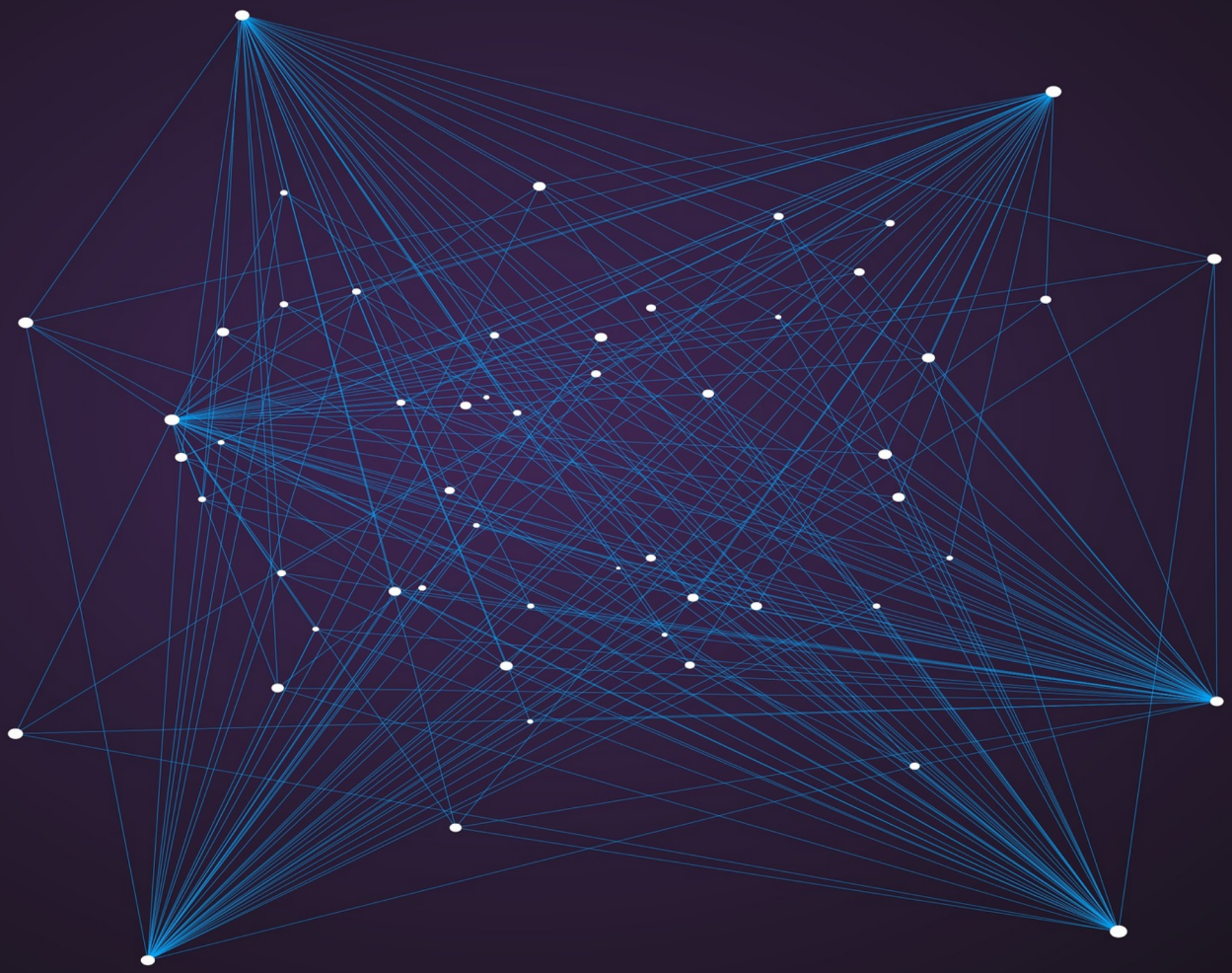

MACROGIOVANI - Digital Edition

June 26th, 2020 on **Microsoft Teams**

A digital meeting for young scientists engaged in the study of macromolecular science and technology

Organized by:

Comitato Scientifico e Organizzatore

Paola Lova – Università di Genova

Andrea Dodero – Università di Genova

Valentina Marturano – Istituto per i Polimeri, Compositi e Biomateriali, CNR

Martina Ussia – Istituto per la microelettronica e microsistemi, CNR

Rocco Di Girolamo – Università di Napoli Federico II

Martina Salzano del Luna – Università di Napoli Federico II

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June 26th, 2020, Microsoft Teams

8:45 - Welcome

	Postdocs	
9:00	Stefano Alberti	PDMS polymeric membrane loaded with TiO_2 NPs with antibacterial properties
9:10	Annalisa Apicella	An innovative route for the valorization of olive industry by-products in antioxidant bio-coatings
9:20	Massimo C. D'Alterio	Stereoselective lactide polymerization: the challenge of chiral catalyst recognition
9:30	Giulia Fredi	Effect of phase change microcapsules on the thermo-mechanical, fracture and heat storage properties of unidirectional carbon/epoxy laminates
9:40	Paolo Giusto	Polymeric carbon nitride thin films: not only photocatalysis
9:50	Anna Liguori	Environmentally friendly approaches for the crosslinking of gelatin electrospun nanofibers
10:00	Angela Marotta	Furan-based bio-epoxy resins and nanocomposites as tinplate coatings
10:10	Alberto Rubin Pedrazzo	Solvent free mechanochemical synthesis of cyclodextrin crosslinked polymers
10:20	Francesco De Bon	Under pressure: electrochemically mediated ATRP of vinyl chloride
10.30-10.50	***Break***	
	Undergraduates & Research fellows	
10:50	Andrea Escher	Use of nanoparticles for morphological control of blends of polyethylene and polypropylene
11:00	Vittoria Ferrara	New Zn(II) complexes with guanidinate ligands as catalysts for the ring opening polymerization of cyclic esters
11:10	Elisa Piccoli	Stretchable strain sensors: characterization of their electromechanical behaviour
11:20	Edoardo Podda	Synthesis and characterization of self-healing hydrogels by micellar polymerization
11:30	Christian Tavella	Synthesis of optical active sulfur-based polymers *via* inverse vulcanization for DBRs fabrication

11.40-12.00	***Break***	
	PhD Students (I year)	
12:00	Andrea Costanzo	Residual alignment and its effect on weld strength in material-extrusion 3D-printing of polylactic acid
12:10	Antonietta Cozzolino	Nanoporous-crystalline polymers for air and water purification
12:20	Viktoria Ilieva	Biodegradable bioplastics: biodegradation study and analysis of the degradation products
12:30	Heba Megahd	Polymer fluorescent films for label-free detection of organic vapors
12:40	Caterina Sanna	Electrospun $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ nanofibers for application in IT-SOFC
12:50	Federica Santulli	Switching between linear and cyclic polylactides with mono or bimetallic zinc complexes
13:00	Libera Vitiello	Thermoplastic laminates: the importance of process parameters
13:10-13:30	***Break***	
	PhD Students (II year)	
13:30	Tiziana Bardelli	Effect of curing thermal history on the mechanical properties of Sylgard 184
13:40	Enrico Carmeli	Continuous cooling curves of polyethylene/isotactic-polypropylene blends
13:50	Raffaella Ferraioli	Valorization of post-consumer plastic waste with environmental friendly additives
14:00	Giulia Gaggero	A rheological evaluation of sodium alginate as thickener for waterborne paints: a focus on the application process
14:10	Bruno Grandinetti	Stimuli-responsive liquid crystalline polymers towards the development of artificial muscles
14:20	Shiva Khoshtinat	Humidity responsive smart textile: from nature to application
14.30-15.00	***Break***	
15:00	Parnian Kianfar	Electrospinning and photo-crosslinking of PEO-based nanofibrous membranes
15:10	Giorgia Pagnotta	Photo-crosslinkable methacrylated alginate hydrogels as natural 3D bioprintable inks with tunable stiffness
15:20	Gaia Urciuoli	Melt- and solid-state behavior of ethylene-based multiblock copolymers

15:30	Francesco Valentini	Production and characterization of EPDM rubber foams obtained through salt leaching
15:40	Gianluca Viscusi	Fabrication of green composites from natural pectins and hemp fibers as novel carriers of green pesticides for agricultural applications
15.50-16.20	***Break***	
	PhD Students (III year)	
16:20	Andrea Dodero	Polysaccharide-based electrospun membranes for wound healing applications
16:30	Stefania Boi	Microchambers arrays for cargo protection and controlled release
16:40	Cosimo Brondi	Influence of air bubbles loading on the reaction kinetics of rigid polyurethane foams
16:50	Elisabetta Brunengo	A smart approach to modify PVDF polymorphism and properties
17:00	Riccardo Chiarcos	Monodisperse polypeptoids in silicon doping applications
17:10	Chiara Gallo	Development and applications of controlled-release materials for the conservation and protection of cultural heritage
17:20	Gustavo Gonzalez	Development of novel photopolymers for the fabrication of microfluidic devices through light-based 3D printing
17:30	Irene Nepita	Fluid dynamic assessment of ultrasound and guillotine vitrectomy probes
17:40	Arianna Pietrosanto	Production and characterization of ecosustainable blown shrink films
17.50-18.15	***Break***	
18:15	**Awards ceremony and greetings**	

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PDMS POLYMERIC MEMBRANE LOADED WITH TIO_2 NPs WITH ANTIBACTERIAL PROPERTIES

STEFANO ALBERTI[1], ANDREA DODERO[1], SILVIA VICINI[1], MAILA CASTELLANO[1], VALENTINA CARATTO[1], MAURIZIO FERRETTI[1]

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Abstract

Antimicrobial multidrug resistance has nowadays become a serious threat for humans' and animals' health and the spread of emerging pollutants (pharmaceuticals and personal care products) results to be the main cause [1]. These pollutants have become ubiquitous because of their use and abuse; the result is a continuative replenishment in the environment which led to their persistent presence in waters and soils. Bacteria have developed antibiotic resistance, which represents an extreme hazard for patients undergoing cures in intensive care units, for the risks of several complications due to the rapid colonization of biofilm-forming pathogens, which are responsible for sustained inflammatory processes by the adhesion to surfaces of man-mad biomaterial. The aim of this work is to study a composite material, prepared by electrospinning technique, which is made up by polydimethylsiloxane, "PDMS", and TiO_2 nanoparticles. PDMS is a highly hydrophobic, mechanically and thermally stable polymer whose features are attributable to its Si-O bonds, which can resist to TiO_2 photo-activity with respect to average carbon-based polymers.
PDMS hydroxyl terminated prepolymers, with two different molecular weights and therefore viscosities (20.000 e 50.000 cSt); TEOS (tetraethyl orthosilicate) as multifunctional cross-linking agent; THF as solvent and HNO_3 for hydrolysis reactions, were used to obtain the polymeric solution. The electrospinning process guarantees a fibrous structure with microscale dimensions. In order to obtain the cross-linked PDMS membranes coupled with TiO_2, a Sn-based catalyst was used. Amorphous TiO_2 NPs were synthesized through a sol-gel synthesis, using titanium tetraisopropoxide, 2-propanol and water (1:35:5, V/V). The coupling was performed by means of dip-coating technique, submerging the membrane's pieces into the amorphous TiO_2 gel and eventually heat-treating the composite to stabilize the adhesion and crystallize TiO_2. This composite appears as a white soft sheet and combines the high adsorbent capacity (with electrostatic features) and the macroscopic handling of the membrane with the photocatalytic antibacterial features of TiO_2 which can be activated by an indoor neon light source [2].
For the present work, several synthetic conditions were investigated in order to be reproducible and scalable, varying the PDMS prepolymers ratio, the temperature and the time of the polymer synthesis and the electrospinning conditions (voltage, flow, distance from the electrodes). The synthesized samples were characterized by means of rheological measurements and FE-SEM while the antibacterial activity was evaluated on the abatement of some controlled E. Coli cultures. This material can be employed in a wide range of fields: it can be applied to many surfaces, it is easily activated under artificial light (without specific UV lamps requirements) and it can be detached without difficulties; furthermore, the composite is recyclable and TiO_2 activity is not limited for the support's high surface area.
This project is co-financed by Por FSE Regione Liguria 2014-2020 Operating Program, code RLOF18ASSRIC/32/1.

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MACROGIOVANI- Digital Edition
26TH June 2020

AN INNOVATIVE ROUTE FOR THE VALORIZATION OF OLIVE INDUSTRY BY-PRODUCTS IN ANTIOXIDANT BIO-COATINGS

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Abstract

Oxidative phenomena are among the most important causes of food degradation, loss of precious nutrients and generation of toxic compounds. Synthetic antioxidants were widely used so far, but these molecules can accumulate in the human tissues, increasing the risk of toxicity to the consumer. An innovative approach concerns the use of natural antioxidants, such as plant and fruits extracts or essential oils, which can be successfully used in the production of active packaging.

In particular, the olive oil industry produces a large quantity of wastes and by-products, which are exceptional sources of phenols with strong antioxidant and O_2-scavenging activity. These phenolic-rich compounds are also very resistant to microbial degradation, generating phytotoxicity and pollution of the groundwaters: therefore, investigating new fields of applications to reuse these products is not only a way to restore their economic and commercial dignity, but also solves a burdensome problem of environmental impact.

These consideration inspired the aim of this research, which aimed at exploring new possibilities to develop eco-sustainable active films, through the valorization of natural antioxidant compounds deriving from olive industry wastes.

The first part of the research, carried out at the Fraunhofer Institute for Process Engineering and Packaging IVV (Germany), as also part of the EU Horizon2020 Project AgriMax- "Agri & food waste valorization co-ops based on flexible multi-feedstocks biorefinery processing technologies for new high added value applications", involved the extraction of polyphenolic antioxidants from olive pomace. The olive pomace extract (OPE) was thoroughly characterized, to evaluate chemical-physical properties, antioxidant and O2-scavenging potential, which provided basic knowledge for tailor-made packaging design. A second-order mathematical model was also applied to describe the oxidation-kinetics of the extract, underlining the potential of the model to predict quite accurately the O2-scavenging performance of a variety of polyphenols.

Then, the OPE (at 5% and 10% w/w) was used to realize active bio-coatings based on Whey Protein Isolate (WPI), spread on a PET substrate film. The produced films combined the environmental advantages deriving from the revaluation of food industry by-products, with the high technical performance offered by the PET film and the high barrier whey protein bio-coating.

The antioxidant activity of the films was evaluated by release tests in fatty foods simulant, and the diffusion kinetic was investigated, suggesting a suitable application of the films for long storage greasy foods. The films compliance to the migration limits established by the European Union Legislation was assessed by overall migration tests. Moreover, the OPE chemical interaction with the WPI matrix was investigated, as well as its effect on the adhesion, wetting, optical and barrier properties of the films. All active coatings showed very high transparency, satisfactory adhesion and tensile properties and excellent gas barrier performance. Films respected the overall migration limits established by the EU Legislation, and the release tests proved their ability to release the antioxidant agent within fatty foods simulant, with possibility to tune the release rate and time.

Outcomes suggest that the formulated bio-coatings can be considered an effective active packaging solution to protect foods from oxygen-induced quality loss, endorsing this route as a promising for the recovery of high-value compounds applied to competitive commercial solutions.

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STEREOSELECTIVE LACTIDE POLYMERIZATION: THE CHALLENGE OF CHIRAL CATALYST RECOGNITION

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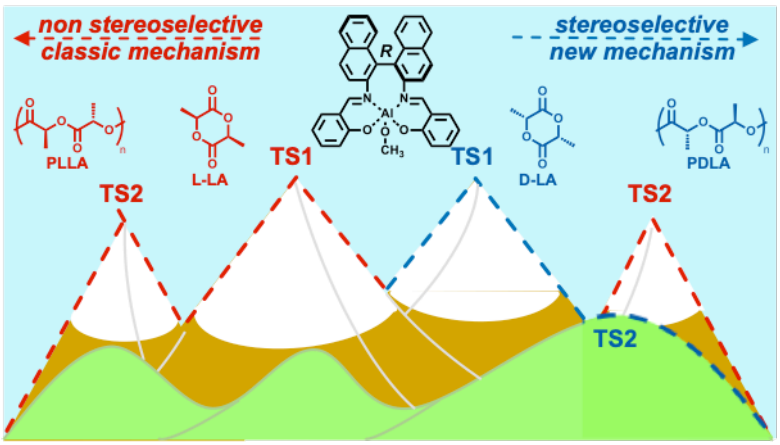
Abstract

A model for stereoselective ring opening polymerization (ROP) of rac-lactide promoted by chiral aluminum systems[1,2] is reported based on DFT calculations. The mechanism of enantiomorphic site control dictated by the chiral catalyst shows unusual features, including active site reorganization on the reaction path, which add complexity and need to be taken into account when addressing the challenge of chiral catalyst recognition. The ROP chiral control to discriminate D- and L-LA in the rac-mixture combines complexity (large number of mechanistic pathways) with novel mechanistic steps different from those of the classical ESM reported to date.



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EFFECT OF PHASE CHANGE MICROCAPSULES ON THE THERMO-MECHANICAL, FRACTURE AND HEAT STORAGE PROPERTIES OF UNIDIRECTIONAL CARBON/EPOXY LAMINATES

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Abstract

This work aims at developing and characterizing unidirectional carbon fiber/epoxy composites containing varying fractions of paraffin microcapsules (MC) for thermal energy storage (TES) and thermal management applications. Such lightweight multifunctional composites could be useful in all those applications where weight saving and temperature regulation are both important, such as the automotive and portable electronics fields [1].
Since the viscosity of the epoxy/MC mixtures increases with the MC content, the matrix flows out of the fiber fabric more slowly during processing, thereby increasing the final matrix weight and volume fraction, at the expense of that of the fibers. This is at the basis of the decrease in mechanical properties of the laminates with high MC concentration, but the application of theoretical models shows that this decrease is entirely due to the lower fiber volume fraction, and not to a decrease in the properties of the constituents.
The MC phase is preferentially distributed in the interlaminar zone, which leads to a thickening of this region and a decrease in matrix-related properties, such as the transverse strength and the interlaminar shear strength. However, a modest MC fraction causes an increase in the mode I interlaminar fracture toughness of up to 48 %, due to the introduction of new toughening mechanisms. On the other hand, an excessive MC content lets the crack propagating through the matrix and not at the fiber/matrix interface, thereby reducing the toughening mechanism provided by fiber bridging.
For the thermal properties, the phase change enthalpy increases with the MC fraction up to of 48.7 J/g, and this is reflected in better thermal management performance, as proven by thermal imaging tests.
This work also investigated the uncommon application of dynamic-mechanical analysis (DMA) to study a melting-crystallization transition and assessed the impact of such transition on the viscoelastic properties of the host composite. In this way, interesting correlations were found between DMA and DSC parameters.
These results are promising for the development of multifunctional polymer composites with thermal energy storage and thermal management properties, and future researches will be aimed at studying the micromechanical properties of PCM microcapsules and at improving of the capsule/matrix adhesion.

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POLYMERIC CARBON NITRIDE THIN FILMS: NOT ONLY PHOTOCATALYSIS

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Abstract

Carbon nitrides (CN) are a class of polymeric materials with ideal formula C_3N_4. The first report for this class of materials dates back in 1834 by Berzelius and Liebig and named "melon", thus being one of the oldest published synthetic polymers to date. Recently, CN materials have attracted much attention especially for photocatalysis with visible light. However, up to now their application in fields like optics and photonics were hindered due to the low quality thin films available. Herein, we present an innovative method to produce CN high quality thin films with tunable thickness from a single-source and commonly available precursor, the melamine, by means of chemical vapour deposition without constraints on the substrate shape.[1] Eventually, the as-prepared CN thin films are highly homogeneous over large areas and possess very high refractive index (n_D=2.43), even in the range of diamond (n_D=2.42), with high transparency in the visible range. Furthermore, the CN films present very intense blue fluorescence and long-living emission that can be tuned by doping with carbon, sulphur and other heteroatoms. This will pave the way for new application of CN materials beyond photocatalysis, in fields like optics and optoelectronics being also very hard and resistant to damage, with hardness of 2.2 GPa and Young's Modulus of 36.5 GPa, significantly higher than those of other hard polymers like Kevlar and polyimides.
Besides the optical properties, CN thin films can be used as a platform for one-step light-induced graftin-from of vynil polymer brushes, allowing to control the surface properties by growing different polymer brushes. By different polymerization time, the vynil polymer thickness can be controlled from few to several hundreds of nanometers. The growth of such thick and dense polymer brushes is exceptional and points to a quasi-living mechanism with low radical recombination. Eventually, the as-grown polystyrene brushes show photoswitchable wettability under UV illumination, which, to the best of our knowledge, is herein shown for the first time. Eventually, the proposed method allows also to grow large area Janus surfaces by photo-grafting-from hydrophilic and hydrophobic polymer brushes on the two surfaces of a free-standing CN film. Introducing simple methods to engineer surface wettability of CN thin films will set the base for tailoring surface properties of great interest for microfluidics, smart devices and lab-on-a-chip.

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ENVIRONMENTALLY FRIENDLY APPROACHES FOR THE CROSSLINKING OF GELATIN ELECTROSPUN NANOFIBERS

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Abstract

Gelatin is a natural polymer obtained from the thermal denaturation or chemical degradation of collagen. These processes involve the loss of the collagen triple-helix structure and the formation of gelatin random coil structure. Gelatin macromolecules can rearrange, under certain conditions, forming again sequences of the triple helix, even if the fibrillar collagen structure cannot be recovered and the material becomes soluble in an aqueous environment. Showing binding sites for cell adhesion, signaling and differentiation, gelatin can be employed in tissue engineering, wound dressing and drug delivery. In these sectors, electrospun nanofibrous mats, having high porosity and specific surface area, are demanded since they mimic the extracellular matrix and promote cell adhesion and proliferation. Due to the water solubility of the polymer, gelatin nanofibrous mats do not maintain their morphology when they come in contact with water. To solve this issue, several approaches have been set up for the crosslinking of gelatin, involving both physical and chemical methods. However, the so far tested physical methods turned out to be ineffective and the most common crosslinking agents often give rise to cytotoxicity problems. In this presentation, two alternative methods for the crosslinking of electrospun gelatin fibers are proposed. The first approach is a physical, environmentally friendly method based on the use of cold atmospheric pressure plasma to crosslink gelatin electrospun mats directly in the solid state [1]. The method was successfully applied to induce crosslinking both in pure gelatin and genipin-containing gelatin electrospun nanofibers, the latter requiring a shorter plasma exposure time. Plasma treatment turned out to trigger crosslinking reactions, as confirmed by the decrease of the deformation at break, as well as by the structural and morphological stability of electrospun mats once soaked in aqueous solution. These effects are ascribable to an increase of the crosslinked ε-amino groups as well as to chemical/physical mechanisms not involving the gelatin free amino groups [1]. The second approach for gelatin crosslinking is a green strategy that makes use of citric acid [2]. Citric acid is a natural acid already employed for the crosslinking of proteins: the carboxylic groups of citric acid can undergo nucleophilic acyl substitution with the ε-amines of lysine, leading to the formation of stable amide bonds. The process was aimed at the obtainment of crosslinked mats by electrospinning a gelatin aqueous solution containing citric acid. Results showed that an increase of the pH of the solution from 1.8 to 3.7 allowed for obtaining fibres that maintained their morphology. A subsequent thermal treatment of the electrospun mat contributes to increase the stability [2]. The obtained materials were characterized by means of SEM, ATR-FTIR, X-ray diffraction and stress-strain analysis; the crosslinking extent was measured by means of a UV assay through determination of uncrosslinked ε-amino groups.

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FURAN-BASED BIO-EPOXY RESINS AND NANOCOMPOSITES AS TINPLATE COATINGS

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Abstract

Thanks to their good properties of mechanical strength, chemical resistance and good adhesion to several substrates, epoxy resins perfectly fit for coating applications. However, the quite majority of epoxy resins are nowadays made by DGEBA, the diglycidyl ether of BPA, which has been banned in the production of materials in contact with food. Therefore, the development of new platform chemicals from renewable resources for the synthesis of bio-based, low environmental impact epoxy resins for can coatings applications is of main interest nowadays.
To achieve the required properties of mechanical and chemical resistance, aromatic epoxy resins are needed; for this reason in the present work a furanic bio-derived molecule was selected as platform molecules. Bio-based epoxy resin based on 2,5-bis[(oxiran-2-ylmethoxy)methyl]furan (BOMF) cured with methyl nadic anhydride (MNA), and its nanocomposites obtained by the addition of titanium dioxide nanoparticles were prepared and tested as tinplate coatings. First, the properties of bulk resins were tested, then coating layers were obtained on a tinplate substrate, previously treated to improve the adhesion.
The effect of addition of titanium dioxide nanoparticles on thermal and rheological properties of coating was studied. Moreover morphology, chemical resistance and pencil hardness of coatings were analysed. Cure kinetic, as proved by calorimetric analysis, and rheological properties were conditioned by the presence of titanium dioxide. Uniform morphology was obtained regardless of presence of filler nanoparticles. Excellent chemical resistance to polar solvent and good chemical resistance to acid solution was guaranteed. Moreover, their chemical resistance is improved by the addition of the filler. Resins showed excellent values of pencil hardness.
The obtained result indicated that BOMF-based resins and nanocomposite coatings had properties comparable with those of DGEBA-based systems and thus can be proposed as a good alternative material for metal can coating industry.

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Solvent Free Mechanochemical Synthesis of Cyclodextrin Crosslinked Polymers

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Abstract

Cyclodextrin nanosponges (CD-NS) are cross-linked cyclodextrin polymers characterized by a nanostructured three-dimensional network. CDs act as polyfunctional monomers thanks to the reactive hydroxyl groups, permitting to crosslinking bi or multifunctional chemicals [1]. The "classic" NSs synthetic pathway involves the solubilization of the CD in closed batch, using a usually suitable organic polar aprotic liquid, that may affect a potential environmental or biomedical application.
Since nowadays research is moving towards more sustainable and green approaches, new syntheses of CD-NS are now being developed.
We are here reporting a new green synthesis of nanosponges through a mechanochemical approach. Mechanochemistry involves the application of mechanical forces to drive and control chemical reactions by transferring energy to chemical bonds. Mechanochemistry applied to inorganic chemistry is well established, but in recent years there has been a growing interest in mechanochemistry applied to organic synthesis: esterification and etherification of starch and the possibility of obtaining CD derivatives with a solid state reaction using ball milling, have been reported recently [2]. The green synthetic route here proposed permits to obtain a cross-linked polymer, exhibiting the same characteristics as CD-NS synthesized in batch, without using any solvent. CD-based carbonate NSs, traditionally synthetized in DMF, which is a toxic and suspected carcinogenic solvent, were synthesized using 1,1-carbonyldiimidazole as a crosslinker.
After the synthesis, moreover, a significant amount of imidazolyl carbonyl groups still able to react was detected within the NS structure. These reactive groups permitted to obtain a covalent bond between the already synthesized cyclodextrin nanosponges and various organic dyes, with different structures (Methyl Red, Rhodamine B and Fluorescein). The possibility to easily mark with fluorophores CDs and consequently CD-Nanosponges, could open many applications in the pharmacological area, image guided therapies or conjugated drug delivery.

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UNDER PRESSURE: ELECTROCHEMICALLY MEDIATED ATRP OF VINYL CHLORIDE

FRANCESCO DE BON[1,2], ABDIRISAK A. ISSE[2], ARMANDO GENNARO[2], ARMENIO C. SERRA[2] AND JORGE F. J. COELHO[1]

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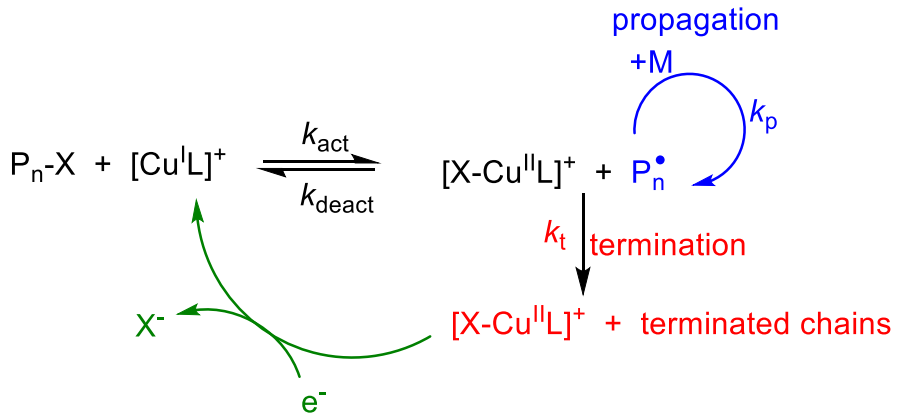
RTDa

Abstract

Polymerization of non-activated monomers, as vinyl chloride, remains one of the major challenges for reversible deactivation radical polymerizations (RDRP), including Atom Transfer Radical Polymerization (ATRP) [1]. Electrochemically mediated ATRP (*e*ATRP) of a gaseous monomer, vinyl chloride, was successfully achieved for the first time in a SS304 reactor using a simplified setup, with an aluminum sacrificial anode and a Pt cathode; the body of the reactor could be used as cathode as well. The control over the polymerization was confirmed by the good agreement of theoretical and measured molecular weight, as well as the relatively narrow molecular weight distributions. Preservation of chain-end fidelity, as confirmed by chain extensions, allowed the synthesis of poly(vinyl chloride) (co)polymers with different topologies: statistical, block fashion, and even stars, where *e*ATRP outperformed SARA ATRP. The possibility of synthesizing poly(vinyl chloride) by *e*ATRP, without any metallic copper excludes SET-LRP mechanism. Considering the importance of PVC in health applications and the problem of metal contamination of final products *e*ATRP could be an alternative way to get cleaner PVC copolymers and the overall simplified setup may be a starting point to polymerize other gaseous monomers.



Mechanism of Cu-catalyzed ATRP with regeneration of the activator complex by external electrochemical control.

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USE OF NANOPARTICLES FOR MORPHOLOGICAL CONTROL OF BLENDS OF POLYETHYLENE AND POLYPROPYLENE

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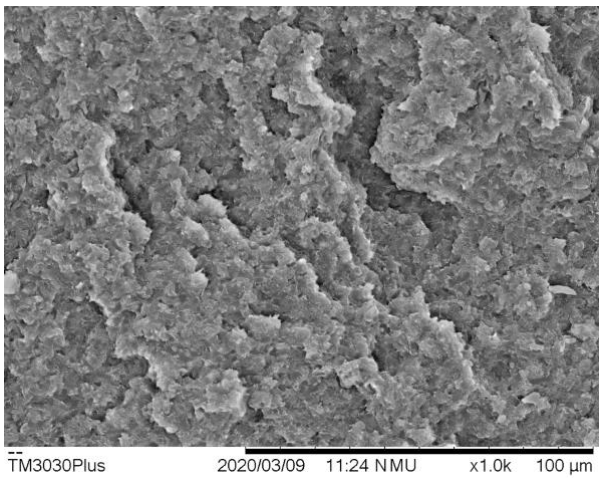
Abstract

My master thesis was carried jointly at the Department of Chemistry and Industrial Chemistry of the University of Genoa and the Department of Chemistry of the University of the Basque Country in San Sebastian.
The work focused on the preparation of blends with immiscible neat and functionalized polyolefins: Polypropylene and Polyethylene. The mechanical blending was operated with different mixers (Brabender, micro-extruder).
Part of the thesis aimed to the compatibilization of these polymers using nanofillers (nano-clay or silica nanoparticles) and polymer functionalized with maleic anhydride.
The assessment of the effective compatibilization were performed with contact angle tests, differential scanning calorimetry and thermogravimetric analysis (DSC, TGA) transmission and scanning electron microscopy (SEM figure:1 and TEM figure:2) were also employed to evaluate the morphology and composition of the blends. The stability of the new composites was also characterized by Large Amplitude Oscillatory Shear and Dynamic Mechanical Thermal Analysis (LAOS and DMTA).



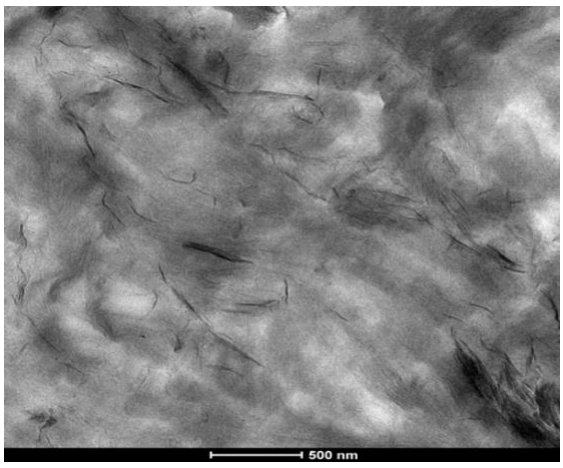


Figure 1 – 2: SEM and TEM image of PE-PEMAH/PP-PPMAH + A20 [70/30 → 10/10 3%A20]

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NEW ZN(II) COMPLEXES WITH GUANIDINATE LIGANDS AS CATALYSTS FOR THE RING OPENING POLYMERIZATION OF CYCLIC ESTERS.

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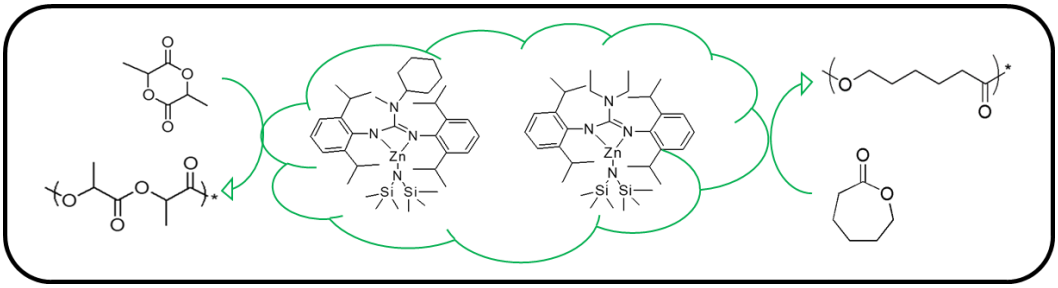
Master's Degree

Abstract

The global concern for the environmental issues, the exhaustion of fossil fuels and the unstable prices of crude oil have pushed scientific research towards the study of biocompatible and/or biodegradable polymers as an attractive alternative to conventional polyolefins.
In particular, aliphatic polyesters, such as poly (ε-caprolactone) (PCL) and poly (lactide) (PLA), because of their excellent physical and mechanical properties, have recently gained considerable attention as an environmentally friendly class of polymeric materials.[1]
Among the different synthetic methods suitable for the production of polyesters, the ring-opening polymerization (ROP) of the related cyclic esters, promoted by metal complexes is the most effective way to obtain polymers with controlled microstructure and narrow distributions of molecular weights.
Specifically, single-site homogeneous metal catalysts of the type LnM-X, are among the most active in the homopolymerization of cyclic esters.
In recent years, Coates and his collaborators have published numerous works on zinc complexes with β-diiminate ligands, highly active catalysts for the synthesis of poly (lactic acid).[2]
Considering the high efficiency of these catalysts, we report the synthesis and structural characterization of zinc complexes supported by guanidinate ligands and their application as initiators for the polymerization of cyclic esters.



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STRETCHABLE STRAIN SENSORS: CHARACTERIZATION OF THEIR ELECTROMECHANICAL BEHAVIOUR

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Abstract

Nowadays the technological progress in different fields, such as soft robotics and bioengineering, causes a growing demand of highly stretchable strain sensors. They respond to mechanical deformation by the change of electrical characteristics such as resistance or capacitance. Many requirements are needed to make high-performance strain sensors including: sensitivity, deformability, response speed, stability, fabrication cost, and simplicity. [1].
This work is part of the project ASSIST, that has the final aim of creating a stretchable strain sensor as component of a valve for biomedical applications. This sensor is made by a membrane of polysiloxane on which a gold layer of few hundreds of nanometres is implanted through the Supersonic Cluster Beam Implantation (SCBI) technique (Cimaina laboratory of Physics Department at University of Milan [2]).
In particular, this work is focused on the mechanical characterization and modelling of the polysiloxane substrate. At first, the Dow Corning polydimethylsiloxane (PDMS) Sylgard 184, one of the most used PDMS in soft robotics, was studied. It consists of two components (a pre-polymer and a curing agent) which are mixed to give rise to a crosslinked elastomer. As mentioned in literature [3,4], the properties of the resulting material depend on the process conditions. So, it was performed a Design of Experiments (DOE) considering the simultaneous changing of some production conditions such as: time, temperature of curing and, as suggested by the study of Liu et al. [5], the thickness of the final sheet. An optimal combination of production conditions was selected. The material thus obtained was characterized performing test under uniaxial and pure shear loading conditions. The experimental data were used to select the proper material constitutive model for numerical simulations. The Ogden's model (3^{rd} order strain energy potential) resulted to better fit of the material behaviour. It was validated with an equi-biaxial tensile test and the mechanical response of the sensor membrane inside the valve. A similar characterization was also performed on a biocompatible commercial silicone, supplied by Guarnizioni Industriali as 0.5 mm thick sheets (product code SIL540080T).
Both silicones were implanted with gold via SCBI technique.
Some promising preliminary cyclic tensile were performed, during which the deformation and the electrical resistance were correlated. More suitable resistance measurements for the valve application were for the SIL540080T. The latter is considered for further investigations both for the numerical modelling and the prototyping of a highly stretchable strain sensor.

Acknowledgements This work has been supported by Fondazione CARIPLO and Regione Lombarida under project ASSIST (2018-1726), under the Program 'Call to support the knowledge transfer in advanced materials research".

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SYNTHESIS AND CHARACTERIZATION OF SELF HEALING HYDROGELS BY MICELLAR POLYMERIZATION

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Abstract

Hydrogels are three-dimensional network of polymers, which have the capability to absorb a large amount of water or biological fluids. These materials consist of hydrophilic crosslinked polymer chain, which are able to swell, having a soft rubbery consistency similar to living tissues. For this reason, hydrogels are used for biomedical, biotechnology and pharmaceutical applications[1,2]. The nature of the used crosslinker divides hydrogels in two large families namely physical or chemical crosslinked. In chemical hydrogel, crosslinking is obtained by covalent bond, either during the polymerization or in a post polymerizzazion process[3]. Physical hydrogels are obtained using physical interaction such as hydrophobic association, ionic bond or hydrogen bond.
In this work we prepared physically crosslinked hydrogels by radical micellar polymerization. This type of polymerization involved the use of a hydrophilic monomer (Acrylamide), a hydrophobic monomer (Octadecylacrylate), a surfactant (Sodium dodecyl sulfate), and a salt (NaCl). The polymerization was initiated using a redox initiator system composed of ammonium persulfate and sodium metabisulfite. In addition, a multifunctional monomer, divinylbenzene, was used with the aim of creating branched chains to evaluate their effect on the characteristics of the materials. Three series of five samples were prepared by varying, within the series, the quantity of Octadecylacrylate (C18A), and, between the series, the quantity of Divinylbenzene (DVB).
The samples were characterized with thermal (DSC) and rheological analysis, both before and after the washing phase. As the concentration of C18A increases, the amount of water present at equilibrium within the hydrogels decreases. In addition, the melting and crystallization enthalpies increases and an increase is also seen in mechanical modulus G '.
On the other hand, as the DVB concentration increases, the water content decreases and the mechanical modulus increases. This phenomenon is probably caused by the formation of chemical cross-linking points within the polymer network. The self annealing behaviour of these materials was also demonstrated by several rheology measurements.

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Synthesis of Optical Active Sulfur-Based Polymers *via* Inverse Vulcanization for DBRs Fabrication

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Abstract

Elemental Sulfur is an abundant by-product of gas and oil industry –that is an inexpensive resource– which recently was demonstrated to be easily converted into innovative polymeric materials with unique functional properties through a simple, solvent-free process called inverse vulcanization (IV). Indeed, IV process proceeds via a free radical mechanism allowing to copolymerize an excess of molten elemental Sulfur (from 50 up to 90 wt%) with minor amounts of small-molecule comonomers bearing reactive vinyl, alkenyl or ethynyl groups to achieve Sulfur-hydrocarbon random copolymers. IV has attracted a great deal of attention because these novel polymeric materials named inverse vulcanized polymers (IVPs) possess intriguing optical properties, such as very high refractive index (n≈1.8) and excellent transparency in the NIR spectral region [1,2].
In this work, new IVPs having noticebly high refractive index (n=1.83) were achieved by copolymerization of elemental Sulfur with 2,5-diisopropenylthiophene (DIT) comonomer and then used in the fabrication by spin-coating of all-polymer distributed Bragg reflectors (DBRs) [3]. DIT molecule, to the best of our knowledge never synthesized before, was obtained by Suzuki-Miyaura Cross-Coupling Reaction (SMCCR) from 2,5-dibromothiophene (Fig.1). DIT comonomer was purposely designed [4] to: (i) enhance the refractive index of the ensuing IVP due to the high electron density of the thiophene ring, (ii) favour the IV process due to the higher reactivity of isopropenyl moieties with respect to vinyl functionalities.

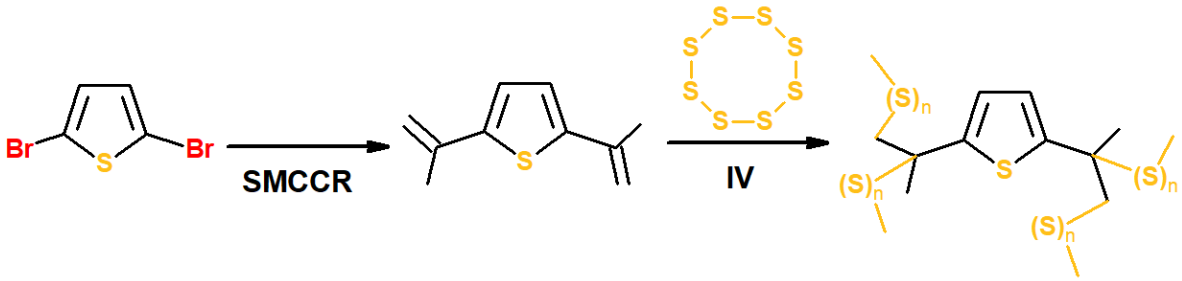

Figure 1. Schematic structure of the synthesized IVP.

Acknowledgment: Compagnia di San Paolo (Turin, Italy) for funding Project "PIVOT - Sulfur-based Polymers from Inverse Vulcanization as high refractive index materials for planar photonic crystals: dielectric mirrors and microcavities" (IDROL 20583). Dr. M. Marsotto and M. Patrini for contribution to polymer characterization.

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Residual alignment and its effect on weld strength in material-extrusion 3D-printing of polylactic acid

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Dottorando 1° Anno

Abstract

Gaining a molecular understanding of material extrusion (MatEx) 3D printing is crucial to predicting and controlling part properties[1]. Here we report the direct observation of distinct birefringence localised to the weld regions between the printed filaments, indicating the presence of molecular orientation that is absent from the bulk of the filament. The value of birefringence at the weld increases at higher prints speeds and lower nozzle temperatures, and is found to be detrimental to the weld strength measured by tensile testing perpendicular to the print direction. We employ a molecularly-aware non-isothermal model of the MatEx flow and cooling process to predict the degree of alignment trapped in the weld at the glass transition. We find that the predicted residual alignment factor, A, is linearly related to the extent of birefringence, Δn. Thus, by combining experiments and molecular modelling, we show that weld strength is not limited by inter-diffusion, as commonly expected, but instead by the configuration of the entangled polymer network [2]. We adapt the classic molecular interpretation of glassy polymer fracture to explain how the measured weld strength decreases with increasing print speed and decreasing nozzle temperature [3].

Keywords: Material Extrusion, Birefringence, Molecular Orientation, Weld Strength, Polylactic acid

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NANOPOROUS-CRYSTALLINE POLYMERS FOR AIR AND WATER PURIFICATION

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Abstract

Nanoporous materials are mainly constituted by amorphous or crystalline inorganic networks such as silica[1] or zeolites[2] but the use of nanoporous organic polymers often adds relevant advantages of robustness, low cost, durability, and in some cases easy processing to suitable products (e.g. films, fibers, foams, aerogels, etc). In particular, fully thermoplastic nanoporous organic polymers, which are suitable for standard industrial melt and solution processing, are based on nanoporous-crystalline phases exhibiting a density lower than the corresponding amorphous phases. Presently NC phases have been found only for two industrially relevant polymers: syndiotactic polystyrene (s-PS)[3] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO).[4] Nanoporous-crystalline (NC) forms can be obtained generally by removal of low-molecular-mass guest molecules from corresponding host-guest co-crystalline (CC) forms.

These NC polymers are able to absorb volatile organic compounds (VOCs) also when present in traces in air or in water and, for low guest activities, guest sorption occurs prevailingly by the NC phases.[5] However, NC PPO films exhibit guest diffusivities much higher with respect to NC s-PS films, comparable with those of NC powders and not far from those of NC aerogels. Particularly high guest diffusivities are observed for PPO films with orientation of the chain axes of their NC phases being preferentially perpendicular to the film plane (c⊥ orientation).

In this communication, we compare sorption kinetics of a same guest molecule, that is perchloroethylene (PCE) a common pollutant,[6] in NC PPO and s-PS samples exhibiting different morphologies (powders, aerogels and films). We also investigate guest diffusivities in NC PPO films showing two different kinds of orientation, with crystalline chain axes preferentially parallel (c//) or perpendicular (c⊥) respect to the film plane.

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BIODEGRADABLE BIOPLASTICS: BIODEGRADATION STUDY AND ANALYSIS OF THE DEGRADATION PRODUCTS

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Polymers, the so-called plastics, are considered one of the most used materials in everyday life. Their production has reached the quotes of 348 Mt per year worldwide, of which over 64 Mt in Europe, and this turns out to be growing in the next future. In recent years, the production, use and disposal of packaging and other "short-term" uses plastics, and the resulting impact on the environment, have become a major focus worldwide. Besides a sustainable consumption and use as well as improved recycling and waste management, the development of biodegradable polymers has become a suitable alternative and a promising option to commodity plastics.[1] The bioplastic innovation seems to be a key solution to plastic pollution. However their growing diffusion is not entirely without unknowns. The current procedures and processes for handling waste are not best suited to managing bioplastics, which are supposed to mineralize into water, carbon dioxide, and biomass once they end up in the environment.[2]

Most of the plastics labelled as biodegradable generally degrade under specific conditions that may not always be easy to find in the natural environment, or in composting plants conditions. The most studied biodegradable polymers are polysaccharides or aliphatic and mixed aliphatic/aromatic polyesters. Recent studies focus on the key factors affecting materials degradation rate and the effect of the degradation on the structural properties[3,4] and less on the identification of degradation products released and their effect on environment[5,6]. Therefore, to provide a sustainable alternative, it is crucial to understand the degradation mechanism in environmental conditions, which depends on the chemical structure, on different abiotic and biotic factors, on the content of additives and the potential effect of degradation products.

Here, the identity of the degradation products formed from the biodegradation of biodegradable polybutylene succinate (PBS) was investigated using a liquid chromatography (HPLC-RI) system. Firstly, a primary solid screening was carried out to select fungal strains capable of growing in the presence of PBS as sole carbon source, in form of three-dimensional electrospun membranes and films of 40 μm thickness. The best representative fungus is a *Purpureocillium lilacinum*. His capability to metabolyze PBS was tested in acqueous media for 32 days, which was analysed for polymer degradation intermediates. During the degradation, a significant growth of the fungal biomass has been observed. From the HPLC analysis just the 1,4-butanediol was detected. Interestingly its concentration increases in the first 20 days, as hydrolysis proceeds, and then falls below the detection limit on the 32nd day of degradation. This leads to suppose that polimers degradation products are a suitable carbon source and there is not accumulation of oligomers and monomers in the degradation media.

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POLYMER FLUORESCENT FILMS FOR LABEL-FREE DETECTION OF ORGANIC VAPORS

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Dottorando 1° anno

Abstract

Human exposure to volatile organic compounds has been proven to cause a range of health complications,[1] thus, their detection is important, both in industrial or urban settings. Nevertheless, commonly used quantitative analysis used for their detection is cumbersome and so, simple and fast sensors are needed for environmental and industrial monitoring. Hence, we present an alternative portable and fast sensing system based on fluorescence-quenching in thin films for the detection of vapors of four volatile organic compounds: chloroform, dichloromethane, toluene and m-xylene.

Optical vapor sensors based on fluorescent thin films present multiple advantages including fast responses, portability and sensitivity that led them to be highly investigated.[2-5] However, the common occurrence of aggregation-induced photoemission quenching in the solid state limits the array of materials suitable for this application.[6, 7] The discovery of the ground-breaking aggregation induced emission (AIE) fluorophores has thus ushered an opportunity for many solid-state fluorescence-based applications.[8, 9] Borelli et al have presented the synthesis of styrene copolymers with 2-[4-vinyl(1,1'-biphenyl)-4'-yl]-cyanovinyljulolidine (JCBF) and demonstrated its potential for sensing volatile organic compounds.[10] This system has a promisingly fast response, but multiple vapors induce quite similar fluorescence variation in kinetics and magnitude, complicating the identification of different analytes. In this work we investigate the effect of a different polymer capping layer placed on top of the JCBF copolymer thin films as an additional selective mechanism. We demonstrate that modifying the diffusion barrier between the vapor and the fluorescent dye embedded in the polystyrene matrix yields a simple but effective mechanism of controlling the selectivity and speed of the sensing response of the system. Indeed, the diffusivity of a vapor analyte can be easily modified using polymer capping layers with different solubility in the analytes themselves.

This straightforward alteration provides a proof of concept for producing fast, affordable and portable sensors that can be tailored for specific applications. Furthermore, these systems can also be utilized for characterizing the diffusion properties in the capping layer.

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Electrospun $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ nanofibers for application in IT-SOFC

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Abstract

Intermediate temperature-solid oxide fuel cells (IT-SOFCs) are under development for operation in the temperature range 600-800°C. Reduction in working temperature is expected to mitigate degradation, reduce sealing problems, enable the use of inexpensive materials and improve response to rapid start-up. However, lowering the operating temperature also lowers the fuel cell performance, since the kinetics of the electrochemical reactions decrease exponentially as temperature decreases. In order to improve the catalytic performance at lower temperature, advanced materials and innovative architectures are intensively investigated [1]. Mixed ionic electronic conductors (MIECs) materials are under investigation due to their ability to carry simultaneously both electrons and oxygen ions. Among MIECs, perovskites, such as $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), and fluorites, such as $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC), are currently the most promising candidates [2]. In parallel, one dimensional (1-D) materials like nanotubes and nanofibers are gaining significance due to their high surface area and mechanical properties. Electrospinning is one of the best methods for large-scale preparation of nanofibers, since it is cost effective, simple and reproducible. The working principle of electrospinning is based on the electrostatic attraction, which is obtained by applying a voltage difference between the starting precursor solution, injected through a syringe, and the nanofibers collector. The process is sensitive to several solution and equipment parameters, The polymer concentration in the precursor solution is an essential parameter. If the polymer concertation is high there are more chain entanglements and the charged jet begins to be stabilized producing fiber-like structures. For low concentrations, the entanglement network is not so strong to stabilize the charged jet producing axisymmetric instabilities and generating drops and fibers with beads.
In the present work, we present the results of our research focused on SOC air electrodes manufactured through the electrospinning technique. Different electrode architectures are investigated: unbroken LSCF continuous ribbons-like nanofibers, disaggregated LSCF nanofibers and mixed LSCF/GDC nanofibers [2]. The morphological characterization is carried out through SEM images. The nanofibers diameter and the porosity of the tissue is investigated using the ImageJ software. Electrochemical characterization is performed through electrochemical impedance spectroscopy (EIS) in the temperature range 600-950°C and with oxygen partial pressure varying in the range 0.2. A correlation between the solution properties and the morphology and electrochemical performance of the electrode, is proposed as well.

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Switching between linear and cyclic polylactides with mono or bimetallic zinc complexes

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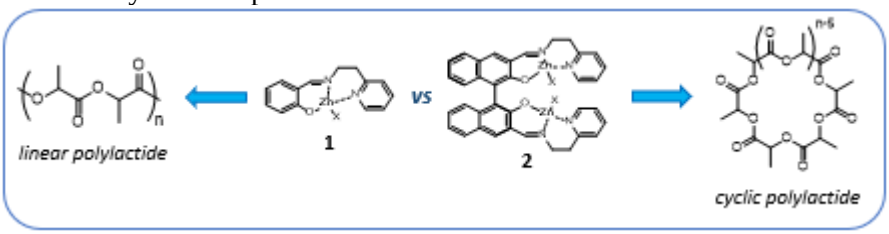
Abstract

Over the past 70 years, the production of synthetic polymers has increased exponentially and, in 2018, the plastics production almost reached 360 million tonnes.[1] Within this market, polyolefins still represent the largest segment, consistently amounting more than half of polymer production. Nevertheless, the durability of these materials and the linear economic model adopted resulted in one of the most severe worldwide environmental problem, i.e. plastic pollution.
During the last years, many efforts have been dedicated in developing biodegradable polymers as efficient and more sustainable alternatives to polyolefins.[2]
Among these, poly(lactic acid) (PLA) is the most commercially promising material because it combines good mechanical properties, biodegradability and biocompatibility, and it is obtained from annually renewable resources.
Different synthetic routes can be used to obtain PLA, such as metal-catalysed Ring Opening Polymerization (ROP) of cyclic esters.[3] This method allows to produce polymers with different chemical and physical characteristics depending on their microstructures but revealed to be scarcely efficient to control the topology of polymers. On the other hand, grafted, cross-linked, and cyclic polymers are attracting considerable interest due to their remarkable properties, such as the high glass transition temperature (T_g), the low melt viscosities and thermal stability.[4]
Among the different classes of metal catalysts, zinc (II) complexes remain an attractive choice because of cheapness and biocompatibility of the metal, while being able to combine high activity and selectivity in catalytic processes.
In this work mono- and bi-metallic zinc complexes with phenoxy-imine-pyrimidine ligands were synthesized and used in the polymerization of rac-lactide, showing different and specific behaviours and a marked selectivity toward specific structural motifs.



Indeed, linear polylactides are obtained with the monometallic complex **1** showing extremely high activity (TOF of 10560 h^{-1}) at room temperature, even in the presence of low catalyst loading and impurified monomer. Instead, the bimetallic complex **2** provides selectively cyclic polylactides, showing the highest activity and selectivity at room temperature.

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THERMOPLASTIC LAMINATES: THE IMPORTANCE OF PROCESS PARAMETERS

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Dottorando 1° anno

Abstract

The hot molding process of film-type thermoplastic composites is based on operator experiences. The use of new polymer matrices requires numerous attempts, often based on a trial-and-error approach, to identify the optimal processing parameters. In this study, a thorough study is performed to rationalize the choice of the hot-pressing conditions for realizing a laminated biocomposite constituted by polyamide 11 (PA11) reinforced with woven basalt fabrics. Rheological analyses of the matrix have shown that the PA11 is characterized by high viscosity which increases rapidly over time at high temperatures. This behavior makes the impregnation of the fabric complex during the hot molding process [1]. To solve the problem, two different procedures were considered: in the so-called “slow” process, low pressure, and long times were applied; in the “fast” process, higher pressures were reached rapidly while shortening the compaction times. Darcy's law, which models the flow of a fluid through a porous medium, has been used to describe the permeation of thermoplastic polymers into reinforcing fabrics [2]. Compared to the "slow" process, the "fast" process increases the apparent velocity of the penetrating fluid described by Darcy's law. SEM analysis showed that the matrix penetrates the pores and channels of the fabric more efficiently when subjected to high pressures and short process times. The mechanical properties of the laminates have been improved by better impregnation. The flexural modulus and strength showed an increase of 74% and 81% respectively, passing from the "slow" to the "fast" procedure. The preliminary results obtained demonstrate that the study of the process parameters is necessary to obtain laminates with the best performance.

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EFFECT OF CURING THERMAL HISTORY ON THE MECHANICAL PROPERTIES OF SYLGARD 184

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Abstract

Sylgard 184 is a polydimethylsiloxane (PDMS) largely used to produce smart soft composites and soft morphing structures which are generally applied in soft robotics[1,2]. In all these applications the mechanical properties of all the components of the composite play a very important role.
Sylgard 184 is provided as a two components system consisting of a pre-polymer (the elastomer base) and a curing agent. Both the components are liquid and when mixed they react forming a tridimensional network of dimethyl siloxane. It is known[3] that the structure of the network formed and, thus, the relevant mechanical properties, are significantly affected by curing conditions but, to the authors' knowledge, no systematic study on the curing conditions effect has been reported in literature. In this work, a systematic study of curing thermal history effects on Sylgard 184 mechanical properties is proposed.

To this aim, and to correlate the mechanical behaviour with the structural features of the PDMS network, two methods have been used: (i) a dynamic mechanical analysis in shear during the curing process and (ii) network swelling measurements on the obtained cured materials. Isothermal curing was performed at different temperatures, and different heating rates were used to reach the curing temperature.
Through both the material characterization methods above indicated, the molecular weight between crosslinks, Mc, could be determined: from rheological measurements, the elastic shear modulus of the crosslinked PDMS can be related to Mc according to the theory of rubber elasticity while from swelling measurements, the volume fraction of the polymer in the swollen network can be associated to Mc following the theory proposed by Flory and then modified by several authors[4]. Mc was then used as index of the tri-dimensional network structure.

The main results obtained are here reported:
(i) the curing temperature has a significant influence on the PDMS mechanical properties which instead are not influenced by the heating rate used to reach the curing temperature. Considering the production process, this is an advantage because, it is easy to control the material temperature in a mould put in an oven, while it is much more complex to accurately control its heating rate.
(ii) the elastic modulus of PDMS increases from a value of about 0.6 MPa, obtained when a curing temperature of 65°C was adopted, to a value about 1.2 MPa for a curing temperature of 150°C.
(iii) Mc calculated from the elastic modulus, in relation to the theory of rubber elasticity, are consistent with Mc calculated from swelling measurements. This confirms that changes in the network structure are strongly responsible of the mechanical properties changes.
(iv) Mc measurement based on the simple swelling experiment could be proposed to be used as an index of the mechanical properties of the PDMS elastomer. To perform a mechanical test it is necessary a dynamometer and relatively large specimen with a proper shape while for swelling measurements it is only necessary a precision weighing scale balance and any shape of a small specimen is suitable for the measurement.

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Continuous Cooling Curves of polyethylene/isotactic-polypropylene blends

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Role: Dottorando 2° anno

Abstract

The role of industrial processing variables (such as cooling rate and flow fields) on the structuring process and on the resulting properties of polymeric materials is of paramount importance, in order to design manufacts meant for specific applications. Continuous Cooling Curve (CCC) diagrams turn out to be a simple method to investigate polymer crystallization under fast cooling [1]. The approach is based on in-situ temperature acquisition, through a micro-thermocouple embedded in the polymer film, coupled with ex-situ characterization of structure, morphology, mechanical or thermal properties.
In the present work, this method is employed for studying the crystallization behavior in blends of isotactic polypropylene (iPP) and polyethylene (PE) sourced from recycling (Figure 1). The two polyolefins are immiscible and, therefore, each of them crystallizes independently upon cooling the phase-separated melt. Despite this, some interesting mutual nucleating effects between the two polymers can arise. In particular, epitaxial growth of PE onto iPP (and viceversa) has been extensively documented [2]. Given the rather different crystallization rate among PE and iPP, the crystallization peaks obtained on cooling for PE and iPP are affected by the cooling rate to different extents and an "inversion point" of the crystallization order can be detected. Depending on which component crystallizes earlier upon cooling, an inverted epitaxial growth or nucleating effect is obtained. The experimental CCC diagrams here presented encompasses a wide range of cooling rates (1-600 °C/s), typical of industrial processes, in the domains of monoclinic structure and mesophase for iPP and orthorhombic structure for PE. The effect of PE and iPP type and amount in prepared blends was investigated and allowed to unveil possible reciprocal effects of the phases during crystallization under industrial processing conditions in recycled PE/iPP blends.

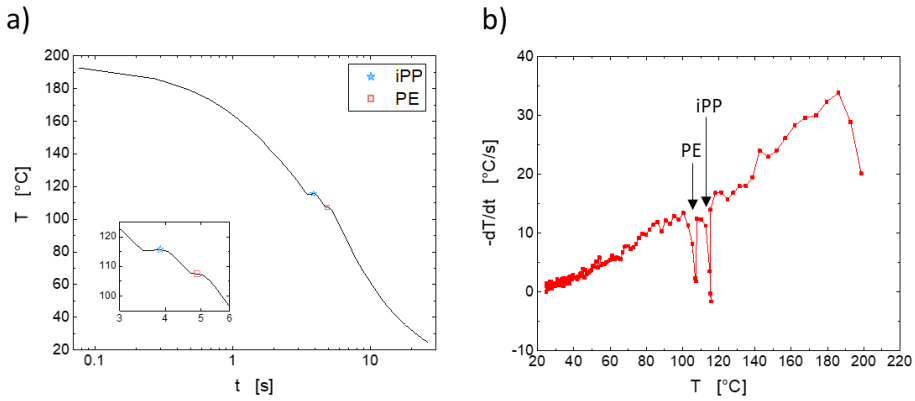

Figure 1. a) Example of temperature vs. time curve obtained experimentally upon cooling for a prepared PE/iPP blend. b) Plot of the derivative of temperature with respect to the time (-dT/dt), i.e., cooling rate, versus the temperature.

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VALORIZATION OF POST-CONSUMER PLASTIC WASTE WITH ENVIRONMENTAL FRIENDLY ADDITIVES

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Abstract

Plastics, once they reach their end-of-life, represent a growing environmental problem, especially if they are not disposed properly and dispersed in the environment. However, issues related to their end-of-life also exist for post-consumer plastic waste (PCPW) collected correctly. Of these, only a small part, equal to 32.5%, mainly from packaging plastic wastes, manages to be recycled[1]. This percentage so low, which according to the new European waste directive (EU) 2018/852 must be increased up to 55% in 2025, is due to the main issues currently presented by some of these materials[2], i.e. (i) the heterogeneity of the flows that cannot be effectively separated, because it is not possible from a technological point of view or because it is not economically advantageous, (ii) the presence of polar contaminant compounds and (iii) the bad smell. Due to heterogeneity of the flows, being their constituents generally not compatible, the recycled products have poor mechanical properties. Additionally, due to the presence of polar contaminant compounds, the PCPW is hygroscopic and must be dried before being processed, so its recycling is often uneconomic. Finally, due to the bad smell, the recycled PCPW is unpleasant and unsuitable for manufacturing of high quality, neutral smelling recycled goods for large-scale market applications.

In this field, our research has the aim to overcome the PCPW limitations by the development of effective valorisation strategies based on the use of different eco-friendly additives. Three plastic waste systems were selected as target PCPW: (i) pulper waste, a residue from the paper recycling process; (ii) packaging collected in seas and rivers; (iii) mixed plastics deriving from urban collection. All the analysed systems were composed of polyolefins, in particular PE and PP in different percentages, with small quantities of low molecular polar compounds. The selected plastic wastes have been added with low environmental impact and low cost substances, commercially available or obtained from other recycling processes. In particular, block polyolefin copolymers grafted with maleic anhydride as compatibilizers; a polyolefin mixture obtained from the recycling of bumpers, mineral (basalt fibre, talc and zeolites) and vegetable fillers (wood plastic compound) as reinforcements; and odour and humidity absorbers (ODOSORB, DESICCO and zeolites) were used.

The study was performed by melt compounding PCPW with different amounts of selected additives, used individually and in combination to evaluate their individual performance and any synergistic effects, by means of pilot scale twin-screw (for the realization of the mixtures) and single-screw (for the realization of the products) extruders. The obtained recycled systems were then tested for their morphology and thermal and mechanical performances. Main benefits obtained for the different plastic wastes and using the different additives were shown and compared.

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A RHEOLOGICAL EVALUATION OF SODIUM ALGINATE AS THICKENER FOR WATERBORNE PAINTS: A FOCUS ON THE APPLICATION PROCESS

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Dottorando 2° anno

Abstract

Paint formulations are complex combinations of chemicals that work together in a synergic way to obtain a high-performance product; the substitution of one traditional component with a non-engineered molecule is atypical in the industrial world because of the difficulties that researchers can encounter to obtain a stable and marketable product. Sodium alginate (SA) is a versatile biopolymer extracted from marine macroalgae extensively used in biomedical, textile and food industries for its viscosity and gelling capability with divalent cations [1]; very little is known about the performances of this natural polymer in the architectural coatings field.
The aim of this work is to investigate the applicability of SA as thickener in a simple paint formulation for interior walls, evaluating the effect of a medium viscosity and a low viscosity sodium alginate, through rheological tests and application tests on a gypsum board.
Preliminary experiments suggested that alginate interacts with the surrounding system; the aim of the present research is to verify how these interactions affect the application process; in particular if they led to surface defects as the presence of brush marks due to bad anti-sagging or bad-levelling behaviour. A cellulosic thickener has been chosen as benchmark.
The rheological characterization was carried out with an Anton Paar Physica MCR 301 rheometer using a parallel plate geometry, d=50, at T=23 °C. The structural recovery immediately after the application phase was investigated with the Three Interval Thixotropy Test, 3ITT, a rheological test that simulates the application process in three steps. The percentage of regeneration achieved in the third interval after 10 s or 60 s is used to analyse the structural recovery [2]. Both rotational and oscillatory conditions were investigated in the 3ITT to link the rheological properties to a brush application test onto a gypsum board. Stereomicroscope images were acquired to evaluate the occurrence of surface defects of the dried surface. The 3ITT provides valuable information; the alginate molecular mass and its concentration deeply influence the shear history of samples. The percentages of recovery after 10 and 60 s have a strong connection to the presence of surface defects, highlighted by the stereomicroscope images; low viscosity alginate samples exhibit the slowest recovery and deep brush mark while medium viscosity alginate samples have a better recovery, comparable to the standard cellulose.

Acknowledgment

This work has been done in collaboration with Boero Bartolomeo S.p.A.; the authors wish to thank Giulio Allegretta for providing the paints raw materials and the technical support received.

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STIMULI-RESPONSIVE LIQUID CRYSTALLINE POLYMERS TOWARDS THE DEVELOPMENT OF ARTIFICIAL MUSCLES

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Dottorando – II anno

Abstract

Our research aims at the design and development of biocompatible photosensitive Liquid Crystalline Elastomers (LCEs) and their 3D structuration. Such materials, thanks to their stimuli-responsiveness and elasticity, will be implemented to develop innovative lightweight and minimally invasive contraction assist devices, towards a new approach in the treatment of damaged heart tissues. Dye-doped LCEs, indeed, can show several types of actuation in relation to their molecular alignment and can generate tension as a consequence to their movement; the actuation is triggered by irradiation with light in the UV-visible range. In particular, planarly aligned polymer films can contract uniaxially and are regarded as smart materials to be used as artificial muscles in the field of regenerative medicine.[1] Our group has demonstrated their muscle-like behaviour and is now investigating on the possibility to use these materials to realize a cardiac contraction assist device, exploiting their biocompatibility and their low rigidity, which is similar to the one typical of biological tissues.[2] Advances and perspectives of the use of LCEs in biomedical engineering and as contraction assist devices will be discussed in this communication.

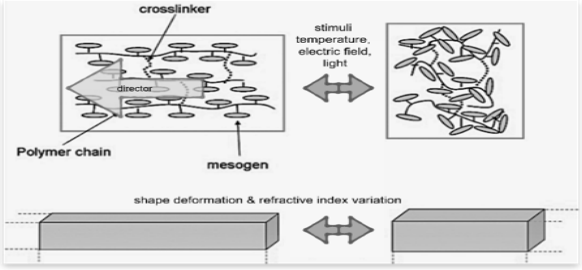

Figure 1. Cartoon representing the shape change in Liquid Crystalline Elastomers in response to external stimuli.

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HUMIDITY RESPONSIVE SMART TEXTILE: FROM NATURE TO APPLICATION

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Abstract

Plants can show an active response to the changes in the humidity level as they contain a great amount of cellulose. Pine cones, in particular, show reversible mechanical bending movement due to the changes in relative humidity [1]. This behavior derives from the difference in dimensional changes due to moisture absorption between the inner and outer layers (bi-layered composite) of pine cone scales. A thin layer of a hygroscopic material, submitted to an increase of the environment relative humidity, expands linearly according to its Coefficient of Hygroscopic Expansion (CHE). If this hygroscopic thin layer is coupled with a layer of another material with a negligible CHE, the variation of relative humidity creates a bending deformation in the bi-layered composite. The scope of this work is to produce a bi-layered textile that can show a spontaneous response to the changes in the environment humidity level. Mimicking this instantaneous self-actuation requires a meticulous study of the hygroscopic behavior of the materials and a proper design of their coupling.
Cellulose-based polymers, such as cellulose acetate, which are known for their sensitivity to the moisture absorption and desorption, are perfect candidates to mimic the autonomous response of plants to humidity changes. The stand-alone membrane of cellulose acetate (53.3% degree of acetylation), presented in this study, has already shown instantaneous response to the variation of environment humidity. Coupling this material as a membrane on textile as substrate can provide bi-layered composite with the desired actuation mechanism.
A detailed model must be foreseen to predict the moisture absorption and the effect on the mechanical behavior of the cellulose acetate membrane and of the bi-layered composite. Although numerical finite element codes could be suitable tools for accurate modeling of the humidity response bi-layers textile-based composites, to the best of the author's knowledge, these codes do not allow direct simulation of the hygroscopic behavior. Such limitation can be overcome considering the similarities of governing equations of conduction heat transfer and moisture diffusion, by substituting the thermal conductivity and temperature with diffusion coefficient and equilibrium moisture concentration, respectively [2]. This substitution is valid when the diffusivity is constant through the process of absorption.
The moisture absorption process for a series of cellulose acetate membranes (65 – 200 μm of thickness) has been monitored at a constant temperature (23° C) and at different relative humidity (RH = 20,30 and 40%). Since cellulose acetate shows a sigmoidal diffusion behavior, the experimental measurements were fitted and extrapolated by an analytical model [3] that can provide a constant diffusion coefficient. Extracted values from the analytical model for diffusion coefficient and equilibrium moisture concentration were used as input data for finite element analysis. Comparing the results of the simulation shows a very good agreement with the extrapolated and experimental data. Finally, a preliminary prediction of hygroscopic expansion of cellulose acetate membrane has been simulated by finite element analysis.

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ELECTROSPINNING AND PHOTO-CROSSLINKING OF PEO-BASED NANOFIBROUS MEMBRANES

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Abstract

Electrospinning is a unique technique for polymer fiber fabrication in nano- or microscale size through electrostatic forces. Electrospun membranes have plenty of applications including tissue engineering, filtration, energy devices and many more[1]. Polyethylene oxide (PEO) with its interesting characteristics such as biocompatibility, non-immunogenicity, stability against heat and hydrolysis, alongside interesting physico-chemical properties is an excellent candidate for applications in biomedical area, biocompatible coatings, and energy storage devices. Accordingly, the incorporation of nanofeatures (e.g. the obtaining of PEO electrospun nanofibrous membranes) can further expand its domain of applicability. However, PEO is soluble in water as well as in organic solvents: as a result, its application in many fields is hindered. As expected, PEO fibrous membranes in contact with water or other solvent first lose their nanostructure morphology and then are completely dissolved. Correspondingly, crosslinking reactions can be used to tackle this obstacle of solubility. Photo-induced crosslinking is particularly interesting as characterized by short conversion time, low energy consumption, ambient temperature operation and control both in time and space. It is thus an accessible and eco-friendly method for the modification of polymeric membranes in order to enhance their physico-chemical properties such as solvent resistance[2,3].

In this study, PEO-based nanofibrous mats were fabricated by electrospinning and subsequent photo-crosslinking reaction. For this purpose, two multifunctional crosslinkers, namely polyethylene glycol diacrylate (PEGDA) and trimethylol propane triacrylate (TMPTA), were introduced to the PEO solution. PEO/PEGDA and PEO/TMPTA with three different (ethylene oxide)/(acrylics group) ratios were electrospun and the fabricated membranes were irradiated by UV light. Photo-DSC measurements allowed to assess the irradiation conditions required for assuring an efficient crosslinking reaction. The effects of amount and type of photo-crosslinker were evaluated by insoluble fraction, structural, thermal, and mechanical characterizations. In particular, it was demonstrated that the membrane fibrous morphology was completely retained after water treatment for both PEO/crosslinker systems (Figure 1). Consequently, the obtained superior water resistance can highly widen the application fields of PEO-based fibrous membranes, especially in the water treatment and biomedical areas.

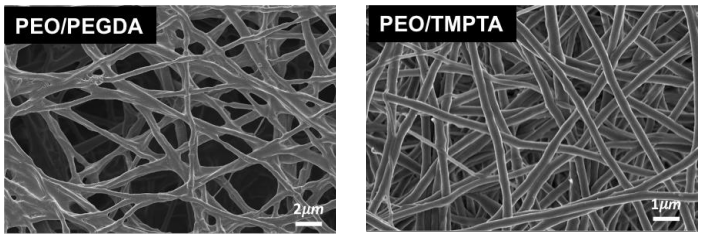

Figure 1. PEO/PEGDA and PEO/TMPTA photo-cured electrospun fibrous membranes after water treatment

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PHOTO-CROSSLINKABLE METHACRYLATED ALGINATE HYDROGELS AS NATURAL 3D BIOPRINTABLE INKS WITH TUNABLE STIFFNESS

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Abstract

Alginate-based hydrogels are extensively used for 3D bioprinting models reproducing *in vitro* features that accurately resemble *in vivo* conditions. Alginates are good candidates to support cell growth and, since they do not contain ECM proteins, their use as scaffolds allows the detection of ECM produced by cells themselves. The most common method to prepare hydrogels from alginate solution is to use divalent cations, such as calcium chloride ($CaCl_2$), which is one of the most frequently used agents to ionically crosslink alginate. In this case, tailoring alginate mechanical properties to simulate a broad spectrum of physiological features, while maintaining printability and biocompatibility at the same time, represents a key challenge, due to the instantaneous and poorly controlled gelation. The introduction of methacrylate moieties into natural polymers backbone chains has been widely demonstrated as an effective way to obtain photo-crosslinkable materials with improved mechanical properties, without altering their biochemical behaviour and cell-viability. However, the few alginate methacrylation strategies available in literature are usually reported as laborious synthetic processes involving numerous pH adjustments, high molar excess of methacrylic anhydride (MAA) or the use of an organic base, thus requiring an additional precipitation step which leads to a low yield.
In this work, an affordable alginate methacrylation process was accomplished by adapting for the first time Shirahama et al.[1] gelatin methacryloyl synthesis to the alginate polymer chains, in order to make the alginate-methacrylate (AlgMa) production easier and more manageable. In particular, the reaction involves basic aqueous carbonate buffer which serves as solvent capable of maintain pH 7 during the whole reaction time (72 h). The reduced molar excess of MAA employed, along with the ability of the buffer to autonomously sustain neutral pH throughout the synthesis, dramatically reduced the number of pH adjustments needed, making this green synthesis easy to handle and more friendly. ^{1}H-NMR confirmed that the chemical modification was successfully obtained after 72 h of reaction under mild conditions. Rheological measurements carried out on both pristine (Alg) and modified (AlgMa) hydrogels after cross-linking with $CaCl_2$ and UV light respectively, were performed with the aim of demonstrating AlgMa mechanical properties improvement with respect to Alg. Results highlighted the possibility to obtain different AlgMa hydrogels with tailored and customizable stiffness, by playing with photo-initiator concentration and UV cross-linking parameters. Rheological analysis coupled with 3D printing studies allowed to predict the optimal printability conditions of AlgMa hydrogels. It is worth pointing out that AlgMa hydrogels with tunable mechanical properties, high-shape fidelity and high stability of the final 3D-printed construct were obtained without making use of additives or blending with other polymers.
In conclusion, in this work we propose, for the first time, a relatively simple and more accessible alginate methacrylation reaction, to obtain photo-crosslinkable alginate-based hydrogels. The obtained AlgMa polymer was suitable for 3D bioprinting application and was used to successfully produce customizable printed platform with gradient stiffness for 3D cell culture.

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MELT- AND SOLID-STATE BEHAVIOR OF ETHYLENE-BASED MULTIBLOCK COPOLYMERS

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Indicate the role: Dottorando 2° anno

Abstract

Olefin block copolymers (OBCs) are high-performance materials that combine apparently irreconcilable properties such as elastic behavior, low density, high melting temperature, and high mechanical resistance. OBCs, and in particular ethylene-based OBCs (EOBCs), are obtained through the chain shuttling process[1] and feature alternating crystallizable hard blocks constituted by polyethylene (HDPE) and amorphous soft blocks constituted by random ethylene/1-octene copolymers. Given that in the chain shuttling process growing-chain transfers occur between active metal centers, a reactor blend of non-uniform chains with differences in block length and number of blocks/chain is obtained. In addition to the intrinsic polydispersity of these systems, it should also be considered that the presence of both hard crystallizable blocks and soft amorphous blocks results in a complex interplay between microphase separation and crystallization.
The solid-state morphology developed at nanoscale by effect of crystallization of two commercial EOBCs characterized by similar microstructure, rather small values of segregation strength χN_{tot} different molecular masses, small differences in the average octene concentration, similar content of hard segments, and similar polydispersity index has been analyzed through transmission electron microscopy.
The different results in the morphology have been correlated to the possible presence of heterogeneities in the melt, probing the state of the melt through rheological measurements, which are sensitive to order-disorder transition and mesophase separation. It is shown that polydispersity, molecular mass and number of blocks values have critical influence on the phase behavior of non-symmetric, multiblock copolymers

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PRODUCTION AND CHARACTERIZATION OF EPDM RUBBER FOAMS OBTAINED THROUGH SALT LEACHING

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Indicate the role: (Dottorando 2° anno)

Abstract

Polymer foams, thanks to the combination of low density and limited thermal conductivity, are widely used for the thermal insulation of buildings[1]. Expanded rubbers are materials consisting of a rubber matrix and of a porosity containing a gas phase (generally air)[2]. A possible alternative to traditional foaming agents is the "particle leaching": it involves the addition of water-soluble solid particles to the polymer matrix at the beginning of the process and the subsequent dissolution, leading to the formation of a porous cellular network[3]. The aim of this work is the production of EPDM foams using the technique of "salt leaching" and the investigation of the main thermal and mechanical properties.

A Vistalon® 2504 EPDM rubber was purchased from Exxon mobil, zinc oxide, stearic acid, and sulphur were supplied by Rhein Chemie, tetramethylthiuram disulphide (TMTD) and zinc dibutyl dithiocarbamate (ZDBC) were obtained from Vibiplast srl, carbon black N550 was obtained from Omsk Carbon group, polyethylenglycol (PEG) was purchased from Alfa Aesar. Sodium chloride was grinded and sieved into different granulometries. Two agents were considered: Micropearl® F82 was obtained from Lehvoss Italia S.r.l., while Expancel® 909DU80 was purchased by Nouryon Chemicals spa. The cryofractured surfaces of the samples were observed through a Zeiss Supra 40 scanning electron microscope (SEM). The thermal conductivity was measured using a Hot Disk thermal analyser. The compression set was evaluated according to ASTM D395-85 after 22h at a temperature of 23 °C.

Scanning electron microscopy and density measurements highlighted that the use of this technique leads to the formation of open-cell porosity with dimensions of around 60-80 µm, while foams obtained with the two traditional foaming agents lead to the formation of a close-cell porosity. The thermal conductivity of the foams allows possible applications in the field of thermal insulations. The compression set demonstrated that the behaviour of the foam produced with salt leaching is more similar to the one of a reference EPDM rubber.

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FABRICATION OF GREEN COMPOSITES FROM NATURAL PECTINS AND HEMP FIBERS AS NOVEL CARRIERS OF GREEN PESTICIDES FOR AGRICULTURAL APPLICATIONS

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Indicate the role: Dottorando 2° anno

Abstract

The interest in the use of natural fibers in the production of composites, as substitutes for traditional synthetic fibers, is finding more and more interest from basic and applied research. Among the numerous vegetable crops, hemp fiber, one of the few with a carbon footprint close to zero, is attracting great interest from the scientific community. From the chemical point of view, hemp fibers consist essentially of cellulose and hemicellulose, proteins, pectins, lignin and waxes. Traditional chemical-physical methods allow the removal of the non-cellulosic component but, simultaneously, they involve a reduction in the mechanical properties of the fibers themselves. Furthermore, the compatibility of the vegetable reinforcement with the polymeric matrix requires the optimization of the surface properties of the vegetable fiber in order to expose a high contact area and improve the fiber-matrix adhesion. To overcome the drawbacks of traditional treatments, it is necessary to develop innovative methods having as a target the selective removal of the non-cellulosic component without reducing the fiber properties. Mechanochemistry could represent an interesting and alternative tool to perform chemical reactions and materials modifications by application of mechanical energy. By using the appropriate processing conditions, it is possible to either drastically reduce the time of processing or to work at ambient temperature. In view of the above, this research concerns the use of a green and time-saving mechanochemical treatment of hemp fibers as green reinforcement in pectin based composites, as carriers of green pesticides for agricultural application. Finally, the work focuses on the low environmental impact, high functional efficiency and improved physical properties (thermal, mechanical, barrier…) of the green composites, in order to allow the replacement of traditional materials.

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POLYSACCHARIDE-BASED ELECTROSPUN MEMBRANES FOR WOUND HEALING APPLICATIONS

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Abstract

Electrospinning is nowadays recognised as an easy, fast and cost-effective technique to prepare polymeric nano- and microfibers.[1] The basic principle behind this technique is the application of a strong electric field to a polymer solution or a polymer melt with the consequent formation of a continuous polymer jet and the collection of the formed fibers on the surface of an appropriate grounded collector.[2] Electrospun fibers find a wide number of purposes in the biomedical and pharmaceutical fields as wound healing patches and drug delivery systems.[3] To this regard, the electrospinning of natural biopolymers, such as polysaccharides and proteins, has gained an increasing interest owing to their superior biocompatibility, biodegradability, and low cost. Moreover, these natural occurring materials exploit a higher biological response with respect to the synthetic ones, thus being extremely promising to promote cell adhesion and proliferation. Nevertheless, polysaccharides and proteins are infamous to electrospun with the obtained membranes often lacking the adequate mechanical and stability properties.[4,5]
Different type of polysaccharide-based electrospun membranes were here prepared with great attention in avoiding toxicity issues.[6,7] More in detail, novel washing-crosslinking approaches were especially developed in combination with various collection set-ups to obtain stable products with proper morphology, mechanical resistance and water-related features.[8–10] Moreover, nanoparticles of different nature were embedded within the nanofibers to enrich the electrospun membranes with antibacterial properties.[11] The possibility to use these products as drug delivery systems was also evaluated by using model drugs molecules, with the results showing the possibility to easily tune the release kinetics depending on the specific purpose. Additionally, a multilayer electrospun membrane consisting of an external layer of polycaprolactone and an internal layer of alginate has been successfully developed, thus obtaining a highly efficient wound healing product with promising applications.

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MICROCHAMBERS ARRAYS FOR CARGO PROTECTION AND CONTROLLED RELEASE

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Abstract

Encapsulation systems are pivotal in active compounds delivery, given the need to control the release in terms of space, time, and dosage. Micro-packing of active molecules and subsequent site-specific release can be achieved via the production of nano-engineered microchambers, obtained by depositing thin polymer films on patterned surfaces[1]. Films composed of microchambers could also be deposited as a microscopic coating on the surfaces of stents or implants[2]. Microchambers are small, hollow reservoirs sizing from one to ten micrometres. The microchambers are formed by depositing the polymer film on top of an ad hoc designed array of micro-wells (Fig. 1a), filling the microwells with the chosen cargo (Fig. 1b) and sealing them with a second layer of polymer film (Fig. 1c). The proposed microchambers arrays system is a film of micrometric thickness. In this work, polylactic acid (PLA) was used to obtain arrays of microchambers containing various low-molecular water-soluble cargos. Confocal microscopy and scanning electron microscopy demonstrated efficient filling of microchambers and cargo stable retention under submerged conditions, up to several weeks. The loaded molecules can be released by enzymatic degradation and diffusion[2] or external stimuli such as ultrasound, laser, pH and magnetic field [1,3].

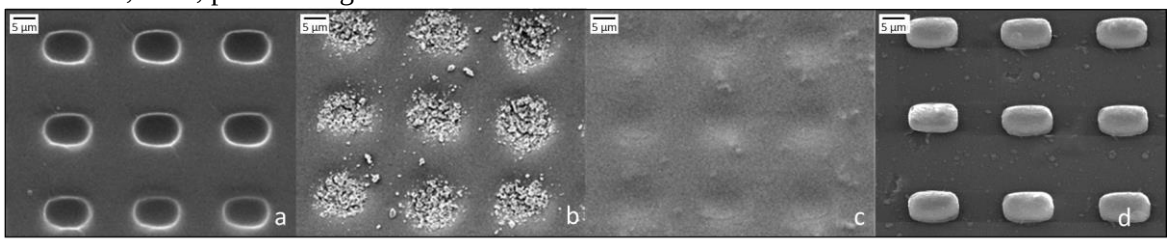

Figure 1. Scanning electron microscope micrographs of microchambers production steps.

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INFLUENCE OF AIR BUBBLES LOADING ON THE REACTION KINETICS OF RIGID POLYURETHANE FOAMS

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Indicate the role: Dottorando 3° anno

Abstract

Rigid polyurethane foams (RPUs) are widely used in many applications such as domestic appliances, constructions and automotive [1] for their excellent thermal insulating [2] as well as acoustic absorbance properties [3]. RPU properties of interest in the respective application fields are, among others, thermal conductivity, compression strength, acoustic absorption, dimensional stability, fire properties and adhesion [4]. These are tightly related to the foam density and morphology (e.g., the bubble size distribution, the open/closed bubble feature and the solid fraction in the struts and walls). To the aim of designing the desired properties, it is key to assess the governing mechanisms in the morphology evolution, both at the early stages, where bubble form, and at the later stages, when they grow, impinge and possibly merge into each other, thereby inducing a morphology coarsening. In this study, we investigated on the foaming process of RPUs obtained at different mixing speeds. In particular, the influence of the mixing conditions on the reaction kinetics of water blown RPUs was monitored by in-situ FTIR spectroscopy. The effect of air bubbles inclusion on the foaming process was monitored by means of an optical camera. Results revealed a significant enhancing effect of the mixing conditions on the polymerization reaction. In addition, in absence of air bubbles, formation of new bubbles was observed during the foaming process, while, in the case of air bubbles inclusion, this occurrence was not detected. The combination of the different reaction rates and the amounts of included air bubbles led to different observed coarsening mechanisms, responsible for the final RPU morphology.

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A SMART APPROACH TO MODIFY PVDF POLYMORPHISM AND PROPERTIES

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Abstract

Nowadays, the investigation of processing methods effective in inducing the electroactive β polymorph of PVDF has become an important research topic in many energy related fields [1].
In this work, an alternative and smart approach to tune PVDF polymorphism was proposed, that is exploiting the compression moulding to induce, within the not completely molten material, internal shear stresses similar to those occurring in a rolling process [2]. The moulding conditions were properly modified to investigate their influence on the crystalline phases obtained. The electroactive phase amount was estimated by ATR-FTIR spectroscopy, after having carried out a principal component analysis in order to verify the representativeness of the two infrared bands usually used in literature for such a calculation [3]. A multiple linear regression was employed to evaluate the trend of the β phase quantity as a function of the plate thickness and moulding temperature, obtaining a non-monotonous trend, due to the effects of two contrasting factors: (i) the effectiveness of compression, which increases by increasing the amount of molten polymer; (ii) the phase transition, which involves only the solid portion of the polymer bulk. Taking into account this, a series of moulding conditions was selected to prepare PVDF samples for further morphological, calorimetric, structural, dynamic-mechanical and dielectric characterization. Gathered results indicate that the processing method, by changing the polymorphism of PVDF, consequently affects the dielectric response of the polymer but also changes its ultimate properties independently from the induced crystalline phases [4]. By hot pressing the PVDF below the melting temperature, an orienting effect (verified by polarized optical microscopy) was obtained, leading to the α to β phase transition and consequent increasing of the dielectric permittivity. On the other hand, the dielectric losses and the dynamic-mechanical properties appear to be not affected so much by the β phase content but rather by a different packing of the polymer chains.

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MONODISPERSE POLYPEPTOIDS IN SILICON DOPING APPLICATIONS

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Abstract

The mad rush to technological enhancement imposes the realization of nanoscopic transistors with complex shapes to increase the power and speed of the microelectronic devices. For an electrical circuit, transistors are the equivalent of cells for our body. To set up these very small and 3D fundamental units, an extreme control of the amount and position of dopant atoms in semiconductive substrate is required. Our research group proposed some year ago a technological solution based on polymers having on one end a phosphorus dopant atom[1-2]. These functionalized polymers bring to the silicon surface phosphorus atoms in different amount simply by changing the molecular weight of polymeric chain. In spite of the success of this approach, some nuisance is present, coming from the molar mass polydispersity and inherent not fully reproducible synthesis.
Nowadays, only nature can synthesize perfectly monodisperse macromolecules selecting carefully any monomeric unit, e.g. DNA and polypeptides. Fortunately, R. Merrifield (Nobel prize in 1984) developed a solid state technology able to automatically synthesize polypeptide with precision very close to nature. In my talk, I will show how this technology can be applied to the synthesis of polypeptoids containing phosphorus dopant atoms. Polypeptoids are close cousins of polypeptides but can be dissolved in organic solvents. The precise control of the synthesis allows perfectly monodisperse macromolecules to be obtained with dopant moieties inserted wherever we want along the chain. This novel class of truly monodispersed dopants promises an effective integration of polymer based deterministic doping into industrial processing lines.

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Development and applications of controlled-release materials for the conservation and protection of Cultural Heritage

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Abstract

Cleaning and protection methods of stone surfaces are most of the main challenges in the field of Cultural Heritage, continuously aimed at researching products and materials which guarantee the preservation of historical heritage for a long time. Cleaning operation is a necessary first procedure which is aimed at removing superficial biological patinas and deposits from stone surfaces and at eliminating the origin of these alterations[1]. Poultices, predominantly based on clays or silica powders, are commonly used by restorers for cleaning operations and disinfection of stone surfaces. However, operators often use poultices without paying particular attention to the release of the used antimicrobial agent from different types of these supporting material. Cleaning procedures with poultices generally require fast and nearly complete release of the active agent. Recent studies carried out on poultices based on smectite intercalated compounds[2], sepiolite and silica powders[3], have shown a different kinetic release of the salt mainly used by restorers (i.e. benzalkonium chloride), showing suitability of these materials in cleaning and disinfecting operations, for instance in the field of heritage conservation, requiring both fast antimicrobial release and long-term biostatic effect.
In the other hand, an innovative material for the controlled-release of antimicrobial molecules, especially for long-term conservation procedures for rediscovered archaeological remains, is based on syndiotactic polystyrene (s-PS)[4,5]. With this inexpensive and reusable material, nanoporous-crystalline structures can be obtained by removal of low-molecular-mass guest molecules, and could be also complemented by inclusion of guest molecules, as molecules with antimicrobial effects[6], in the crystalline cavities of the structure, which are able to controlled-release over time. It is worth noting that fragile remains are usually covered by sheets and textiles, made of natural or synthetic materials (e.g. cellulose and polyesters), which modify the environment by creating conditions for the development of biodeterioration, with the growth of microorganisms, algae, fungi and infesting weeds on the archaeological surfaces[7]. Therefore, a comparison of different fibers and staples immersed in eugenol (a natural antimicrobial molecule recently used also in stone conservation field[8]) solutions was made, including s-PS, PET and cotton fibers.
The main result of this recent study evidenced that the highest amount of eugenol is absorbed in the nanoporous-crystalline phases of s-PS, which define a first rapid-release with a successive very slow-release for long time. This behavior ensures a long-term antimicrobial protection against microorganism activity and biological degradation which usually affect archaeological surfaces.

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Development of novel photopolymers for the fabrication of microfluidic devices through light-based 3D printing

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ABSTRACT:

Over the last years, microfluidic devices (or lab-on-a-chips) have attracted the attention of the scientific and industrial communities, particularly in the medical and pharmaceutical area. In fact, those devices can perform accurate and fast laboratory analyses on a much smaller scale if compared to traditional procedures, leading to reduced sample consumptions and costs [1]. Typically, microfluidic devices are fabricated through Soft lithography, which is quite expensive and time-consuming technique. Besides, Soft-Lithography allows only the manufacture of 2.5D microfluidic devices [2]. Therefore, 3D printing has recently emerged as a promising alternative for the fabrication of microfluidic chip in shorter times, at lower costs and maintaining the good precision [3]. Among the 3D printing technologies for processing polymers, those based on the photopolymerization of liquid resins upon light irradiation are the most versatile (i.e. digital light processing or DLP and stereolithography or SLA) and precise [4]. A typical liquid resin for light-based 3D printers is made of three main ingredients: (i) oligomer/monomer, which determines the final characteristic of the printed structure (i.e. mechanical strength), (ii) photoinitiator, which establishes the reactivity of the resin and (ii) a dye, which regulates the light penetration during improving the final resolution of the printed objects.

Therefore, in this work, we report the preparation and printability of custom-made photopolymers for the fabrication of complex-shaped and personalized 3D printed microfluidic chips. By selecting and combining the proper materials during the preparation of the resins along with the freedom of design of light-based 3D printers, 3D microfluidic chips were obtained with excellent optical features, high chemical stability and good mechanical properties. Furthermore, by taking advantage of unreacted functional groups exposed on the sample's surface, the superficial properties of the devices were easily and selectively modified, giving an added value to the printed devices in terms of surface treatment compared to classical methods.

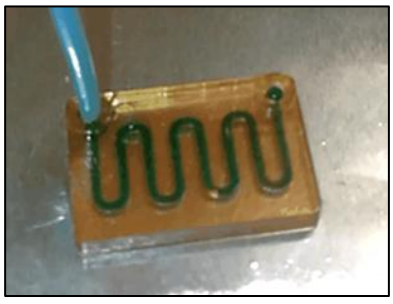

Figure 1. a) 3D printed microfluidic chip with a coloured liquid passing through it. Diameter of the channel 800 micrometres.

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FLUID DYNAMIC ASSESSMENT OF ULTRASOUND AND GUILLOTINE VITRECTOMY PROBES

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Abstract

Vitrectomy is a surgical procedure by which the vitreous humor of the eye is removed from the vitreous chamber and replaced with a transparent tamponade fluid. Vitrectomy is performed by means of a system consisting of several components, including a vitreous probe, which aspirates the vitreous body, the viscoelastic fluid that occupies the vitreous chamber of the eye.
The geometry and mechanics of vitreous probe ports may have great influence in vitrectomy surgery from the fluidics and safety standpoints. The main issue associated with this surgical procedure is the generation of retinal tractions by the vitreous probe, with the possible occurrence of retinal breaks and inadvertent tissue removal. Flow rate and fluid acceleration have been shown to be significantly related to efficiency and retinal tractions in vitreous removal[1]. Therefore, for a safe and efficient vitrectomy, optimization of fluidics can be achieved by maximizing the flow rate and minimizing the acceleration around the vitreous probe port. Moreover, it has been hypothesized that the use of UVPs can induce increase of vitreous temperature through the heat transferred by the probe to the fluid, thus, potentially causing thermal damages to the retina[2].
Purpose of this study is to assess the fluidics of ultrasound vitrectomy probes (UVPs) compared with guillotine vitrectomy probes (GVPs) of various diameters (23G, 25G, and 27G) and geometries. Also, to identify the working parameters that provide the best balance between acceleration and flow rate, and, for UVPs, to measure temperature variations in the fluid.
We used particle image velocimetry to measure flow fields in balanced salt solution and viscoelastic artificial vitreous (AV), in order to simulate both liquefied and healthy vitreous conditions. The rheological properties of each AV solution have been tested with the rotational rheometer Physica Anton Paar MCR 301 and were fairly consistent with those reported for porcine vitreous.
We analyzed acceleration, kinetic energy, and volumetric flux. The parameters considered were vacuum pressure, ultrasound stroke and cut rate. Temperature measurements were taken using an infrared thermal camera.
Our results showed that the flow rate was significantly higher for UVPs than GVPs. In particular, in the tested AV, UVPs were found to be more efficient in terms of generating lower acceleration for a given flow rate. Moreover, for UVPs the increase in temperature was small.
Under the present experimental setup and fluids, UVPs offered better fluidics compared with GVPs in terms of flow and acceleration; however, the flow structure for UVPs is more complicated and unsteady. The slight increase in temperature observed with UVPs is unlikely to be clinically significant.

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PRODUCTION AND CHARACTERIZATION OF ECOSUSTAINABLE BLOWN SHRINK FILMS

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Dottoranda 3°anno

Abstract

Shrink films are polymeric films that, when exposed to a source of heat, contract tightly over whatever they are covering. They are employed in a wide range of applications and with different functionalities and they are commonly produced on an industrial scale by blowing extrusion.
However, shrink films are mainly made by polyolefins, which are non-biodegradable materials [1].
Nevertheless, the problem related to the disposal of plastics has directed the research towards concrete eco-compatible solutions, aimed at improving the environmental sustainability. In this context, the use of biodegradable polymers in the packaging sector as potential substitutes for traditional polymers represents one of the most competitive challenges. Among the biopolymers, polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT) blends, compatibilized with a chain extender named as Joncryl, proved to achieve mechanical properties close to those of polyethylene [2].
However, investigations on shrink films based on these biopolymers are still limited.
Therefore, the aim work was the development of mono-oriented thin shrink films based on PLA/PBAT blends. To this end, films from blends of amorphous PLA and PBAT at different relative mass ratios (60/40 and 40/60 by weight) and compatibilized with Joncryl, were produced by means of a lab-scale blown film extrusion machine varying the take-up ratio (TUR), the blow-up ratio (BUR), the mass flow and the cooling speed. The physical-mechanical characterization of the films revealed that both the blends had adequate performance as packaging materials, that could be tailored varying the PLA content in the blend. Particularly, at the same process conditions, increasing the percentage of PLA in the blend resulted in higher transparency, stiffness and shrinkage and in lower ductility of the films. The increase of the TUR/BUR ratio led to an increase in the MD shrinkage following a linear trend up to a certain value, after which the shrinkage was almost constant. The lower cooling speed in the blowing extrusion process affected not only the thermal shrinkage, that increased mainly in the TD as a result of the higher orientation of the amorphous PLA chains, but it also led to a change in the morphology of the PBAT crystals with a negative impact on the optical and mechanical properties. However, in conclusion, results revealed that the produced films, proved to be successful candidates as biodegradable mono-oriented shrink films.

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