers of biological origin. Vegetable originated substrates deriving from the agri-food sector are of particular interest. The intent is to transform waste materials characterized by low cost and wide availability into high added value products[1].

In accordance with the growing environmental awareness of the scientific community, all synthetic procedures will be environmentally sustainable. All procedures will be optimized to have excellent atom economy and reduced waste production, to avoid the use of toxic reagents and solvents, and will be conducted with reduced energy input, such as low temperature and pressure. The so-produced monomers and polymers will be characterized in terms of their chemical and mechanical properties.

Particular focus will be put on the production of vinyl monomers which will then be employed in atom transfer radical polymerization (ATRP) processes. The ATRP technique relies on the establishment of a reversible activation/deactivation equilibium between dormant species and growing chains mediated by a complex of a transition metal, which is usually copper. Furthermore, it allows to retain control over the molecular weight distribution by altering the reaction conditions. The so-produced polymers are pseudo-living, giving the possibility of producing alternating block copolymers. ATRP processes take place under mild reaction conditions and require minimal amounts of catalyst in order to function, making them environmentally bening[2].

At the current state, olefins are almost entirely of petrochemical origin, with a limited number of publications focusing on their production which do not involve the use of sensitive and/or toxic reagents and handling techniques that are incompatible with industrial applications[3].

Biobased substrates often have complex molecular architecture, bearing various functional groups. Consequently, the deriving vinyl monomers will be bear more functional groups than their petrochemical analogues despite structural similarities, and so the corresponding polymers will. The deriving polymers will, consequently, have additional properties compared to their analogues. Also, those polymers can undergo further transformations involving their functional groups once the polymerization processes have ended, allowing the production of high added value materials[4]. As so, the topic of polymer derivatization will be studied as well during the course of this PhD project.

Another research topic that will be pursued in this PhD project is bisphenol A (BPA) replacement in the production of epoxy resins. BPA has been banned all across Europe due to its endocrine system interference, so its use is currently prohibited in the construction sector, which relies on DGEBA epoxy resins. Therefore, there is a need for developing a less toxic alternative to BPA and bisphenols, in general. Research efforts will be directed towards substrates able to assist the formation of mechanically strong resins. For instance, those bearing rigid aromatic rings and hydroxyl moieties, which will be exploited to afford the proper epoxy functions.

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STARCH FILMS PLASTICISED BY NOVEL DICATIONIC IMIDAZOLIUM-BASED IONIC LIQUIDS

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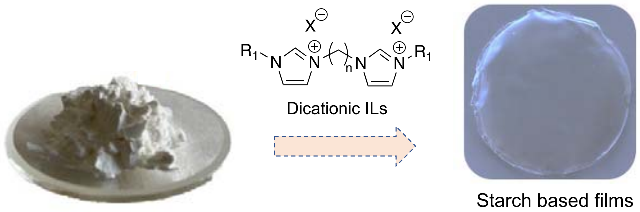
Abstract

Over the years the use of petrol-based plastics has increased about 20 times in the last 50 years[1] and their usage in many sectors has resulted in environmental problems. Natural polymers have been considered a replacement for common plastics due to their degradability, relative abundance, non-toxicity, and low cost. In this sense, starch is one of the most abundant polysaccharides found in plant storage organs and it is readily available. Nevertheless, starch is a brittleness material due to strong interactions among chains which confine their mobility[2]. To obtain effective starch films some plasticizers may be introduced that can improve the polymeric segmental mobility.



Recently, imidazolium-based ionic liquids (ILs)[3] have been studied as new plasticizers due to their unique properties. In addition, ionic liquids, besides acting as plasticizers, can impart several useful properties to prepared films due to their antioxidant, antibacterial and conductive activities[4]. Lately, dicationic ionic liquids (DILs), a new category of ILs family, attracted great concern as it represents an interesting variation of the cationic partner. Dicationic liquids are more tunable in comparison to monocationic ILs because of large number of possible combinations of various anions, cations, and linker. In this work, the influence of the type and the length of the linkage chain on film properties will be discussed through different techniques, such as the Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction analysis (XRD), Electrochemical Impedance Spectroscopy (EIS) and performing mechanical and antimicrobial activity tests.

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CHEMICAL RECYCLE OF PLASMIX

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Abstract

Waste management is a global issue which impacts the sustainability of environmental and economic developments. In particular, plastic wastes, nowadays indispensable in many fields, including packaging, construction, automotive, electronics, sports, agriculture, medicine and others, are problematic materials for treatment as they are highly resistant to biodegradation. Now these wastes are conventionally disposed in landfills and incinerators. In addition, their combustion releases pollutants such as furans, dioxins, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), which are harmful to human health.[1] Among plastic recycling methods, such as mechanical recycling, thermal decomposition or chemical treatments, pyrolysis seems very promising because of its high versatility and its potential of material and energy savings.[2] Pyrolysis technology thermally decomposes plastics or other organic wastes (e.g., biomass) in an inert atmosphere at temperatures of about 350–600°C or higher, to obtain liquid pyrolysis oil, solid char and pyrolytic gas as products. The resulting products can be further and selectively upgraded to fuels or value-added chemicals.

In this context, it was considered of interest to evaluate the possibility of recycling plastic waste of different formulations by pyrolysis process. In order to study the possible synergistic effects between different polymers, a preliminary study of the thermal degradation of each material constituent the plastic waste was performed, and then continued on more or less complex multicomponent mixtures.

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BIFUNCTIONAL ATRP INITIATORS FOR THE SYNTHESIS OF α,ω-DICHLOROPOLYSTYRENE: NEW FUNCTIONALITIES AND THERMAL STABILITY STUDY

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Abstract

Atom Transfer Radical Polymerization (ATRP) allows to obtain living polymers with a well-defined molecular weight distribution, as well as control over topology, composition, and functionality, enabling to develop advanced materials for specific applications[1]. Functional groups can be introduced into the polymer by post-functionalization of the halogenated chain-end moieties, or on the alkyl residue of the initiator, or by direct introduction of punctually functionalized (co)monomers – greatly enhancing the targetable applications[1,2]. In addition, the desired functional group can also be carried by the ATRP initiator, provided that the functionality is impervious to radical reactions. For example, some authors explored the use of initiators containing hydrolysis- or heat-sensitive functionalities such that the final polymer exhibits self-healing properties.[3] Thermoplastics, like polystyrene, require thermal and thermomechanical stability under extrusion conditions (150-220°C) in order to be reprocessed. Therefore, it is important that the initiator employed is also thermally stable, otherwise there would be a reduction in chain length and consequently a loss of telechelecity. Unfortunately, the aliphatic halide esters typically employed as initiators have shown poor thermal stability.[4] Thus, in this study we demonstrate the enhanced thermal stability of α,ω-dichloropolystyrene synthetized via ARGET ATRP (**Figure 1**) using a novel bifunctional benzamide-containing initiator instead of the formerly reported aliphatic esters. Emphasis was placed on investigating the reason why the structure and functionality of the initiator improved thermal stability.

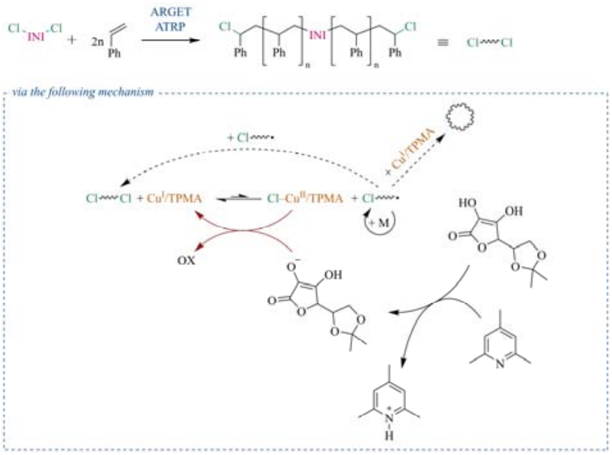

Figure 1 – Mechanism of ARGET ATRP of styrene

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EXPLORING THE EFFECT OF THE APPLIED THERMAL TREATMENT ON THE FRACTURE BEHAVIOUR OF A NBR/SILICA COMPOUND

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Role: Master student

Abstract

This work is part of a research activity of broad interest in the scientific community aimed at furthering the knowledge on the fracture behaviour of elastomer compounds. It is well known that filled rubbers are subjected to what is known as the Mullins effect, which consists in a softening of the material that occurs during the first deformation; for this reason, it is also referred to as strain-induced softening. In literature, this phenomenon is only studied by performing uniaxial tensile tests; to our knowledge, how the strain-induced softening changes the fracture behaviour of the compound has never been studied in a systematic way. As such, this work starts with investigating the Mullins effect in uniaxial tension loading conditions and defining a thermal treatment that, as suggested by literature, can recover the tensile behaviour of the pristine material. The material under investigation is a silica-filled NBR compound supplied by Arlanxeo Germany GmbH. The effect of the strain-induced softening on the material's fracture behaviour is explored too: following a fracture mechanics approach, tensile tests using notched pure shear specimens have been performed, and the fracture toughness has been evaluated using the J-integral energetic parameter. The same thermal treatment used to recover the Mullins effect in uniaxial tension is investigated for its ability to recover the pristine material's fracture behaviour. The results show that the strain-induced softening causes a reduction in the fracture toughness evaluated at the crack onset that is not recovered by the thermal treatment. In order to better understand if the thermal treatment used for the recovery of the pristine material's behaviour can have any effect on the structure of the material, how it affects the fracture behaviour of the silica-filled NBR compound is studied in detail. The whole fracture process has been investigated. The results show that the thermal history significantly affects the crack propagation, which results to be faster when more severe thermal treatments are applied to the material. Its effect on the crack onset, instead, is quite limited. An attempt is made to correlate the behaviour observed in the crack propagation phase with a higher propensity of the material to cavity formation when a more severe thermal treatment has been performed.

VIRAL-ASSISTED DELIVERY OF POLYTHIOPHENE-BASED NANOPARTICLES TO RESCUE NEURODEGENERATION

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Abstract

Neurodegenerative diseases (like Alzheimer and Parkinson's diseases) affect about 50 million people worldwide with no definitive cure and represent a major social and economic burden.[1] There is therefore urgent need for alternative therapeutic strategies to alleviate symptoms in patients suffering from these conditions.

It has been previously shown that semiconductive polymeric nanoparticles made of Poly(3-hexylthiophene) (P3HT-NPs) are able to stimulate denervated neurons "on demand" upon visible light excitation.[2,3] Thanks to their properties, P3HT-NPs constitute an excellent candidate for the non-invasive treatment of neurodegenerative diseases, if a suitable delivering system is made available.[4]
In this work, we aimed at developing an innovative therapy based on the viral-assisted delivery of polythiophene-based nanoparticles in the brain.

Our strategy makes use of an engineered M13-bacteriophage virus as cargo for the P3HT-NPs. Bacteriophage viruses are ideal for this purpose because they possess lack of toxicity towards mammalian cells, capability of crossing the blood-brain-barrier, and can be genetically engineered to achieve neuronal-targeting specificity.[5]

Here, we optimized a protocol for the synthesis of 40 nm, monodispersed nanoparticles from a P3HT derivative possessing one N-succinimidyl-ester (NHS) group for each repetitive unit of the polymer (PolyT2-NPs).[6] We made use of NHS-protein coupling, a well-known cross-linking chemistry reaction, for successfully bioconjugating PolyT2-NPs with molecules of increasing complexity (ethylenediamine and antibodies), before moving to the M13 phage. The phage will be re-directed towards a target exogenously expressed in neuronal membranes using cellular transfection methods. This model system will allow to assess the achievement of effective M13 phage-mediated delivery of PolyT2-NPs on specific neuronal subpopulations.

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SYNTHESIS OF FINE AND CONDUCTIVE FILMS OF PEDOT BY LIQUID PHASE AND VAPOR PHASE POLYMERIZATION

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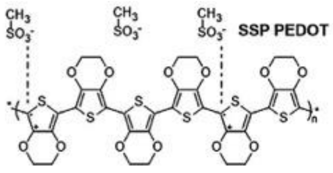
Abstract



Conductive polymers (CPs) are organic materials that are able to conduct electric current. Since their discovery at the end of the 70s they have aroused considerable interest both from the point of view of research and from the industry level. Those materials exhibit interesting characteristics such as transparency, mechanical resistance, good environmental stability and electrical conductivity, as well as for their useful optical and electronic properties.

In this project, the synthesis reaction of a conductive polymer, poly-(3,4-ethylenedioxythiophene) (PEDOT), was studied by means of two oxidative chemical polymerization processes, one in the liquid phase and one in the vapor phase.

The liquid phase process involves the sequential deposition of an oxidant solution (vanadium pentoxide) and a monomer solution (EDOT) on a glass substrate treated with a piranha solution. The film thus formed is washed in solvent to eliminate the excess monomer and finally undergoes an annealing heat treatment.

The main parameters varied in this reaction were the deposition time of the oxidizing solution and the concentration of the oxidizing solution.

The vapor phase process instead involves a first deposition of an oxidizing solution (iron tosylate) on a glass substrate treated with a piranha solution which undergoes a thermal treatment to eliminate the solvent.

The oxidizing film thus formed is placed in a temperature-controlled, vacuum reaction chamber where it is exposed to monomer vapors to form the polymeric film. This is finally washed in solvent and dried with nitrogen flow.

The main parameters varied in this reaction were the deposition time of the oxidant solution and the reaction time in the reaction chamber.

The analysis showed that, for both synthesis methods, the thickness of the polymeric film is mainly influenced by the deposition time of the oxidant solution.

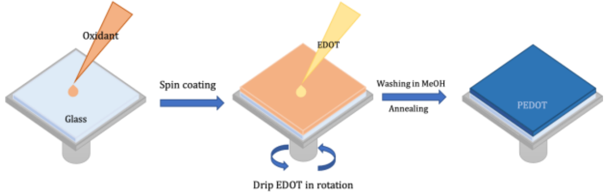
In particular, in the solution method the concentration of oxidant marginally influences the thickness of the polymer due to the different viscosity between more or less concentrated solutions.

Similarly, in the vapor phase process, the reaction time does not affect the film thickness.

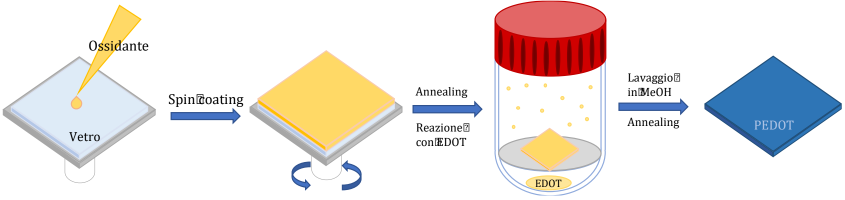
The morphology and thickness of the samples were determined by optical profilometry, while the conductivity of the samples by the Van der Paw method through a 4-point probe placed in electrical contact with the polymeric film. A direct current is applied between the outer test leads, while a voltage drop is measured between the inner ones. What is obtained from the measurement is the resistance value of the sheet (Rs, measured in Ω/□) which, together with the film thickness data, is used to calculate the conductivity of the polymeric film.

The analysis showed that the vapor phase method is much more reproducible than the liquid phase method and, for both, that the thickness decreases as the deposition time of the oxidizing solution increases.

Finally, the treatment of polymeric films in sulfuric acid solutions was tested, from which a significant increase in the conductivity of the polymeric films was found.



Liquid phase polymerization



Vapor phase polymerization

MECHANOCHROMIC PERFORMACES OF PERYLENE DIIMIDE-DOPED POLYURETANES: COVALENT BONDING VS. BLENDING APPROACHES

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Abstract

Recent advancements in the scientific research on mechanochromic polymers have explored the use of aggregochromic dyes incorporated into various polymeric matrices as additives.[1–2] However, a promising new approach has emerged: covalently integrating the dyes into the polymeric chains themselves, offering highly sensitive mechanochromic materials while maintaining low dye concentrations.[3–4]

This study evaluated the mechanochromic properties of thermoplastic polyurethanes containing a perylene diimide derivative: an aggregochromic dye characterized by absorption and emission properties that are susceptible to the dye's intermolecular distance. In particular, a mechanical stress can induce dye disaggregation, thus leading to a variation in the emission spectra.

The dye was either covalently linked to the main polymeric chains or used as an additive. The objective was to evaluate how the concentration of the dye and the two different incorporation methods influenced the mechanochromic performance. Hot-pressed films were tested under tensile mode carrying out stress-strain analysis and stress relaxation while sample emission was measured in situ. As expected, upon deformation the ratio between the intensity of the monomer band and that of the aggregate band increases, thus indicating the occurrence of the disaggregation process. By comparing the different systems, it comes out that bonding the chromophore to the polymeric chains did not improve mechanochromic sensitivity in stress-strain experiments. Moreover, when the dye was covalently linked to the polymeric chains, it exhibited a reduced tendency to aggregate, resulting in a less noticeable color change than in dispersed-dye systems. Conversely, in stress-relaxation experiments, it was demonstrated that the covalent incorporation of the dye led to heightened sensitivity and improved correlation between the stress relaxation process and the mechanochromic response.

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MICROWAVE ASSISTED EXTRACTION OF HEMP SEEDS OIL AND ITS USE FOR FOOD PACKAGING SYSTEMS

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Abstract

The effect of Microwave-Assisted-Extraction (MAE) on hemp seed oil (HSO) yield and its antioxidant activity have been investigated. The aim of this work is to set up tailored extraction conditions to obtain HSO showing the best performing properties, and to employ the extracted oil for the preparation of bioactive biodegradable food packaging films. Polybutylene Succinate (PBS) was chosen as polymer matrix, since it exhibits suitable processing and chemical-physical properties for this application. The hemp seeds were first washed to remove any soil residue, then dried and powdered with a laboratory mill. MAE tests were carried out using hexane as solvent, at different extraction times at constant power (W). MAE extraction products were characterized by Thermogravimetric analysis TGA and by Fourier Transform Infrared Spectroscopy (FTIR-ATR). Moreover, their antioxidant activity was evaluated through DPPH assay. The obtained results were compared with those relating to an product obtained by Soxhlet extraction in the same solvent. Preliminary results indicated that, although the oil extraction yields were comparable between the two different methods, (about 30% in weight), very-shorter operating times were sufficient by using MAE methodology: only 15 minutes against 6 hours of the Soxhlet method. Antioxidant activity was attested to be around 70%, according to literature (Chaymae Benkirane et al. 2022). Physical blend PBS/HSO with an oil concentration of 0,5% (w/w), was prepared by compression molding to investigate its applicability in food packaging. This concentration was selected to avoid oil exudation phenomena. Films were characterized by TGA and FTIR-ATR. The migration of the hemp seed oil from the PBS film into different food simulants was investigated.

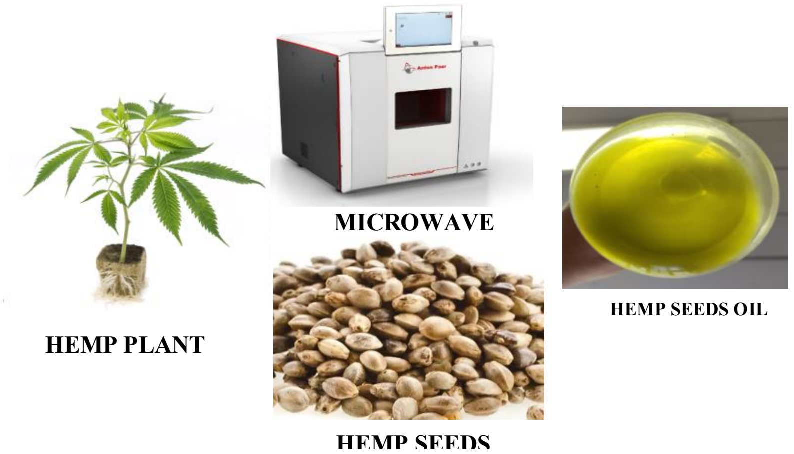

Fig 1. Graphical abstract of MAE process

Reference

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IDENTIFICATION OF MICROPLASTICS IN DIFFERENT MIXTURES AND BLENDS THROUGH PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

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Abstract

The characterization of plastic in soils and waters is key to understand its environmental impact and both destructive and non-destructive methods are being used for this purpose. Molecular spectroscopy technologies, as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy, show promising results in identifying qualitatively different microplastics simultaneously, but the former suffers from spatial resolution [1] and the latter from background noise and organic matter [2], even though they do not damage the sample. Among destructive techniques, differential scanning calorimetry (DSC) allow to identify not only qualitatively, but also quantitatively different polymers; however, it exhibits some limits with multicomponent mixtures [3].

Pyrolysis-gas chromatography/mass spectroscopy is able to identify single polymers in blends and mixtures. The aim of this work is to investigate the likelihood of detecting qualitatively single polymers in mixtures of few milligrams, in particular polyethylene (PE), polypropylene (PP), polyamide (PA), polycarbonate (PC) and polystyrene (PS) and quantitatively blends of PE, PP and PS with varying weight percentages of the individual constituents from 10 up to 90, that have undergone compounding process.

The results show the possibility of detecting the main characteristic products of PE, PP, PS, PC and PA in mixtures, as well as in PE-PP, PP-PS and PE-PS blends, after choosing their main peaks so as to avoid overlapping between them. Signal-to-noise (S/N) ratio is always greater than 3, which validate their identification [4].

Moreover, the quantification of PP in blends is always achieved and its trend can be considered as linear with R^2 higher than 0.9 when considering the variation of the peak area of its characteristic pyrolysis product as a function of its percentage weight change. Regarding PS and PE in blends, it has been possible to quantify them only from 30%wt, since the ratio between signal and noise with 10%wt of these polymers is lower than 10, which represents the limit of quantification (LOQ) [4].

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DEVELOPMENT OF PP-BASED MATERIALS WITH FLAME RETARDANCE AND THERMAL CONDUCTIVITY PROPERTIES FOR 3D PRINTING

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Abstract

The aim of this thesis was to determine the 3D printability of polypropylene (PP) formulations functionalized with different fillers, and then study and compare the thermal conductivity and fire-retardant properties of the material processed both with a 3D printer and a conventional compression molding machine. Two different additives were used to obtain the aim, in particular boron nitride (BN) and Cloisite-20A (C-20A). A polypropylene-polyethylene random copolymer (PP COPO) was used as the polymer matrix. At the same time two commercial filaments from Filoalfa®, a thermally conductive PLA-based filament addicted with graphene (Grafylon®3D) and a self-extinguishing filament based on ABS (ABS V0) were used as references.

The work can be divided into four parts. In the first one, samples produced with commercial filaments were studied, from which it easily emerged that 3D printing, compared to compression molding, does not generally bring to a deterioration of material properties and, in some cases, even leads to an improvement.

In the second part, the two PP COPO-based formulations were produced with a twin-screw extruder. To investigate the processability of the materials, and in particular their 3D printability, rheological tests were performed and from the viscosity curves it was observed that the addition of both fillers led to an increase in the non-Newtonian behavior of the material. Consequently, the composites have better 3D printability than the starting PP COPO. It was therefore possible to extrude the two compounds with a single-screw extruder and obtain smooth filaments with a constant diameter and circular section. Characterization by SEM also showed that both fillers were well dispersed and distributed in the polymer matrix.

The third part of the study focused on the combustion behavior of PP COPO/C-20A samples. Results from cone calorimeter tests showed that the addition of Cloisite-20A greatly improved the combustion behavior of PP COPO. However, a more interesting comparison was observed between pressed and 3D printed samples. The latter exhibited slower combustion and significantly lower HRR peak. This indicates that 3D printing improves alignment and arrangement of fillers, resulting in a more compact layer with better barrier properties. The superior properties of 3D printed samples were also observed in UL94 horizontal burning tests, where all ±45 patterned 3D printed samples passed, while none of the pressed samples did.

In the last part, the thermal conductivity properties of PP COPO/BN samples were studied. Hot disk tests showed that the addition of 12% BN increased the thermal conductivity of the polymer matrix. Comparing the results of BN-additivated samples, the 0-90 filling pattern in 3D printed samples resulted in a significant decrease in thermal conductivity values, while ±45 patterned samples had values similar to those of pressed samples. Moreover, light flash tests revealed that the in-plane thermal diffusivity of the material was much higher than the cross-plane diffusivity.

In conclusion, this study demonstrated that it is possible to develop and use functionalized polypropylene filaments for 3D printing, and that 3D printing can yield comparable or even superior properties to traditional compression molding process.

MIXED-MATRIX MEMBRANES FOR SOPERATION OF TWO-COMPONENT CO_2-CH_4 GAS MIXTURES

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Abstract

Separation of CO_2 from CH_4 is important in many industrial processes such as natural gas sweetening, biogas refining, enhanced oil recovery, and purification of gases that develop in landfills[1]. The search for economical and effective techniques for CO_2 removal from gaseous streams containing mainly CH_4 and for CO_2 capture over a wide range of concentration levels and flow velocities has undergone strong development over time and has attracted much interest[2]. The separation of gases using membrane modules possesses advantages over conventional separation methods in the use of easy-to-make equipment and low production costs[2].

Although the trade-off between permeability and selectivity is the main challenge for polymeric membranes for gas separation, the phenomenon of plasticization, physical aging, swelling[3] and competitive adsorption[4] are other factors that limit the performance of polymeric membranes, especially over a long period of module use[3].

Beginning in 1990, in order to make up for the shortcomings of polymeric membranes, mixed-matrix membranes (MMM). MMM are a type of membrane for which the introduction of organic, inorganic, metallorganic, or graphene-derived additives, in the form of small particles, as a dispersed phase within a continuous phase consisting of the polymeric matrix is provided. In many cases, this membrane production strategy has yielded promising results by increasing both permeability and permselectivity while also ensuring that the two upper limits (1991 and 2008) of Robeson's plot are exceeded[1].

In this work, a mixed-matrix membrane was produced using a polymer matrix of polyether sulfone with *cardo* group (PES-WC) to which a β-cyclodextrin (β-CD) derived additive like β-cyclodextrin nanosponge (β-CDNS) was added by cross-linking β-CD with 1,1'-Carbonyldiimidazole (CDI) in a 1:4 ratio. The actual amount of additive dispersed in matrix was determined by thermogravimetric analysis (TGA). In order to evaluate the effect of additivation, the mixed-matrix membrane and the corresponding blank membrane were characterized by scanning electron microscopy (SEM) analysis, by wettability measurements, by mechanical stress-strain tests, and by performing CO_2 and CH_4 permeability tests. Following additivation, an increase in the separative performance of the PES-WC polymer matrix could be observed over a wide range of ΔP.

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TWO-WAY SHAPE MEMORY POLYMER AS A PLATFORM FOR LIGHT-INDUCED REVERSIBLE ACTUATION: FROM FILM TO FIBERS

MICHELE ZANONI[1], ALESSIO CREMONINI[1], MAURIZIO TOSELLI[2], MARCO MONTALTI[1], MARIA LETIZIA FOCARETE[1], STEFANO MASIERO[1], CHIARA GUALANDI[1]

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Abstract

The field of soft robotics has gained significant attention as researchers work on developing precise machines using soft actuators. These devices aim to assist or surpass human manufacturing capabilities, offering a safer and more user-friendly alternative to rigid machines [1]. One promising application is the use of soft actuators in artificial muscles, which can replace biological or mechanical components with high energy conversion efficiency. Most artificial muscles rely on shape memory polymers that can temporarily change shape and return to their original form when triggered by external factors like heat, light, moisture, or magnetic fields [2]. Light-responsive shape-changing materials are of particular interest, with ongoing research focusing on their structure, properties, and fabrication methods. Light activation provides precise and non-invasive control over the shape of shape memory polymers, offering versatility and remote operability for various applications, further enhancing their potential in the field of soft robotics.

This study focuses on the development of a shape memory system based on a crosslinked poly(ε-caprolactone) (PCL) network with silica-based netpoints [3]. The system exhibits one-way and two-way shape memory behavior triggered by thermal stimuli. To enhance its functionality, an azobenzene compound (AZO) was incorporated to confer photo-responsiveness. The AZO compound undergoes a fast thermal cis-to-trans isomerization, facilitated by push-pull electron-donating/withdrawing substituents, and shows photo-switching capabilities. The shape memory actuation, induced by the photothermal effect, involves the melting of the PCL crystal phase under UV irradiation, leading to a decrease in Young's modulus and deformation of the sample. By switching off UV light, the polymer crystallizes under stress, causing crystallization-induced elongation. By repeating this process, the shape memory actuation can be cycled. Films and electrospun fibers were successfully produced and crosslinked. The occurrence of crosslinking, a key parameter for controlling the actuation performance, was verified by gel content measure, DSC and SEM analyses. Being the photothermal effect at the basis of the actuation, the sample temperature during irradiation was carefully monitored and significant differences emerged when comparing non-woven electrospun fibers and films. Actuation experiments demonstrate reversible strain elongation/contraction The actuation amplitude increases with pre-stretching up to a certain point, while actuation recovery remains close to 100%. Overall, this study provides insights into the design and characterization of photo-responsive shape memory materials for potential applications in various fields.

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Toughening effect of 2,5-furandicaboxylate polyesters on polylactide-based compatibilized renewable fibers

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Abstract

Bioplastics, being biodegradable and/or derived from renewable resources, can represent a more sustainable alternative to conventional plastics in terms of carbon footprint reduction and possible alternative routes for waste disposal[1]. Fully bioderived and biodegradable polymers such as poly(lactic acid) (PLA) have a promising future in the field of sustainable packaging and textiles. Nevertheless, PLA suffers from some severe drawbacks that have been generally addressed via additives such as plasticizers and chain extenders and/or through physical blending with other traditional and bioderived polymers. An attractive class of biobased polymers that can be blended with PLA is that of the furanoate polyesters or poly(alkylene furanoate)s (PAFs). Those polymers are synthesized from furan-2,5-dicarboxylic acid (FDCA) (obtained from sugar fermentation) and present outstanding mechanical, thermal, optical, and gas-barrier properties, comparable or even superior to those of the corresponding terephthalate counterparts.

This work aims, for the first time, at producing PLA/poly(propylene 2,5-furandicarboxylate) (PPF) and PLA/poly(butylene 2,5-furandicarboxylate) (PBF) compatibilized fibers via melt spinning. The PPF and PBF concentration ranged between 0 and 20 wt%, while the concentration of the employed commercial compatibilizer (Joncryl® ADR 4468, J) was fixed to 1 phr. The work first involved the melt blending of the constituents in an internal mixer to produce 2-mm-thick sheets, which have been characterized. Then, those blends have been pelletized to feed a single screw extruder to produce single filaments through melt spinning, collected at different take-up speeds.

The characterization involved a thorough rheological analysis, a detailed evaluation of the microstructure, thermal properties, and mechanical performance, both on bulk (sheets) and fiber samples. Both blend types, although immiscible, are successfully compatibilized by Joncryl (J), which improves the interfacial adhesion and reduces the size of PPF and PBF domains. Mechanical tests on bulk samples show that only PBF (specifically at 5-10 wt%) is able to effectively toughen PLA, showing a distinct yield point, remarkable necking propagation, and increased strain at break (up to 55%). For fiber samples, increasing PPF and PBF fractions improved elastic modulus and mechanical strength, particularly for PBF-containing fibers collected at higher take-up speeds. Remarkably, plasticizing effects were observed for both PPF and PBF, with significant strain at break values compared to neat PLA (up to 455 %), likely due to a further microstructural homogenization, enhanced compatibility, and load transfer between PLA and PAF domains following the fiber spinning process. SEM analysis confirms the deformation of PPF domains, which is probably due to a "plastic-rubber" transition during tensile testing. The orientation and possible crystallization of PPF and PBF domains contribute to increased tensile strength and elastic modulus. This work showcases the potential of PPF and PBF in tailoring the thermo-mechanical properties of PLA in both bulk and fiber forms, expanding their applications in the textile industry.

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IN SITU ANIONIC POLYMERIZATION OF CAPROLACTAM FOR POLYAMIDE6-BASED THERMOPLASTIC COMPOSITES

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Abstract

Thermoplastic continuous-fiber composites have emerged as strong competitors of their thermosetting counterparts, as they can be more easily recycled, post-thermoformed, repaired, and welded, exhibit an infinite shelf life, and feature higher toughness and impact properties. However, the high viscosity of polymer melts may hinder a full impregnation of the reinforcement. An effective solution is represented by reactive processing techniques such as liquid composite molding (LCM): the reinforcement is impregnated with a low-viscosity monomer, which is then in-situ polymerized thanks to catalysts and/or moderate heating[1]. This work aims to employ the in-situ anionic polymerization of caprolactam (CL) to produce thermoplastic composites having a polyamide 6 (PA6) matrix and continuous fibers of different types. The properties of the prepared composites were investigated to evaluate the microstructural features, the degree of conversion, and the mechanical properties as a function of the processing parameters and the type and amount of continuous fibers.

CL (AP-Nylon, Bruggeman S.A.) was melted in a round-bottom flask at 110 °C under nitrogen flow, and then commercial initiator and activator (C10 and C20P, Bruggeman S.A.) were added in a variable concentration. The stirred mixture was injected in a mold preheated at a variable temperature (140-170 °C) containing the reinforcing fibers, and left polymerizing for 20 minutes.

The microstructural evaluation showed that the CL was able to fully impregnate most of the selected fiber types. All prepared composites showed little unreacted CL (<2%), measured through thermogravimetric analysis (TGA) as the mass loss at 250 °C. Unreacted CL decreased with an increase in the content of activator and initiator and was higher for the composites than for the neat PA6 samples, probably because the contact with the fiber surface hindered the polymerization of CL. Tensile tests on the PA6 samples showed that optimal mechanical properties were found at intermediate polymerization temperatures (150-160 °C) and low initiator and activator concentrations. The characterization of the fiber-reinforced composites showed that the elastic modulus generally followed the mixture rule in the fiber direction. This work evidenced the advantages of in-situ anionic polymerization as a method to produce continuous-fiber-reinforced thermoplastic composites. The process proved feasible with several types of reinforcing fibers. Future works will deal with a detailed characterization of the interfacial fiber/matrix adhesion as a function of the polymerization parameters and the fiber type.

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AN ANTIBACTERIAL AGENT BASED ON POLYMER-GRAPHENE DERIVATIVE DECORATED WITH SILVER NANOPARTICLES

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Abstract

The polymer-based materials are ubiquitously applied for structural applications in everyday use objects and value-added devices: from kids' toys manufacturing to biomedical devices (such as catheters, ureteral stents and prostheses). Due to bacterial surface contaminants, severe infections could occur, especially through the use of in-body applied biomedical devices. Usually, to provide a long-term antibacterial effect besides the preparatory materials sterilization, low-molecular-weight organic molecules are used as antimicrobial agents. The application of such molecules occurs through spray coating techniques or blending with a polymer matrix, but their low adhesiveness on the substrates resulted in leakage in the environment, where they bioaccumulate and act as endocrine disruptors. These well-known adverse effects have led to the ban on some of them. On the other hand, hybrid nanocomposites obtained by decorating graphene-based materials with silver nanoparticles (AgNPs) have received increasing attention because of their excellent antimicrobial activity. However, complex synthetic methods for their preparation have limited practical applications.

This communication aims to describe the synthesis of novel NanoHybrid Systems based on graphene, polymer, and AgNPs (namely NanoHy-GPS) through a straightforward microwave-assisted synthetic approach, without the use of reductants and surfactants[1]. In this new system, the polymer moiety plays a crucial role since it assures the coating layer/substrate compatibility, making the platform easily adaptable for a specific substrate. Thus, the synthetic strategy was chosen to ensure the interchangeability of the polymer moieties. The loading of AgNPs (from 5% to 87 %) was easily tuned by adjusting the Silver salt amount used during the microwave-assisted reaction, obtaining a homogeneous distribution of AgNPs size (ranging from 5 to 12 nm) on the polymer-graphene nanosystem. Interestingly, the microwave treatment partially restored the graphene sp^2 network without damaging the polymer-rGO linkages.

The structural, morphological, and chemical composition studies of NanoHy-GPS and its precursors were performed through several techniques (UV-Vis, thermal analysis, DLS, SEM-EDX, AFM, and HRTEM). Finally, a preliminary assay was performed to assess the antibacterial properties of NanoHy-GPS against a typical bacterial population present on common hand-contacted surfaces. The experimental data evidenced a significant reduction in the spread of bacteria colonies.

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COMPOSITE ELECTROSPUN MATS AS SUSTAINABLE PHOTOTERMAL SYSTEMS FOR ARTWORK RESTORATION

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Non-woven electrospun (ES) nanofibers have found application in various technological fields and recently have been proposed as cleaning means for the restoration of cultural heritage[1,2]. The cleaning procedure is one of the most delicate procedures as it is irreversible, thus it must be selective towards the layer to be removed and non-invasive towards the one to be preserved. Traditionally, the procedure is carried out employing cotton swabs coupled with cleaning agents (*e.g.* organic solvents), however this approach presents drawbacks due to the uncontrolled release of solvents, which may interact with the object and damage it even more. Moreover, a new complex challenge that conservators-restorers are facing is the removal of highly insoluble paints, such as reticulated alkyd spray paints, from historic buildings and contemporary mural paintings, as more aggressive treatments are necessary for their removal[3]. A promising solution is the use of ES non-woven fabrics as retentive media, thanks to their high interconnect porosity and permeability[4].

In this work, composite electrospun mats of pullulan nanofibers and melanin nanoparticles have been developed and studied as potential devices for the removal of alkyd-based spray paints. Melanin is widely known for its photothermal properties[5]; thus, when incorporated in polymeric nanofibers, a local temperature increase in the mat is expected upon light irradiation. The morphology and photothermal behaviour of the as-prepared materials were assessed and the effect of light irradiation on varnish removal was investigated by using γ-valerolactone (GVL) as cleaning agent. In particular, it was proven that the light-induced local temperature rise leads to increased mobility of polymeric binders present in the spray paint varnishes, which facilitates the removal of the paint when GVL is added. It was also proven that the local temperature variations influence the retention of the solvent in the cleaning device, leading to a more controlled release both in space and time and thus to a decrease in the application time, which represents a significant advantage both in terms of efficacy and safety of the artwork.

The cleaning procedure here presented makes use of sustainable materials and processes: the solution for electrospinning is prepared in water, pullulan is a natural polymer, melanin nanoparticles are sourced from cuttlefish sacks and GVL is a green organic solvent [5-7].

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DEVELOPMENT OF A NOVEL HYALURONIC ACID HYDROGEL SYSTEM FOR ENHANCED LOADING AND CONTROLLED RELEASE OF ACTIVE MOLECULES

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Abstract

Osteoarthritis (OA) is a prevalent joint disease affecting millions of people worldwide. Among the current treatments, which mainly focus on the mitigation of OA symptoms, Hyaluronic Acid (HA) injections have emerged as a popular therapeutic intervention, as it has been observed that its concentration and its molecular weight decline during the advancement of the disease. HA is a natural, linear, endogenous polysaccharide that plays important roles in the human body; in the treatment of arthritic diseases, it is often employed as starting material for hydrogels, three-dimensional hydrated polymeric networks, with high affinity for water and biological fluids[1]. HA hydrogels have been employed as controlled intra-articular delivery systems for bioactive molecules because of their biocompatibility, biodegradability, lack of immunogenicity, as well as their ability to act as a binding site for molecules. However, conventional HA hydrogels often face challenges related to limited loading capacity, uncontrolled release of active molecules and injectability.

This work presents a novel system based on HA hydrogels for the delivery of Glucosynolates (GLs), a class of nutraceuticals renowned for their well-documented anti-inflammatory, antioxidant, immunomodulatory and antinociceptive properties that are particularly beneficial in mitigating OA progression. The developed HA hydrogel system is comprised of a dispersion of cross-linked HA hydrogel particles embedded within a of non-cross-linked HA solution. Particles were obtained through a water-in-oil emulsion, using 1,4-butanediol diglycidyl ether (BDDE) as the cross-linking agent. Concurrently, the non cross-linked HA solution was integrated into the system to improve injectability of the formulation and to synergistically facilitate GLs controlled and sustained release. A preliminarily evaluation of drug loading capacity and release was carried out using Rhodamine B as representative model drug. Additionally, comprehensive rheological analyses were conducted on the hybrid system employing amplitude sweep and viscosity flow tests to assess its mechanical properties, and the obtained results were compared with those of commercially available hyaluronic acid hydrogels. Preliminary results showed that this hybrid system maintains favourable rheological characteristics, including suitable viscosity and shear-thinning behaviour, crucial for ease of injection and optimal tissue distribution, thus showing its promising potential for efficient delivery of GLs within osteoarthritic sites.

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POLYMER BASED PHOTONIC SENSORS FOR THE DETECTION OF TOLUENE IN WATER

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Abstract

Rapid and effective analysis of ground- and surface water is an ongoing need, especially in today's environment, where pollution from aromatic compounds is a serious concern. Current analytic methods require complex sampling and dedicated laboratory equipment, new methods for monitoring pollution on-site are becoming of increasing importance.[1]

Multilayered polymer photonic sensors have proven to be very valuable for the detection of aromatic compounds and other molecular species in vapors, [2-3] reaching a lower detection limit of a few parts per billion. [4] These structures, also known as distributed Bragg reflectors (DBRs), are composites that alternate high and low refractive index media. This sub-micrometric lattice is responsible for creating photonic bandgaps (PBGs) where light propagating at specific frequencies is reflected or diffracted by the structure, producing a typical chromatic response. On a laboratory scale, if made of polymer building blocks, these structures can be fabricated by spin-casting. This allows an easy yet fine tuning of the photonic bandgap spectral features by modification of number of layers and their thickness.[5]

The DBR molecular detection relies on the swelling of the polymer layers upon analyte intercalation, which affects the optical thickness of layers and therefore the spectral position of the PBG. In this work, we report on polymer photonic crystal sensors made of cellulose acetate and polystyrene as active sensing medium for the detection of toluene traces in water. The sensors are probed with portable optical set-ups and show a concentration dependant response, with a lower detection limit of 100 ppm of toluene in water, thus promising new reliable monitoring system for environmental waters.

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FUNGI-MEDIATED BIODEGRADATION OF POLYBUTYLENE ADIPATE TEREPHTHALATE (PBAT)

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Abstract

Biodegradable polymers have gained increasing importance in the last decades and their production is constantly growing. However, biodegradation is a complex process, involving a large number of variables, which is why the study of biodegradation under different environmental conditions is still a debated research topic. PBAT is one of the most diffused biodegradable polymer, with wide applications in packaging and mulch films[1]. Although it meets the conditions for biodegradation in industrial composting, the existing studies mostly focused on thermophilic and diverse biome conditions[2,3].

The present study aimed at investigating the role of filamentous fungi in the biodegradation of PBAT, at low temperature (24°C), in simple cultural media, to extend the investigations to less favorable conditions and to gain information on the ability of microorganisms to proliferate in the presence of the polymer as sole carbon source. The biodegradation tests were structured in order to study both the depolymerization and assimilation phases of the degradation products, using two fungal strains, hereinafter referred to as F81 and F75, which had already demonstrated a good performance in the degradation of polyesters in a previously study. Along with the biodegradation tests, monitored through gravimetric measurements, FTIR spectroscopy, scanning electron microscopy (SEM), thermal analyses and HPLC of the culture medium extracts, an assimilation test was performed with the monomers (1,4-butanediol, adipic and terephthalic acids), to investigate the effective capacity of the microorganisms to assimilate the final products of biodegradation.

The results showed that the biodegradation of PBAT proceeds through a mechanism of surface erosion, which mainly concerns the amorphous phase of the polymer. The monomer assimilation tests showed that adipic acid is easily assimilated by both fungal strains, even in minimal culture medium, while the assimilation of butanediol is favored by the concurrent presence of easily assimilable carbon sources, that is, in enriched culture medium; terephthalic acid, on the other hand, shows only partial assimilation, even in the presence of additional carbon sources, and tends to accumulate in the culture medium, following the biodegradation of the polymer.

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FROM DRUG DELIVERY POLYMERIC SYSTEM TO GREEN POLYMERS FOR *AUTOMOTIVE* MANUFACTURING

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Abstract

The research projects can be divided basically into two different pathways: the creation of an eco-friendly Drug Delivery System cyclodextrin-based and the characterization and development of innovative materials for automotive applications.

As far as the first part of the projects is concerned, different hyper-crosslinked polymers were synthesized employing cyclodextrin or maltodextrin as a monomer, citric acid as a cross-linker agent and water as a solvent and melatonin as a drug. After getting the powder samples, they were incorporated in "home made" creams and in other cosmetic formulations. Drug releases were evaluated with HPLC-UV detector. Moreover all experimental part was combined with theoretical simulation aimed to study in-depth the structures involved and the interaction inside inclusion complex obtained.

As far as innovative materials for automotive applications, green adhesives and polymers derived by bio source and by chemical recycle were considered.

a) A new material consisting of a percentage of polyester obtained from chemical recycling and a percentage of virgin polycarbonate were studied and the purpose is to find a proper formulation that will compliant with automotive requirements to replace virgin plastic components with this innovative recycled blend.
b) Two commercial resins, a cardanol-based epoxy resin (27% bio-content) and an epoxy novolac resin (84% bio-content), were mixed to obtain four different resin mixtures. In particular, the higher bio-content novolac resin was mixed with the cardanol epoxy resin in different weight percentages in order to reach a total bio content higher than 27%. The resins obtained by this procedure are characterized by a total bio-contents of 27%, 31%, 41% and 51%, calculated on biomass used in production. Quasi-static and dynamic tensile tests have been carried out to assess the mechanical behaviour of the different resins at increasing bio-contents.
c) Many adhesives were synthesized with different amounts of bio-based monomers: the bio-based methacrylate isobornyl (IBOMA) monomer to replace the "hard" monomer methyl-methacrylate (MMA) and geraniol, terpenic alcohol extracted from plants, without any chemical modification into a reactive monomer, to replace the "soft" monomers butyl-acrylate. The chosen technique for the formulation of adhesives was emulsion polymerization, to eliminate VOCs. Isobornyl methacrylate (IBOMA) was a valuable substitute for hard monomer methyl methacrylate derived from oil; the DSC's results were crucial to determining that if IBOMA can adjust the Tg. By aqueous emulsion, the incorporation of IBOMA in the adhesive system was verified through ^{1}H-NMR spectroscopy, while through FT-IR (ATR mode) analysis, the functional groups of copolymers were highlighted.

MULTIPOTENT PRECURSORS FOR CONJUGATED POLYMERS WITH COMPLEMENTARY ELECTRONIC PROPERTIES

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Abstract

Indubitably, the development of semiconductors technologies that characterized last century was the turning point that allowed the rise of modern-day electronics and the information revolution we are living. However, despite their success in applications such as OLEDs, OFETs and flexible electronics, organic semiconductors did not live up to the expectations researchers had 50 years ago. One unrivaled advantage of silicon-based technology over these latter, lies in the possibility of obtaining regions defined by complementary electronic and transport properties - n and p - on a single substrate, which are at the base of integrated circuits and complementary logic configurations (CMOS). This approach cannot be replicated with organic semiconductors due to their intrinsically different nature, which adds up to other shortcomings such as the lower charge mobility and the often non-efficient charge injection from metallic materials. Unlike silicon, organic compounds are characterized by a precise chemical structure which localizes the frontier orbitals and dictates, in principle, its transport properties.

To avoid these limitations, we developed a novel class of polymeric precursors that can undergo two different transformations to yield two different conjugated polymers, characterized by complementary electronic properties, from the same starting materials. While a precursor is usually designed to yield a unique compound, we propose a novel approach, based on highly-processable substituted 9,10-dihydro-anthracene compounds, that generate two different molecular structures, i.e. high-HOMO 9,10-diethynyl-anthracene units and low-LUMO anthraquinone units. Such transformations are achieved by different chemical treatments, which can also be applied orthogonally and on the solid state, thus generating different phases on a single substrate.

We characterized the systems proposed and show several examples of how this methodology can be applied for the fabrication of OFETs, redox polymers, and multicolored electrochromic displays.

ONLINE MONITORING OF MIXING QUALITY OF RUBBER COMPOUNDS

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Abstract

Rubber processing includes a series of different transformation steps, the first of which consists in combining the ingredients of a compound, namely elastomers, reinforcing fillers, plasticizers, stabilizers, processing aids and curing agents, and in a mixing device. Both batch/discontinuous technologies (internal mixers) and continuous lines (extruders) can be used for this purpose. The complexity of the mixing process arises from the different physical form of the raw materials and the numerous physical and chemical interactions among them. Such interactions must be kept under control by dividing the process into different mixing phases and choosing, for each of them, the proper sequence of ingredients addition and final temperature.

Aiming at the achievement of increasingly challenging targets for compound processability and performances and to guarantee their reproducibility and efficiency, accurate quality control systems are needed focusing on (*i*) proper compound composition and homogeneity, determined by the dispersion and distribution of the ingredients within the polymer matrix, and (*ii*) correct geometrical features of the rubber semifinished and final products. In particular, online monitoring techniques of uncured materials show the advantages of being less time-consuming and almost non-destructive and allowing a higher sampling frequency compared with traditional offline checks. The resulting fast feedbacks can bring about major improvements in mixing quality, with the possibility of promptly reacting to any detected processability issue and deviation from correct formulation and pushing towards process auto-regulation.

During rubber processing, the geometrical uniformity of rubber parts may be compromised by the occurrence of flow instabilities, that are surface and volume defects whose severity depends on the shear rates involved and the reactivity among the ingredients of the compound.[1,2] In this work, methodologies based on rheo-optical tools for the online monitoring of flow instabilities in rubber materials are presented. Geometrical descriptors for the instabilities, such as their characteristic wavelength and height, can be quantified to determine the onset of defect formation and deepening the investigation at the lab-scale allows to build correlations among compound processability and material-related features such as the molecular architecture and rheological fingerprint of the polymer matrix, the amount of reinforcing filler and other chemicals and their extent of dispersion. This approach can be pursued to develop prediction models for processability of novel formulations. Also other combinations of optical, rheometric and spectroscopic techniques have been reported in the literature to be effective in assessing the mixing quality of rubber compounds.[3]

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BRAN OR HAZELNUT SHELL POWDER REINFORCED COMPOSITES PROCESSING AND RECYCLING BY BIOBASED CHAIN EXTENSION

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Abstract

The valorization of agro-food waste in biobased and biodegradable materials is a strategy to apply circularity concepts and at the same time to boost the use of biopolymers in applications with a short life cycle. Wheat bran is an abundant waste of the cereal food chain, representing the external part of wheat grain. The powder obtained by grinding hazelnut shells is another underutilized waste of the food industry. Wheat bran was added to polylactic acid (PLA)/poly(butylene succinate-co-adipate) (PBSA) blends to produce biobased and biodegradable composites by twin screw extrusion, but an evident chain scission of biopolyesters occurred. This was detrimental for both processing and recycling of this material. Thus, biobased chain extenders were developed for this composite using dicarboxylic acids coming from fruits and epoxidized vegetable oils. This biobased chain extender system could work well only in a specific range of composition and showed inferior performances with respect to commercial fossil-based chain extenders.

Similar composites were produced by using as reinforcing filler the hazelnut shell powder. Two different dimensions of the powder were considered. In this case it was found that only a limited chain scission occurred. Results of this study evidenced a modest increase in melt viscosity due to biobased chain extension system, but only for the hazelnut shell powder with the lower dimension. The observed differences can be tentatively ascribed to the different compositions of the two fillers.

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PERFORMANCE, BIODEGRADATION, AND SUSTAINABILITY OF POLYLACTIC ACID-BASED GREEN COMPOSITES FILLED WITH NATURAL FIBERS

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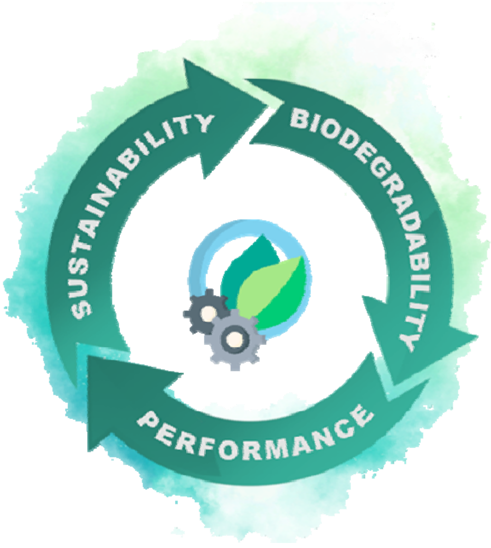
Abstract

To mitigate the plastic pollution problem, biopolymers represent one of the most interesting solutions. These “green” plastics have the inherent advantage of being produced from renewable resources and, more important, they can be biodegradable or compostable. The latter point is highly desirable to reduce the environmental footprint. Many plastics are biodegradable, but the time needed to complete the process can be very long. The challenge is shortening this time as much as possible while preserving the plastics properties.

In our group, this goal is pursued exploiting hygroscopic natural fibres, which are able to exert a pro-degradative action when embedded into biopolymeric matrices susceptible to hydrolysis. The hemicellulose fraction of the fibres acts as water vehicle that triggers the hydrolysis of matrix. The shortened polymer chains can be hence mineralized by microorganisms. To exploit the full potential of the pro-degradative effect of the fibres without compromising mechanical performances can be achieved by fine tuning of material-related parameters. Experimental analyses on green composites are carried out in parallel to life cycle assessment studies aimed at assessing the actual environmental impact of raw materials and processing for the development of truly sustainable composites.



PIRELLI'S OPEN INNOVATION MODEL TOWARDS MORE SUSTAINABLE TYRES

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Abstract

Tyre integrates hundreds of raw materials and diverse technologies: tyres are then complex engineered products.

Tyre development is driven by the requests of vehicle manufacturers, legislation, and market forces: Pirelli integrates the former inputs into an Open Innovation Model, involving collaborations with OE customers, selected suppliers and research institutes.

Pirelli is strongly committed to the development of high-performance products and to their continuous improvement in terms of safety and environmental impact, according to its "green performance" strategy "safe for People, safe for the Planet".

Pirelli set itself ambitious objectives on product and raw materials:

- Products: to reach by 2025 A/B class in rolling resistance for 70% of the products and A/B class of wet performance in 90% of the products
- Raw materials: renewable materials to reach 40% of the weight of the tyre within 2025 and 60% within 2030, on selected products.

New Materials and Technologies are a fundamental part of Pirelli's Innovation Strategy - main developments in new materials are:

1. New Polymers able to solve trade-offs between Rolling Resistance, Wet and Winter performances.
2. Materials from renewable feedstock with potential use as plasticizers, protective agents, curing and coupling agents - in particular a bio-based "universal coupling agent" was developed in cooperation with Politecnico of Milano.
3. New nanofillers, exhibiting a low environmental footprint and enabling the formulation of compounds with exceptionally low hysteresis.
4. Biopolymers from renewable sources, focusing on lignin and cellulose. In the past, various attempts have been made to be able to use some of these materials as reinforcing agents, which also have a lower specific weight than traditional reinforcing fillers. Such efforts were long undermined by difficulties in dispersion and compatibilization. Pirelli is now introducing Lignin as a reinforcing filler in tire compounds following a proprietary approach, while significant R&D effort is still devoted to further improve the interaction of lignin with the elastomer matrix.

FROM CONTROLLED POLYMERS TO PRECISION POLYMERS: ADVANCES IN MONOLAYER DOPING USING GRAFTING TO PROCESS

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Abstract

Interfacial reactions between end-functionalized polymers and suitable substrates are generally defined as "grafting to" reactions and are commonly employed to cover inorganic surfaces with chemically anchored thin polymer layers. Since the number of polymer chains included in the brush (i.e. the grafting density, Σ) is reaction-limited and predicted proportional to $M_n^{-0.5}$, with M_n being the average molecular weight of the polymer, "grafting to" reactions were recently exploited to deliver controlled amounts of dopant atoms (typically phosphorus, P) on silicon substrates. Silicon substrates have been doped using controlled polymers, including polystyrene and poly(methyl methacrylate) with narrow dispersity and containing a terminal phosphate group[1]. Even if a M_n-based control of P dose can be achieved, it has been demonstrated that partitioning by molecular weight occurs at interfaces, with lower molecular weight species being preferentially incorporated into the polymeric brush. This preferential incorporation also affects polymer dopants with relatively narrow molecular weight distribution ($Đ < 1.1$), thus limiting the capability to effectively control the number of polymer chains in the brush layer and, consequently, the dopant atoms dose[2].

To facilitate the incorporation of polymeric materials into the complex processes of the microelectronics industry, a significant technological advancement is required to achieve the production of monodisperse and highly reproducible polymers. Precision polymers have emerged as a promising solution to address this new challenge. In this context, monodispersed bioinspired phosphorous-terminated polypeptoids with different backbone length have been obtained by solid phase sub-monomer synthetic approach and grafted onto silicon oxide substrates (SiO_2). The monodisperse nature of the synthesised polymers has been confirmed by MALDI-TOF characterization. The deposited amount of P has been evaluated by TOF-SIMS analyses. An inverse correlation was found between the phosphorus dose and the polypeptoid length[3].

Overall the use of polypeptoids for doping of semiconductors through monolayer doping allows to control the amount of P dose in the phosphorous δ-layers by changing the polymer chain length. The monodisperse nature of these precision polymers prevents the partitioning process driven by the molar mass distribution, thus ensuring perfect control of the characteristics of the brush layer.

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DESIGN OF POLYMERIZED IONIC LIQUID ELECTROLYTES FOR MORE SUSTAINABLE RECHARGEABLE BATTERIES

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Abstract

With global battery demand projected to increase by 25% per year till 2030, it is urgent to overcome the limitations of commercial Li-ion batteries in terms of energy density, safety, cost and carbon footprint. Batteries based on multivalent ion chemistries (*e.g.*, Mg^{2+}, Ca^{2+}, Al^{3+}) can reach significantly higher energy densities at lower costs, employing metals that are significantly more abundant than Li and more geographically widespread.[1] The major barrier toward the development of effective multivalent metal-based rechargeable batteries is the lack of suitable electrolytes that allow reversible, charge efficient plating/stripping of the selected metal.

Herein, the rational design of polymerized ionic liquids (PILs) as potential electrolytes for multivalent-ion batteries is presented. IL-based electrolytes have emerged as non-flammable alternatives to more conventional liquid electrolytes, with improved electrochemical stability. PILs further offer the advantages of improved chemical and mechanical stability. Moreover, their structure can be carefully engineered to determine the impact of various functionalities and features on their properties and performance when employed as electrolytes. Two different PILs will be synthesized by means of controlled radical polymerization procedures to obtain polymers with pre-defined molecular weight (Figure 1). PEO-PIL differs from PIL for the presence of an oligomeric ethylene oxide (EO) side chain. EO units are known to coordinate several monovalent and divalent metal ions. Therefore, the comparison between the performance of PIL- and PEO-PIL-based electrolytes is expected to offer improved understanding on the mechanisms of conduction of multivalent metal ions.

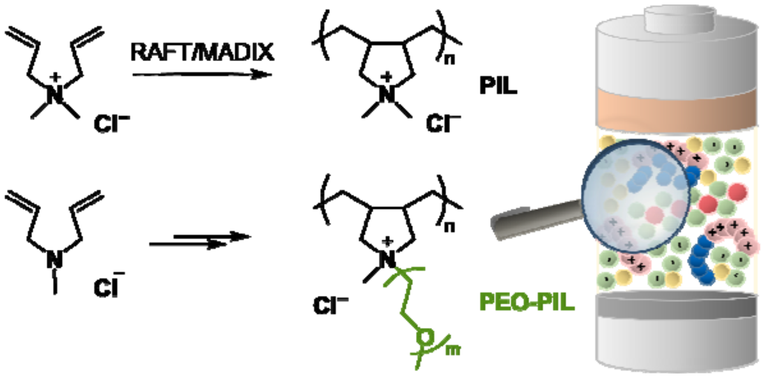

Figure 1. Structure of PIL and PEO-PIL for use as electrolytes in multivalent metal batteries (RAFT/MADIX indicates reversible addition-fragmentation chain transfer/macromolecular design via the interchange of xanthates polymerization).

Acknowledgements. This work is funded by the European Commission through the MSCA-PF-2021 project “ION-MAN” (Grant agreement n° 101068538)

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Responsive Polymer and Solution Processed Nanophotonics

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Abstract

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Photonic crystals are very well known nowadays and are used for a variety of applications such as lasers, modulation of light emission and even sensing. In the past, these structures were made from inorganic media, which offer great dielectric contrast but poor mechanical properties and complicated fabrication processes.
Solution-processed polymers[1] and hybrid polymer-inorganic[2] structures promise to simplify growth methods, reduce cost, and improve mechanical properties. This work focuses on the design and fabrication of functional solution-processed photonic crystals and demonstrate applications in molecular species recognition,[3] mechanical stimuli detection, light emission control,[4] lasing, and thermal shielding.[5]

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CAN THERMOSETTING MATERIALS WITHSTAND THE CIRCULAR ECONOMY?

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Abstract

Attention to the environmental impact of all human activities, and more specifically to sustainability, is at the heart of the agendas of politicians, the strategies of companies, and current scientific research. As a matter of fact, in 2020, the European Commission developed an action plan for a new circular economy that includes suggestions about the design of more sustainable products and waste reduction.[1] The circular economy is a production and consumption paradigm that promotes the reuse, repair, restoration, and recycling of existing resources and goods for as long as feasible so that the life cycle of products is prolonged.

Thermosetting materials, such as epoxy resins, due to their impossibility to melt, high mechanical and chemical resistance, ensured by their covalently crosslinked structure, hardly fit into the concept of a circular economy. However, the scientific community found a key to solving this dilemma by developing the so called Covalent Adaptable Networks (CANs): materials with a three-dimensional network containing dynamic covalent bonds that, under a given stimulus, can be broken and reformed.[2] In this way, some properly conceived thermosets can also be remoulded, repaired, and reused, according to circular economy requests.

Another issue, concerning the huge amount of epoxy resins earlier produced and distributed worldwide, remains open. Fortunately, this concern too can be fixed by resorting to CANs. The addition of suitable substances (e.g. catalyst) to unrecyclable epoxy resins by different techniques, such as reactive blending, mechano-chemical functionalization, or infusion, can ensure reprocessability of a large amount of materials already existing.[3]

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LIGHT RESPONSIVE POLYMERIC MATERIALS FOR MICROBOTICS AND PHOTONIC APPLICATIONS

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Abstract

The use of light in polymer science opens up to multiple opportunities. Among them, exploiting photopolymerization processes, specifically designed materials can be printed allowing for 3D structures preparation at different scales.
In this communication, the use of Direct Laser Writing, a technique based on two photon absorption polymerization, will be presented to realize 3D polymeric objects with a resolution up to 150 nm.
Furthermore, light was demonstrated to specifically modify selected properties of some materials, such as to control the shape of Liquid Crystalline Networks (LCNs). LCNs are polymers used as responsive actuators able to convert energy from external stimuli (as light irradiation) into mechanical actions. The use of LCNs for micrometric robots (controlled by light) or cell scaffolds (able to control cell alignment or some differentiation processes, see Figure below) realization will be also presented.
Finally, functional polymers can be explored to control light. The already mentioned LCN can be used to create optical element such as diffraction gratings, ring resonators or 3D photonic crystals. Some application of LCNs for photonics will be shown.

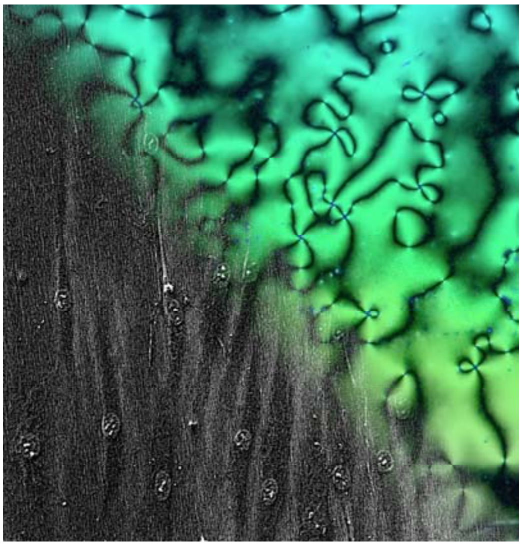

Figure 1. Combination of a polarized optical image of a LCN with a SEM picture of cells on a LCN scaffold. The cells grow aligned along the director of the liquid crystal molecules.

D. Martella acknowledges INRiM for financial support (Next-Generation Metrology project).

EXPLOITING FLUORESCENCE IN POLYMERS

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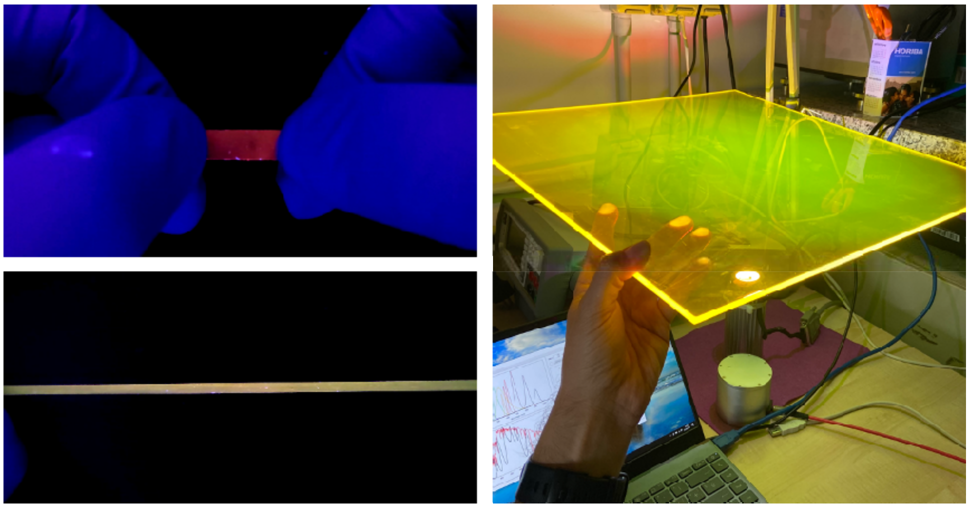
Senior

Abstract

Incorporating luminescent dyes into polymers has effectively provided materials showing optical response to visible light. The basic principle of these materials is founded on colour changes in emission associated with the structural modifications of the molecular assemblies of dyes dispersed in the polymer phase. Fluorescent polymers can respond to various stimuli *via* a macroscopic output in which the energy of the stimulus is transduced into optical variations. For example, mechanochromic, thermochromic or vapochromic fluorescent polymers were designed and prepared to be applied for the development of chromogenic polymers for different stimuli.

Fluorescence is also pivotal in luminescent solar concentrators (LSCs) for photovoltaics. LSCs are waveguides in which sunlight penetrates the top surface of inexpensive plastic and is then absorbed by the embedded luminescent molecules. Most of the re-emitted light is trapped in the waveguide by total internal reflection and then collected at the edges of the device to produce electric power. In this technology, fluorophore features are fundamental in solar harvesting.

This contribution provides the most illustrative examples developed in our group of fluorescent polymers in sensing and solar harvesting.



CARBON DOT/POLYLACTIC ACID ELECTROSPUN NANOFIBROUS MEMBRANES FOR SOLAR-MEDIATED OIL-WATER SEPARATION

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Abstract

Solar-heated oil absorbents have attracted growing attention as effective platforms for separating and recovering oils from water. Carbon dots (CDs) are promising nanoparticles with photothermal properties that can be utilized in environmental treatments.[1] CDs possess advantageous physicochemical characteristics, such as low toxicity and chemical stability. Moreover, they are produced from environmentally friendly components by green manufacturing processes.

In this study, ultrafine fibrous membranes composed of CDs and polylactic acid (PLA) were produced exploiting the electrospinning technique and their efficiency in removing oil from oil/water mixtures was tested.[2] PLA was chosen to endow the membranes with biodegradability and good affinity with oil, given the hydrophobic character of the polymer. PLA membranes with different CDs contents (5-20 and 40 wt%) were fabricated and thoroughly characterized in terms of their morphology, thermal and mechanical properties. Experimental results using solar radiation demonstrated that the CDs/PLA composites exhibit superior oil absorption compared to pure PLA membranes due to the photothermal effect induced by CDs. In fact, by harnessing absorbed solar energy, carbon nanoparticles effectively generate heat, causing a rise in temperature that leads to a decrease in the viscosity of the oil, thus facilitating the diffusion of the oil into the nanofibrous membrane. The newly developed CDs/PLA membrane demonstrated efficient oil adsorption and regeneration capabilities through multiple uptake/release cycles. Additionally, the environmental impact (ISO 14040 and ISO 4044 standards) and the eco-compatibility of this novel oil-adsorbent system were evaluated.

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MALTODEXTRIN-BASED ELECTROSPUN MAT AS ADSORBENTS FOR THE REMOVAL OF ATENOLOL AS EMERGING POLLUTANTS FROM WATER

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Abstract

In recent years, the anthropogenic water pollution has raised a great concern due to potential risks to aquatic ecosystems and human health. In this frame, the "emerging pollutants" are defined as synthetic or naturally occurring chemicals characterized by slow kinetics of biodegradation and resilience to the conventional water treatment processes which have the potential to enter water bodies and reservoirs causing undesirable effects on the environment or human health.

Pharmaceuticals are considered as emerging pollutants; among them, atenolol, a beta-blocking drug used for the treatment of cardiovascular diseases, hypertension, and arrhythmias, is frequently detected in different type of waste waters such as treatment plants, hospital waste, pharmaceutical industry effluents, and surface water. For this reason, its removal is of great importance.[1]

Electrospinning is a facile, cost effective, and flexible technique which allows the production of fibres at micron, sub-micron and nano-scale, from an electrically charged jet of polymer solutions. The development of this technique has now consolidated its role in the processing of a rich variety of polymers mostly for filtration, biosensors, drug delivery, tissue engineering, and wound dressings applications.[2]

In this work, membranes obtained from the electrospinning of water solutions of a commercial corn starch-derived maltodextrin (Glucidex 2®) mixed with citric acid were successfully obtained and thermally cross-linked post-processing, allowing their use as adsorbents in aqueous media.[3]

The membranes were subsequently screened for the removal of atenolol from water solutions in batch conditions, and the effect of different experimental parameters such as the amount of pollutant and adsorbent, pH, and the presence of other chemical species in solution was also studied.

Eventually, the possibility of using the spun mat in column adsorption tests, aiming for a potential industrial scale-up of the process, was evaluated.

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PEI-PCL COPOLYMERS AS NON-VIRAL NANOVECTORS FOR CANCER IMMUNOTHERAPY

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Abstract

One of the emerging therapeutic approaches for cancer treatment is immunotherapy, which requires an effective gene carrier to induce an immune system response against tumor cells. Compared to viral vectors used for gene delivery, non-viral vectors, such as cationic polymers, represent a promising alternative for their biocompatibility, low toxicity, and versatility through different synthetic strategies. As drowbacks, their clinical application is still limited due to low transfection efficiency and poor gene expression.[1]

Polyethyleneimine (PEI) is a synthetic cationic polymer proposed for non-viral vector; due to its very high density of amine groups, it is able to form stable polyplexes with DNA and protect it from degradation within the cellular environment. Unfortunately, its high charge density also results in a high cytotoxicity, so various approaches have been attempted to reduce PEI toxicity.

In this work, copolymers of branched PEI (25 kDa) and polycaprolactone (PCL, 4 kDa) at different PEI-PCL ratios have been synthesized (Fig.1). The insertion of PCL blocks should reduce PEI cytotoxicity and impart self-assembling properties.[2] The copolymers were characterized by NMR and FT-IR/ATR spectroscopy and GPC chromatography.

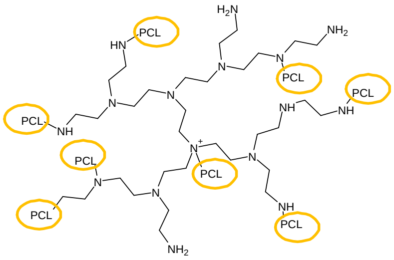

Fig.1: general structure of synthesized PEI-PCL polymers

PEI-PCL nanoparticles (NPs) were prepared though nanoprecipitation technique and their physical properties, such as size, superficial charge and stability were analyzed through Dynamic Light Scattering (DLS). The *in vitro* cytotoxicity was evaluated by MTT assay on human dermal fibroblast (HDM) cells, proving the potential application of the NPs as carriers. The ability of NPs to complex the DNA was investigated by using pSLCAR-CD19-28z as plasmid model, varying the NPs-pDNA ratio and confirmed by agarose gel electrophoresis. Further studies will focus on *in vitro* evaluation of NPs-pDNA polyplexes features, such as stability in different media, cellular uptake and transfection efficacy.

Acknowledgments:

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This work has been partly funded by a grant from the Italian Ministry of Foreign Affairs and International Cooperation (MAECI), in the frame of the NANOARBO project.

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