

Macrogiovani 2022

16-17 June 2022, Firenze



Workshop for Young Researchers on Macromolecular Topics



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Macrogiovani 2022

Aula Magna, University of Florence

Program

Thursday, June 16th 2022

13:00 – 14:00

Registration

14:00 – 14:10

Opening Ceremony

Undergraduates & Research fellows

14:10

Bisio Francesco

Synthesis of fine and conductive films of PEDOT by liquid phase polymerization

14:20

Di Lisa Luana

Rheological assessment of a hyaluronic-based injectable hydrogel for disease treatment

14:30

Fuochi Neri

Synthesis of shape-changing smart polymers by chain transfer

14:40

Palmieri
Francesco

An experimental model for fibrosis based on polyacrylamide hydrogels

14:50

Rotondo
Benedetta

POMOPLA: bio-based composite with tomato by-products for circular packaging application

15:00

Scognamiglio
Stefano

Realization of thermoplastic composites from recycled wind turbine blades

PhD Students (1st year)

15:10

Arese Matilde

Study of antibacterial treatments applied on soft trims materials for automotive application

15:20

Cappitti Alice

Bio-based polymers for treatment of degraded wood and paper

15:30

Di Matteo Pietro

Chemical and mechanical characterization of virgin and recycled polypropylene reinforced with talc and glass fibers for automotive application

15:40

Ferrentino Nancy

Light-sensitive poly(ϵ -caprolactone)-block-poly(ethyleneglycol) copolymers for drug delivery system

15:50

Ferri Martina

Fully bio-based polyhydroxyalkanoates/tannin films with potential application for food packaging

16:00

Gravina
Giuseppe

Zinc and magnesium catalysts for the synthesis of PLA and its degradation: a contribution to the circular economy of bioplastics

16:10-16:40

Coffee break

16:40	Lamberti Elena	Hemp fibers modified with graphite oxide as a sustainable solution for removal of methylene blue from wastewaters
16:50	Lanfranchi Andrea	Multilayer polymer photonic aegises for thermal shielding
17:00	Lenzi Luca	Glycerol trillevulinate as fully bio-based plasticizer: synthesis and effects on thermo-mechanical properties on several polymeric matrices
17:10	Luzzi Enrica	Designing of highly filled polymeric gels for 3d printing by direct ink writing
17:20	Miravalle Edoardo	Polystyrene biodegradation in <i>Zophobas morio</i> larvae: in vivo and ex-situ evaluation of microbial guts community activity
17:30	Moramarco Antonella	Polyethylene/polypropylene blends: study of their miscibility using compatibilizing agents
17:40	Niccolai Francesca	Next-generation composite polymeric membranes for semi-organic redox flow batteries
17:50	Picchi Alberto	Poly(cyclohexyl methacrylate-co-methyl methacrylate) as host polymer matrices for luminescent solar concentrators
18:00	Rea Mariangela	Development of a GelMA/alginate interpenetrating polymer network (IPN) hydrogel for 3D-bioprinting of liver models
18:10	Rollo Marco	Chemical depolymerization of polyethylene terephthalate by hydrolysis using Lewis-Brønsted acid mixtures
18:20	Rossi Elisa	Computational insights into the carbon dioxide-promoted polyethylene terephthalate depolymerization
18:30	Rossi Ruggero	New photoswitches bearing heterocycles for smart photoresponsive polymers

20:45

Social dinner

Friday, June 17th 2022

PhD Students (1st year)

9:30	Salvestrini Serena	Polymer dispersed Liquid Crystals for highly secure cryptographic keys
9:40	Sarotto Elio	Conductive polymeric nanocomposite based on carbonaceous fillers for integrated metal-free cabling and sensing
9:50	Scittarelli Doriana	Synthesis and characterization of polyester-urethanes from tomato cutin for applications as protective and/or aesthetic coatings
10:00	Togliatti Elena	Viscoelastic properties and degradation of poly (butylene-adipate-terephthalate)-calcium-phosphate glass composites

PhD Students (2nd year)

10:10	Donato Simone	How to mimic biological muscles with polymers
10:20	Escher Andrea	Polymer photonic crystals for the assessment of food degradation
10:30	Ospina Viviana	Polypeptoids for the deterministic doping of semiconductors
10:40	Pecorini Gianni	Additive manufacturing of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-based composites for bone regeneration
10:50	Podda Edoardo	Self-healing and shape-memory hydrogels by micellar polymerization

11:00-11:30

Coffee break

11:30	Prandi Francesco	Development of cellulose-based food packaging materials
11:40	Roggi Andrea	Polymeric anion exchange membranes for green hydrogen production
11:50	Scurti Stefano	Highly electron-donor copolymeric ligands as promotor/inhibitor agent in redox nanocatalysis

PhD Students (3rd year)

12:00	Balestri Arianna	New amphiphilic block copolymers as stabilizers for lipid drug delivery nanoparticles
12:10	Vitiello Libera	Effect of natural fibers on degradation of polylactic acid biocomposites

Postdocs

12:20	Franceschini Alessandra	The role of polymeric hydrogels for biological tissue clearing
12:35	Gelli Rita	Shaping gelatin-based hydrogels: from the cross-linking mechanism to the preparation of microparticles for biomedical applications

12:50	Hirschmann Max	Main chain azobenzene polymers: does sequence control enable control of degradation?
13:05	Impemba Salvatore	Ring-opening polymerization catalyzed by new NSSN-type group IV metal complexes
13:20-14:30	Lunch	
14:30-15:30	Awards ceremony and greetings	



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

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Abstract

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

In this project, the thin film synthesis reaction of a conductive polymer, poly-(3,4-ethylenedioxythiophene) (PEDOT), was investigated by a chemical oxidative polymerization process in the liquid phase by spin coating.

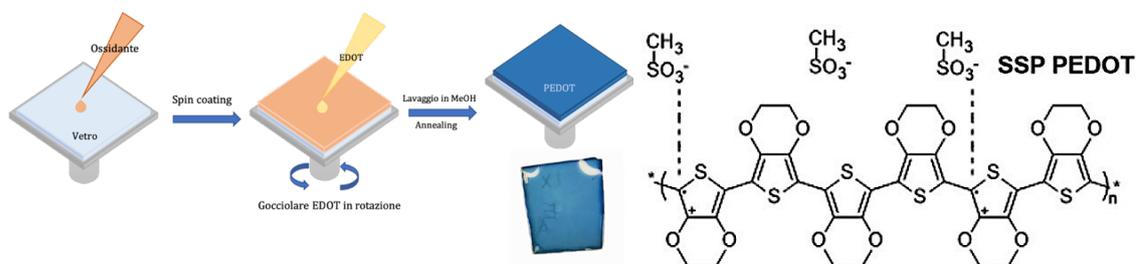
This process involves the sequential deposition of a solution of an oxidant (vanadium pentoxide) and a monomer solution (EDOT) on a glass substrate treated with piranha solution. The film thus formed is washed in a solvent to eliminate excess monomer and finally undergoes a thermal annealing treatment. The main parameters varied in this reaction were the concentration of the monomer solution, the deposition time of the oxidant solution and the concentration of the oxidant solution.

The analysis showed that the thickness of the samples obtained is fundamentally influenced by the deposition time of the oxidant solution and the concentration of the same.

The morphology and thickness of the samples were determined by AFM microscopy, while the conductivity of the samples by the Van der Paw method. The method involves the use of a probe with four equally spaced co-linear points, placed in electrical contact with the polymer film. A direct current is applied between the outer tips, while a voltage drop is measured between the inner ones. What is obtained from the measurement is the sheet resistance value (R_s , is measured in Ω/\square) which, together with the thickness data of the film, is used to calculate the conductivity of the polymer film.

The analysis showed that the technique is very reproducible, that the thickness decreases with increasing deposition time of the oxidant solution and that the conductivity increases with increasing concentration of the oxidant solution.

Finally, the treatment of polymeric films in sulfuric acid solutions was tested from which a sample with a thickness of about 100 nm and conductivity of 680 S / cm was obtained, a very good result even if compared to the values present in the literature.



RHEOLOGICAL ASSESSMENT OF A HYALURONIC-BASED INJECTABLE HYDROGEL FOR DISEASE TREATMENT

LUANA DI LISA¹, GIORGIA PAGNOTTA¹, GIOVANNA DESANDO², CHIARA GUALANDI¹,

MARIA LETIZIA FOCARETE¹

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²RAMSES Laboratory, Rizzoli RIT - Research, Innovation & Technology Department, Istituto di Ricerca Codivilla Putti, IRCCS, Istituto Ortopedico Rizzoli, Via di Barbiano, 1/10, 40136 Bologna, Italy

Abstract

Hydrogels are physically or chemically crosslinked 3D polymeric networks derived from natural or synthetic origin, with an intrinsic hydrophilic character due to their functional groups. Thanks to their unique properties, such as high-water uptake capability, high porosity, and biocompatibility, they can be used in various biomedical applications¹. In particular, injectable hydrogels have the suitable physicochemical properties to be injected *in situ* into the body via minimally invasive surgical procedures. Hyaluronic acid (HA) is one of the most employed natural polymers in viscosupplementation treatment for mild-moderate osteoarthritis (OA), a common degenerative joint disorder. Beyond its biological properties, the rheological characterization of HA hydrogel is clinically relevant and allows simulation of how it behaves during and after the entire injection process into the joint space. In general, this process can be divided into three phases: (i) the rest phase of HA, when the hydrogel is in the syringe at room temperature, prior the injection; (ii) the high shear phase, when the hydrogel is injected into the body; (iii) the new rest state of HA at body temperature (37 °C), after the injection². In this work a commercial hexadecylamide derivative of hyaluronan (Fidia Farmaceutici, Italy)³ was selected for a rheological characterization. To this aim, a measurement of viscosity as a function of shear rate was firstly performed to evaluate the hydrogel shear thinning behaviour, an important feature that ensures good injectability. Amplitude sweep was carried out to measure both storage (G') and loss (G'') moduli and to determine the linear viscoelastic region of the sample. Frequency sweep was performed to further characterize the inner structure of the material and the presence of either chemical or physical crosslinks. Finally, the full injection process was simulated by testing the material at the desired values of shear rate, followed by a recovery test. Results showed that HA is a solid-like gel, supported by physical entanglements probably generated by the high molecular weight and by the presence of alkyl branches in the polymer chain. The simulation of the injection process shows that HA has a good shear thinning behaviour, which favours a good injectability at 25°C and, at the same time, it completely recovers its properties at physiological temperature of 37°C after the injection. In sum, our findings support the relevance of rheological characterization of HA for injective treatments in osteoarticular diseases.

Acknowledgments

This work was supported by the Italian Ministry of Health (Grant Number: GR-2019-12370030 “A novel functionalized NUTraceuticals-laden hyaluronic hydrogel for gender-based PERsonalized treatment for osteOArthritis care: a novel proof-of-concept in viscosupplementation – NUTperOA).

¹ J.M. Alonso et al., Injectable Hydrogels: From Laboratory to Industrialization, *Polymers*, **2021**, 13,650.

² Minna H. Chen et al., Methods To Assess Shear-Thinning Hydrogels for Application As Injectable Biomaterials, *ACS Biomater. Sci. Eng.*, **2017**, 3146 – 3160.

³ I. Finelli et al., A new viscosupplement based on partially hydrophobic hyaluronic acid: A comparative study, *Biorheology*, **2011**, 48, 263 – 275.

SYNTHESIS OF SHAPE-CHANGING SMART POLYMERS BY CHAIN TRASFER

NERI FUOCHI¹, SIMONE DONATO¹, DANIELE MARTELLA^{1,2} AND CAMILLA PARMEGGIANI^{1,3}

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² *National Institute of Metrological Research (INRiM), Strada della Cacce 91, 10135 Torino (Italy)*

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Abstract

Liquid Crystalline Networks (LCNs) are smart materials that combine the properties of liquid crystals (such as the response to stimuli) with mechanical properties of elastomers. The most peculiar properties of LCNs is the ability to perform a reversible shape-change during the liquid crystalline to isotropic phase transition. Different kind of movements (e.g. contraction, bending, torsion) can be achieved by playing on liquid crystal (LC) molecular alignment thus opening to the design of different functional devices.

Our research group has focused its research activity on the use of LCN prepared by radical polymerization of LCs bearing acrylate groups demonstrating different application from robotics to tissue engineering.

Such materials are characterized by a side-chain architecture (with LC units attached to the backbone as pendant groups) and new synthetic method to obtain main-chain structure are desirable to improve the material responsiveness.

In this communication, we will show the first results on the synthesis of thermoresponsive LCNs prepared by photopolymerization of a mixture of acrylate based LCs and dithiols used as chain transfer agents.

Under thermal stimuli, contraction up to 50% of the original length was observed thus overcoming actuation generally observed in classical acrylate based LCNs.

**AN EXPERIMENTAL MODEL FOR FIBROSIS BASED ON
POLYACRYLAMIDE HYDROGELS**

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ROBERTA SQUECCO¹

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Abstract

Fibroblast-myofibroblast transition represents a key process during the physiological tissue repair upon an injury. Myofibroblasts are indeed the cells primarily responsible for the production and deposition of the extracellular matrix (ECM) components leading to the formation of a transient scar essentially required to restore tissue integrity and preserve its function. However, the generation of myofibroblasts and their persistence in an activated functional state are recognized as “core cellular mechanisms” of fibrosis, a complex disease affecting multiple organs possibly eventually leading to serious alterations of their functionality. A deeper understanding of myofibroblast biology is imperative in a clinical perspective for the identification of smart targets and development of effective antifibrotic therapy.

To this aim, we explored the use of polymeric hydrogels for the development of reproducible *in vitro* experimental models that mimics the *in vivo* condition as best as possible, enabling myofibroblast generation.

Different mechano-mimetic substrates of polyacrylamide gels have been prepared and characterized as scaffold for myofibroblast differentiation. The materials have been prepared by free radical polymerization with an accurate tailoring of water content and crosslinking degree to modulate the mechanical properties (with bulk compression modulus ranging from 29 to 1 kPa).

Murine NIH3T3 fibroblasts were cultured on these substrates in the absence or presence of TGF- β 1 (able to induce the differentiation) demonstrating how the scaffold stiffness play a crucial role for the fibrosis model formation. In particular, our preliminary results indicate that the best myofibroblastic differentiation appears on scaffolds with modulus around 1 kPa, suggesting a better differentiation on soft rather than on stiff substrates. Experiments are ongoing to evaluate the electrophysiological cell responses on the different culture substrates.

POMOPLA²: BIO-BASED COMPOSITE WITH TOMATO BY-PRODUCTS FOR CIRCULAR PACKAGING APPLICATION

BENEDETTA ROTONDO¹, ARKADIUSZ ZYCH¹, ROMINA SANTI², ANDREA MARINELLI^{2,3}, GIOVANNI PEROTTO¹, ATHANASSIA ATHANASSIOU¹, BARBARA DEL CURTO^{2,3}

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Abstract

The low availability of fossil resources, increased pollution caused by traditional plastics, and new regulatory restrictions pushed companies to adopt more sustainable solutions, especially for short lifetime applications such as packaging^{1,2,3}. The present research focuses on the development of a performing biocomposite that enhances the by-products of agri-food industries: POMOPLA² is an innovative material based on a plasticized polylactic acid (PLA) matrix filled with tomato scraps for both rigid and flexible packaging applications. PLA is a versatile bio-based and biodegradable polymer with high strength and stiffness, and good processability. However, brittleness limits its industrial applications where plastic deformation at high impact rate is required.⁴ To overcome this drawback, a renewable and biodegradable plasticizer (named LABD) obtained from esterification of butanediol with linseed fatty acids was mixed with the PLA. Once the optimal extruded formulation (PLA + 5% w/w LABD) was identified, powdered and dried industrial tomato waste composed mainly of tomato peels was added as filler to the matrix. POMOPLA² showed a significant toughness increase of about 485% and a consequent greater elongation at break of 177% (compared to 17% of pure PLA). The addition of tomato peels improves the internal morphology of the material decreasing the phase separation between PLA and plasticizer. The cooperative Finagricola (Battipaglia, Salerno, Italy) was selected as possible future partner interested in recovering its by-products. Following the principle of circular economy, the concept was to give a second life to tomato waste through the development of POMOPLA², representing a promising substitute for current fossil-based plastics (e.g., PP, PE, PET) used by Finagricola to pack and sell fresh tomatoes.

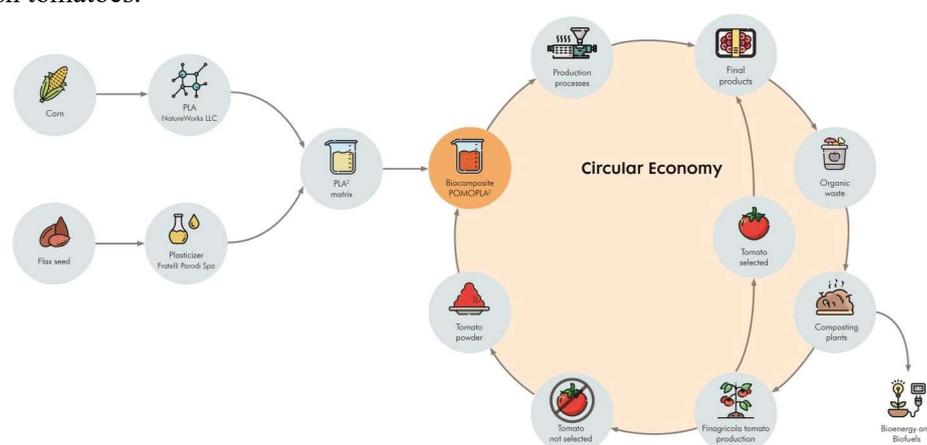


Figure 1: Ideal POMOPLA² life cycle

¹ European Commission, “Single-use plastics,” 2019. https://ec.europa.eu/environment/topics/plastics/single-use-plastics_it (accessed Feb. 18, 2022).

² United Nations, “La nuova Agenda 2030 per lo Sviluppo Sostenibile,” 2021. <https://unric.org/it/agenda-2030/> (accessed Aug. 11, 2021).

³ European Commission, “Circular economy action plan,” 2021.

https://ec.europa.eu/environment/strategy/circular-economy-action-plan_it (accessed Aug. 11, 2021).

⁴ Omnexus, “Polylactide (PLA): Complete Guide to Accelerate your ‘Green’ Approach,” 2022.

<https://omnexus.specialchem.com/selection-guide/polylactide-pla-bioplasic> (accessed Aug. 23, 2021)

REALIZATION OF THERMOPLASTIC COMPOSITES FROM RECYCLED WIND TURBINE BLADES

STEFANO SCOGNAMIGLIO¹, ROBERTA CAPUANO, RACHELE CASTALDO, MARIACRISTINA COCCA, GENNARO GENTILE, MARIA EMANUELA ERRICO, FEDERICO OLIVIERI, ROBERTO AVOLIO

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Wind turbines represent one of the largest source of renewable electrical energy, providing a valuable alternative to fossil fuels and contributing to the decarbonization of the energy production system worldwide. While most components of turbines can be readily recycled at their end-of-life, the recycling of turbine blades (WTB) is a serious challenge, as they are generally constituted by thermoset fiber-reinforced polymer composites. Wind turbines have a designed service life of 20 – 25 years, meaning that an increasing number of installations is currently being dismantled with increasing disposal issues.

In this frame, a mechanical recycling approach for thermoset materials obtained from dismantled WTBs has been setup, aiming at the realization of thermoplastic composites.

This approach is based on a first milling step of WTBs, followed by traditional melt processing with virgin and/or recycled polyolefins, to obtain new thermoplastic composites contain up to 50 wt% of WTB powder as a filler.

Different WTBs fractions, one fine fraction (dust) recovered from cutting and milling operations and the others with nominal granulometry of 250 μ m and 1mm, have been tested for composite preparation, to evaluate the effects of particle size on mechanical properties.

Composites realized by the described approach have been characterized in terms of morphology (SEM), thermal (DSC, TGA) and mechanical properties to validate and compare the results.

According to the parameters recorded by mechanical (tensile and flexural) tests, a higher modulus value is correlated to the grater fiber size (1mm); otherwise, strain at break increases as fiber granulometry reduces.

In order to improve mechanical properties, systems containing polymeric coupling agents have been factored in, with the aim to improve filler/matrix interfacial adhesion. The effectiveness of the coupling agents has been demonstrated by the large increase in tensile and flexural strength recorded materials containing the additive.

In Figure 1, a micrograph of milled WTB and some examples of tensile stress/strain curves are reported.

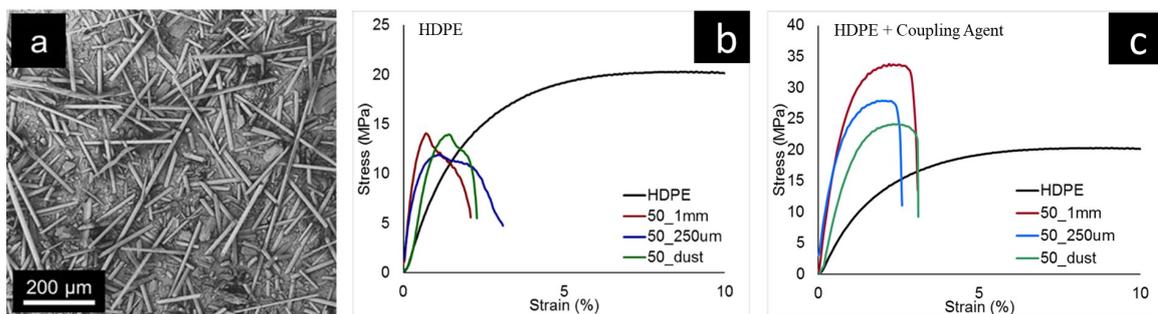


Figure 1. SEM micrograph of milled WTB (a); stress/strain curve for HDPE/WTB composite (b); stress/strain curve for HDPE-Coupling Agent/WTB composite (c).

Acknowledgement: This research is supported by ENEL Green Power SpA, in the frame of the Research Contract “POC per la sperimentazione di processi di riciclo di materiali compositi in fibra di vetro provenienti da pale eoliche a fine vita”.

STUDY OF ANTIBACTERIAL TREATMENTS APPLIED ON SOFT TRIMS MATERIALS FOR AUTOMOTIVE APPLICATIONMATILDE ARESE¹

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Abstract

In the automotive sector, soft trims materials are the textile components that are used inside the cabin, the main types are fabrics, leathers, and fake leathers.

Over the last few years, versions of soft trim materials have been developed with the addition of antibacterial treatments, initially for hygiene reasons, but recently their use has spread more and more due to the advent of car sharing and even more because of the Coronavirus.

Antibacterial fabrics could inhibit the growth of the bacteria and microbes or even kill them, thus reducing the transmission of infectious diseases. Incorporating some antibacterial moieties into fabrics has been extensively adopted by either chemical or physical treatment, such as metal and oxide nanoparticles (Ag, ZnO, TiO₂, Cu₂O, and SiO₂), nanocomposite particles (TiO₂ (MgO or ZrO₂)/SiO₂, Ag@ZnO, TiO₂/Fe₃O₄/Ag, and MgO/Al₂O₃), hybrid particles (ZnO/chitosan and N-chloramine/SiO₂), organic quaternary ammonium salts (QAs), guanidine, N-chloramines, chitosan, etc.¹

Particularly, in the automotive sector, most soft trims materials have antibacterial agents incorporated in the polymeric coating to form a composite coating. Antibacterial agents mainly include inorganic, organic and natural antibacterial agents.²

One challenge in the field is that the antibacterial ability may be gradually decreased over time, where the live/dead bacteria could adhere on the fabrics' coating.

In a new car the effect of antibacterial treatment has its maximum effectiveness; however, how does the efficiency of antibacterial treatments change over time as a result of the stresses to which soft trim materials may withstand during the life cycle of a car?

The goal of this project is to assess the life of antibacterial treatments applied on soft trim materials that are used in the cabin as interior (seat, steering wheel, armrest).

The first sample we tested was a fake leather made of PVC with polyethylene coating that is used as a steering wheel application. The effectiveness of the antibacterial treatment was assessed in accordance with the standard ISO 221963, in particular, tests were carried out on the material as new and after mechanical stress, thermal stress and light aging.

It was possible to confirm the efficacy of the antibacterial treatment on the sample non aged, however there was a decrease in the antibacterial effectiveness after the above-mentioned stresses.

The next steps of the project will include the evaluation of different antibacterial treatments applied on different soft trims materials, focusing on the causes of the decrease in the effect of antibacterial treatment as a result of the above-mentioned stresses.

In conclusion, based on the failures recorded, we will work on the coating formulation to improve its resistance over time.

¹ Jing Lin, XiaoYu Chen, ChunYan Chen, JieTao Hu, CaiLong Zhou, XianFang Cai, Wei Wang, Cheng Zheng, PeiPei Zhang, Jiang Cheng, ZhanHu Guo, and Hu Liu Durably. Antibacterial and Bacterially Antiadhesive Cotton Fabrics Coated by Cationic Fluorinated Polymers. ACS Appl. Mater. Interfaces 2018, 10, 6124–6136

² Yu Chen, Yong Ding, Junping Zheng. A polymer nanocomposite coating with enhanced hydrophilicity, antibacterial and antibiofouling properties: Role of polymerizable emulsifier/anionic ligand. School of Materials Science and Engineering, and Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300350, China

³ ISO 22196:2011(E), Measurement of the antibacterial activity on plastics and other non-porous surfaces (2011)

BIO-BASED POLYMERS FOR TREATMENT OF DEGRADED WOOD AND PAPERA. CAPPITTI¹, G. POGGI^{1,3}, G. DI GIULIO², M. FIORAVANTI², R. GIORGI^{1,3}, A. SALVINI¹¹*Department of Chemistry “Ugo Schiff” University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Italy) – Email: alice.cappitti@unifi.it*²*Department of Management of Agricultural, Food and Forestry Systems (GESAAF), University of Florence, via San Bonaventura 13, 50145 Firenze (Italy)*³*CSGI and Chemistry Department, University of Florence, Via della Lastruccia 1 – 50019 Sesto Fiorentino (FI), Italy***Abstract**

Saccharides were used as feedstocks to synthesize new biopolymers able to be used in the conservation of cellulose-based artefacts. Due to the fact that these materials lose their original mechanical properties upon natural aging, a reinforcement is usually needed.

To perform treatments with products with a high affinity to the cellulosic materials, new biopolymers were synthesized and tested as consolidants for the degraded paper and wood. Saccharides were chosen as starting materials in order to introduce in the final products units with a structure similar to that of the cellulosic substrate and the synthetic methodologies were selected taking into account the principles of the Green Chemistry and the future application in the preservation of the cultural heritage. In particular, α,α' -trehalose is a non-reducing disaccharide with high chemical stability which can be used as an interesting substrate in the synthesis of biocompatible and biodegradable monomers, due to its wide presence in nature. In fact, this saccharide can be found in many organisms or more interestingly can be obtained from starch to a relatively low cost using enzymatic methods. Allyl saccharide monomers were synthesized using allyl bromide to functionalize α,α' -trehalose obtaining products whose degree of functionalization varies according to the molar ratio between the reagents¹. These bio-based monomers were used for the synthesis of vinyl acetate copolymers and three different molar ratios between the two monomer units were selected to evaluate the influence of the composition on the chemical and consolidating properties. Vinyl acetate copolymers were subsequently hydrolyzed to the corresponding vinyl alcohol copolymers in order to obtain water soluble products suitable to be used in the treatment of wood and paper and to prevent the hydrolysis of the vinyl acetate groups after the application on the degraded material.

After characterization, the efficacy of the copolymers as consolidants was evaluated using a properly optimized diagnostic protocol. The performance in the strengthening of degraded paper was evaluated with preliminary tensile tests. The most effective system was thus selected for further testing, including the application on naturally aged paper, whose original mechanical properties are completely lost². On the other hand, the performance of the best product was tested for archeological waterlogged wood, taking into account his affinity for degraded wood, his penetration ability into the wood, the reversibility of treatment and certain physical properties of treated samples³.

¹ A. Papacchini, M. R. Telaretti Leggieri, L. Zucchini, M. A. Ortenzi, F. Ridi, D. Giomi, A. Salvini, *Royal Society Open Science*, **2018**, 5:171313.

² A. Papacchini, S. Dominici, G. Di Giulio, M. Fioravanti, A. Salvini, *Journal of Cultural Heritage*, **2019**, xxx-xxx

³ G. Poggi, A. Papacchini, S. Baracani, A. Cappitti, G. Marini, M. Marrini, R. Giorgi, A. Salvini, *Journal of Applied Polymer Science*, **2022**; 139:e52011

CHEMICAL AND MECHANICAL CHARACTERIZATION OF VIRGIN AND RECYCLED POLYPROPYLENE REINFORCED WITH TALC AND GLASS FIBERS FOR AUTOMOTIVE APPLICATION

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²*MSE SE - Polymers, Centro Ricerche Fiat, Turin, Italy
Corso Giovanni Agnelli, 200, 10135 Turin (TO)*

Abstract

Today about 13% of a car weight is made of plastic materials and automotive industries are constantly looking for new compounds, obtained from recycling processes or from biological sources, in order to develop new ecological materials with quality standards comparable to those of virgin materials, to implement a circular economy model in which more waste is converted into useful raw materials.

The focus of this paper is the chemical and mechanical characterization of different polypropylene compounds in order to find the best compromise between percentage of recycled material, mechanical properties and price for non-aesthetic dashboard applications.

Mechanical characterization was performed by using Digital Image Correlation¹. Compared to classical techniques, such as the use of strain gauges, it is able to measure what happens to the sample even at high speeds. Furthermore, it allows to obtain the Poisson's ratio, the true stress-strain curve and the elasticity modulus since it correctly follows the deformation of the material.

Tensile tests were performed at different speeds (0.1-10-100 mm/s) and dog bone samples were obtained from injection-moulded specimens, considering crosswise, longitudinal and twenty degree angle direction.

The intent of this work is to define a test procedure to obtain tensile characteristics of plastic materials at high strain rates. These characteristics are necessary to predict the mechanical behavior in non-static conditions (e.g. car crash).

The chemical characterization of material was performed with Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning electron microscope (SEM) to obtain information about tacticity of sample, thermal stability², crystallinity and filler dispersion respectively.

Interesting results have been obtained with Py-GC/MS for the purpose of finding a standard analytical method to discriminate recycled samples from virgin ones.

Further developments will be in the direction of combining all these results with chemometric methods, such as the Principal Component Analysis (PCA) and the Partial Least Square Regression (PLS).

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²Zhou, Yuanxin, et al. "Experimental study on thermal and mechanical behavior of polypropylene, talc/polypropylene and polypropylene/clay nanocomposites." *Materials Science and Engineering: A*, **402.1-2**, 2005, 109-117.

LIGHT-SENSITIVE POLY(ϵ -CAPROLACTONE)-BLOCK-POLY(ETHYLENE GLYCOL) COPOLYMERS FOR DRUG DELIVERY SYSTEM

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DANIELA PAPPALARDO¹

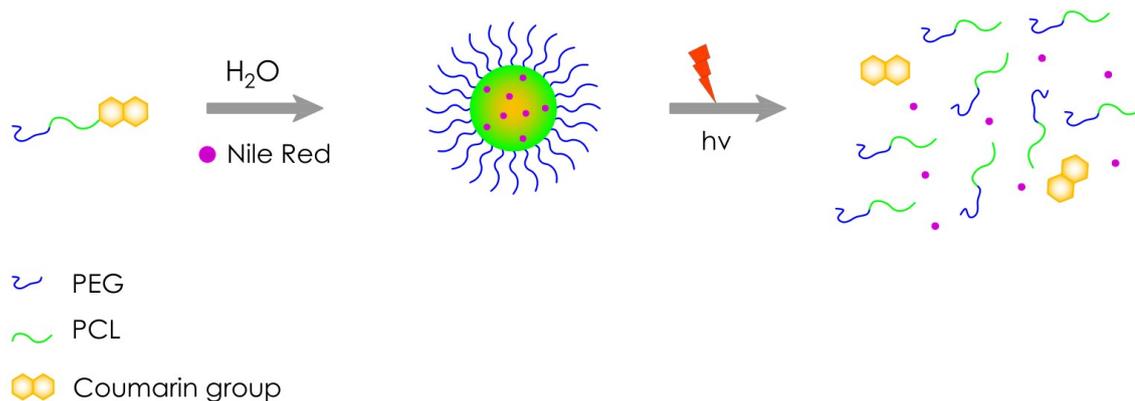
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Abstract

Drug treatment of tumors is often hindered by the rapid elimination and degradation of the drug. To overcome these problems, there are targeted therapies that allow the control of drug distribution by suppressing side effects. Drug delivery systems (DDSs) are supramolecular assemblies that incorporate drugs intended to treat a disease¹. DDSs are made of nanoparticles, liposomes, or natural or synthetic polymers. Polymeric nanocarriers responding to *external* or *internal* stimuli have received great interest for controlled drug release. In particular, by introducing in the DDSs photochromic groups, the light may be used as external stimulus, to ensure that the drug arrives at the specific site and at the right time. The irradiation could be carried out by ultraviolet (UV), visible or near infrared light (NIR)². The NIR spectrum is considered an ideal light source for monitoring drug release due its safety and strengthened tissue penetration. Coumarin has an high two-photon absorption cross section, suitable for NIR triggered drug release³.

We have designed DDSs made of biocompatible poly(ϵ -caprolactone)-*block*-poly(ethylene glycol) copolymers,⁴ acting as light sensitive polymeric materials due to the presence of coumarin on the polymer backbone. When dialyzed against water, coumarin-functionalized polyesters assembled into nanoparticles having a hydrophobic core and a hydrophilic shell, which were characterized by DLS, SEM and NMR. The hydrophobic Nile Red, used as a model guest molecule, was encapsulated in the nanoparticles and then released by UV, vis and NIR irradiation.



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² Zhao, W.; Zhao, Y.; Wang, Q.; Liu, T.; Sun, J.; Zhang, R., Remote light-responsive nanocarriers for controlled drug delivery: Advances and perspectives. *Small* **2019**, 15 (45), 1903060.

³ Hang, C.; Zou, Y.; Zhong, Y.; Zhong, Z.; Meng, F., NIR and UV-responsive degradable hyaluronic acid nanogels for CD44-targeted and remotely triggered intracellular doxorubicin delivery. *Colloids Surf., B* **2017**, 158, 547-555.

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FULLY BIO-BASED POLYHYDROXYALKANOATES/TANNIN FILMS WITH POTENTIAL APPLICATION FOR FOOD PACKAGING

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Abstract

The transition towards a circular economy needs the development of plastic materials that completely fulfill the requirements of sustainability. Due to their biodegradability and renewability, biopolymers embody a potential way to replace petroleum-based plastics, but the presence of non-renewable additives makes their actual renewable carbon content much lower than expected.

This research aims to develop an innovative bioplastic formulation for food packaging applications using polyhydroxybutyrate-co-valerate (PHBV) as the biopolymer matrix and plant-derived tannins as the renewable additive. With their well-known antioxidant, antimicrobial, and UV-blocking activities¹ tannins represent interesting additives to develop fully bio-based materials for food conservation.

Bio-based and biodegradable PHBV/tannin films with increasing concentrations of tannins (1, 5, 10 phr) were prepared by using the solvent casting method (Figure 1a-e). Formic acid was used to reach a homogeneous distribution of the tannins into the polymer matrix and as a greener alternative to PHA common solvents such as chloroform. The antioxidant properties were investigated using the DPPH assay. Samples containing 5 and 10 phr of the bio-additive achieved 100% of scavenging in 10-30 minutes, revealing a strong radical scavenging activity (Figure 2a-b). Moreover, both work extremely well as UV protectors, as proven by the UV-visible measurements. Despite not showing significant improvement in mechanical properties, which were evaluated through the tensile test, Dynamic Scanning Calorimetry (DSC) analysis revealed that all the films can be used at the fridge and room temperatures. Finally, by the naked eye, a color darkening of the sample during the exposition to ammonia vapors was easily observable, showing that the produced films might be used as smart indicators for food spoilage, e.g., to detect fish degradation. The presented study outcomes suggest that the addition of tannins positively affects the final material properties, making it an attractive alternative to petroleum-based plastics for food packaging applications.

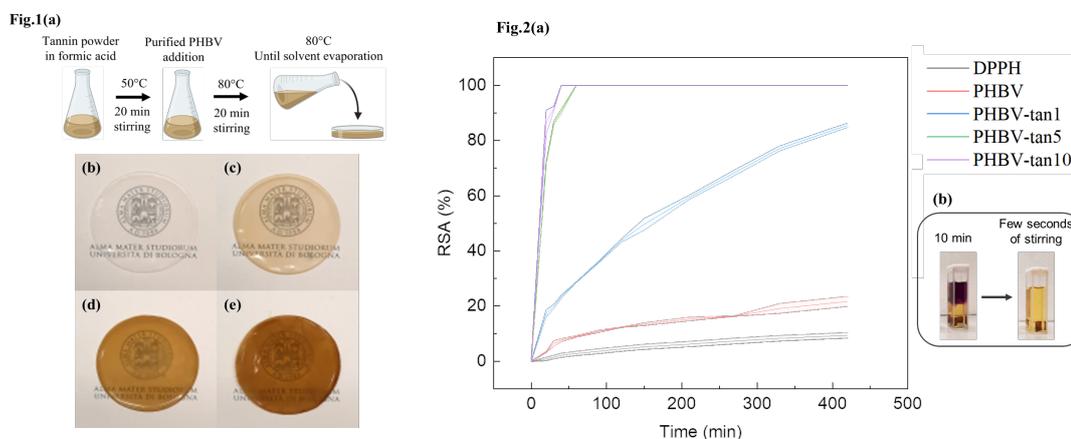


Figure 1. (a) Solvent casting conditions; Films (70 μm thickness) prepared by solvent casting: (b) PHBV, PHBV with tannins at (c) 1 phr, (d) 5 phr, (e) 10 phr. **Figure 2.** (a) Radical scavenging activity results; (b) Color transition of DPPH solution with the PHBV-tan10 film.

¹ A. Pizzi, "Tannins medical/pharmacological and related applications: A critical review", *Sustain. Chem. Pharm.*, vol. 22, no. June, p. 100481, 2021

ZINC AND MAGNESIUM CATALYSTS FOR THE SYNTHESIS OF PLA AND ITS DEGRADATION: A CONTRIBUTION TO THE CIRCULAR ECONOMY OF BIOPLASTICS

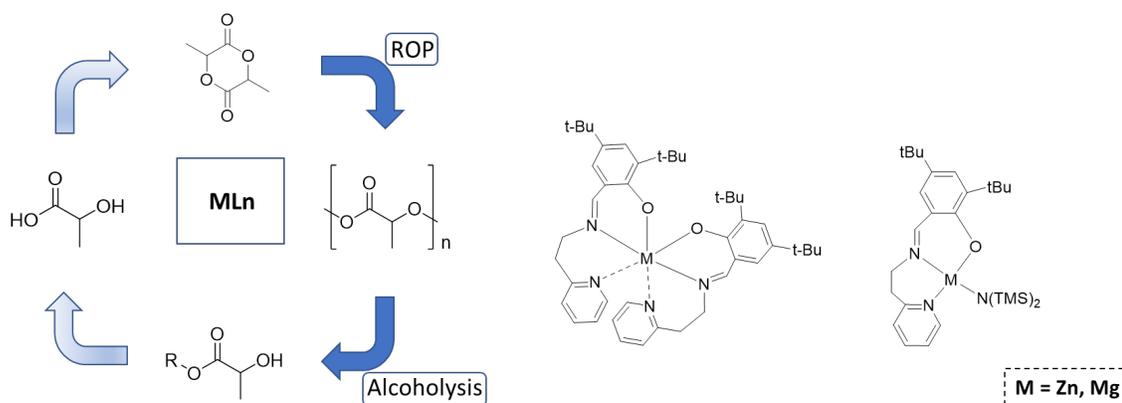
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Abstract

Poly(lactide) (PLA) is a biodegradable plastic derived from renewable resources that shows mechanical properties comparable to those of traditional polyolefins. For these characteristics, PLA may offer a concrete opportunity to implement a virtuous model of circular economy for plastics. However, despite its potential sustainability, there are some limitations about its life cycle; PLA is industrially produced by ring opening polymerization of lactide catalyzed by tin(II) 2-ethylhexanoate, a toxic catalyst¹. Moreover, although PLA is a biodegradable material, it causes environmental damage if dispersed into the environment^{2,3}; industrial composting conditions are required for its degradation. Recently chemical depolymerization by alcoholysis is emerging as a powerful method for recycling of PLA⁴.

In my master's thesis work, homoleptic and heteroleptic zinc and magnesium complexes were synthesized, characterized, and studied as a possible solution to the limitations described above for synthesis of poly(lactide) (PLA) and its chemical degradation to contribute to the circular economy of PLA.



The ancillary ligand, nature of the metal centre and coordination geometry were investigated for identifying design elements to improve the catalytic activity in both reactions. Moreover, some mechanistic aspects and the role of pyridine pendant were investigated.

High efficiency and control degree were reached with zinc catalysts while magnesium ones showed lower activity and a weak control degree. Significantly, the complexes that showed the best activity in the ROP of lactide revealed to be the most efficient also in the degradation reaction.

¹ Tanzi, M.C., Verderio, P., Lampugnani, M.G. et al. Cytotoxicity of some catalysts commonly used in the synthesis of copolymers for biomedical use. *J Mater Sci: Mater Med* 5, 393–396 (1994).

² Nazareth, M.; Marques, M.R.C.; Leite, M.C.A.; Castro, Í.B. Commercial plastics claiming biodegradable status: Is this also accurate for marine environments? *J. Hazard. Mater.* 2019, 366, 714–722.

³ A. R. Bagheri et al. "Fate of So-Called Biodegradable Polymers in Seawater and Freshwater" *Global Challenges*, 1 (2017) 1700048.

⁴ McKeown, P.; Jones, M. D., The Chemical Recycling of PLA: A Review. *Sustainable Chem.* 2020, 1, 1.

HEMP FIBERS MODIFIED WITH GRAPHITE OXIDE AS A SUSTAINABLE SOLUTION FOR REMOVAL OF METHYLENE BLUE FROM WASTEWATERSELENA LAMBERTI¹, GIANLUCA VISCUSI¹, GIULIANA GORRASI¹¹*Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy – Email: ellamberti@unisa.it***Abstract**

Nowadays, the presence of synthetic dyes in industrial effluents is leading to environmental concerns due to the impact of such contaminants on ecosystems and human health. Dyes are substances used in many industrial fields. Among all, methylene blue is a cationic dye with high water solubility. Many methods have already been applied to remove synthetic dyes from industrial wastewaters¹. Adsorption process is the most used one since its technological simplicity, low cost and wide availability of adsorbents. The use of common sorbents and their regeneration could noticeably increase the cost of the adsorption process². In our case, in an effort to address the need to develop more sustainable biomaterial-based sorbents, modified and engineered hemp fibers are fabricated to be a versatile class of sorbents. The use of hemp fibers modified with graphite oxide for the removal of methylene blue (MB) from aqueous solutions was investigated. The use of hemp fiberboards will allow to easily handle the adsorbent facilitating the desorption and reusability processes and limiting, in this way, the operating costs. Parameters such as contact time, pH, temperature, initial concentration of dye and ionic strength were varied and their effects on the adsorption recovery were evaluated. The adsorption process attained the equilibrium within 30 min while the adsorption capacity was found to increase with increasing contact time. The experimental data were fitted through a pseudo-second order model. Maximum adsorption capacity slightly increases with temperature changing from 54 mg/g to 58 mg/g at pH = 7.5, from 37 mg/g to 45 mg/g at pH = 3 and from 44 mg/g to 49 mg/g at pH = 12, by increasing the temperature from 20 °C to 80 °C indicating that the process is slightly endothermic ($\Delta H = 3.43$ kJ/mol). The thermodynamic parameters were even calculated demonstrating that the process is spontaneous ($\Delta G \approx -4.4$ J/mol K and $\Delta S = 3.16$ J/molK). Finally, a mathematical algorithm was applied to forecast the response surface model. A second order model was chosen to fit the experimental data and the statistical effect of the process parameters were estimated. A numerical optimization was even performed to individuate the optimal set of process parameters (pH = 9.25, T = 53.8°C and $C_0 = 13.2$ mg/L) which maximizes the removal capacity. A possible adsorption mechanism was even presented. So, it was proved the efficiency of the adsorption of a novel, inexpensive and sustainable composite material obtained from agro-waste resources by performing reusability cycles.

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MULTILAYER POLYMER PHOTONIC AEGISES FOR THERMAL SHIELDING

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Abstract

Thermal shielding, as a passive method of cooling, has seen an increase in its importance in multiple applications, year by year. These include, for instance, reduction of energetic consumption in vehicles and buildings, and conservation of foods and beverages along the production, transportation and storage chain.^{1,2} Here, we report on the use of all-polymer photonic crystals as selective reflectors for near-infrared radiation (NIR) spectral region, which is responsible for about half the total radiative heating caused by sunlight. Indeed, thanks to molecular vibrations, several materials (including water) absorb these light frequencies and generate heat upon absorption.³

Planar photonic crystals are multi-layered structures where the refractive index is modulated periodically with periodicity on the same order of magnitude of visible (VIS) and NIR wavelengths. The interaction between light and these structures generates characteristic optical responses, with high reflectance values at specific wavelength ranges and relative transparency between those regions. The spectral position of these ranges depends on the periodicity and the refractive index of the photonic crystal's building blocks. Therefore, it is possible to design and build structures that are transparent or partially transparent to VIS radiation, but highly reflecting in the NIR, efficiently shielding light absorption (Figure 1).^{4,5}

In this work, we report on the design and fabrication of thermal shields made of flexible polymer films, which we call “aegises” referencing the mythological goat pelt worn by the goddess Athena. The structures were fabricated by spin-coating deposition of poly(*N*-vinylcarbazole) (PVK) as the high refractive index medium and either cellulose acetate (CA) or polyacrylic acid (PAA) as the low index one. Different structures were realized to match the absorbance spectrum of materials showing NIR absorption. All the structures were tested as thermal shields measuring the temperature variation of different materials upon irradiation. These tests demonstrates that our simple polymer structures can reduce the heating phenomenon more than 20% with respect to clear glass. As polymer photonic crystals are also processed by co-extrusion on very large areas, these results are promising for lowering building energetic consumption and for conservation of food and beverages.

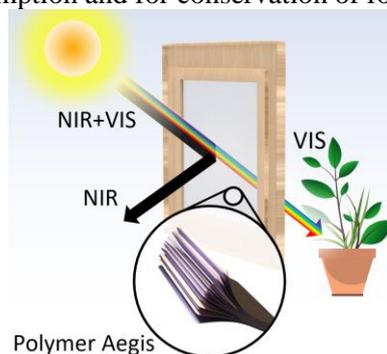


Figure 1. Schematic of aegises' functioning.

¹ K. L. Kownacki, E. D. Hornyanszky, T. A. Chu, J. A. Olsson, P. Becker. *Int. J. Biometeorol.* 62, 2017

² C. Bach, X. Dauchy, I. Severin, J.-F. Munoz, S. Etienne, M.-C. Chagnon. *Food Chem.* 139, 672, 2013

³ X. Cheng, W. Yang, C. Lin, Y. Ding, Z. Jiao. *Appl. Phys. A*, 123 644, 2017

⁴ P. Lova, G. Manfredi, D. Comoretto. *Adv. Opt. Mater.* 6, 1800730, 2018

⁵ A. Lanfranchi, H. Megahd, P. Lova, D. Comoretto. *ACS Appl. Mater. Interfaces* 14, 14550, 2022

GLYCEROL TRILEVULINATE AS FULLY BIO-BASED PLASTICIZER: SYNTHESIS AND EFFECTS ON THERMO-MECHANICAL PROPERTIES ON SEVERAL POLYMERIC MATRICES

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Abstract

Conventional plasticizers such as phthalates are the most used additives for polymeric materials. In particular, phthalates arouse several concerns due to their renewability, biodegradability, cytotoxicity¹. The use of phthalates have been restricted and monitored worldwide, however they are still been used in innumerable consumer products due low their cost, attractive properties, and lack of valuable alternatives. Hereby, in this work, we present a fully bio-based alternative plasticizer synthesized from Glycerol, which is a by-product of the biodiesel supply chains², and Levulinic Acid which is produced from lignocellulosic wastes³. A mild-condition solvent-free esterification have been used to synthesize Glycerol Trilevulinate plasticizer (GT). The product has been characterized by FT-IR and NMR (Figure 1). Reaction parameters such as the excess of Levulinic acid and catalyst amount have been optimized before testing the new additive with various polymers. Poly(vinyl chloride) (PVC) is the most compounded polymer, which makes PVC the perfect model polymer for testing new additives and comparing them with the nowadays industrially used ones (Figure 2a and 2b). GT has also been tested with several biopolymers, which typically lack of processability due to their high crystallinity. Different ratios of GT have been tested with Poly(3-hydroxybutyrate), Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), Poly(lactic acid) and Poly(caprolactone). The additive miscibility in the different polymers have been investigated by migration tests (figure 2e) and SEM imaging. Tensile tests (Figure 2e) and DSC investigations showed a very high plasticization effect of GT in terms of glass transition temperature (T_g), melting temperature (T_m) and crystallinity reduction on all tested polymer (Figure 2c), proving to be a promising and effective alternative plasticizer.

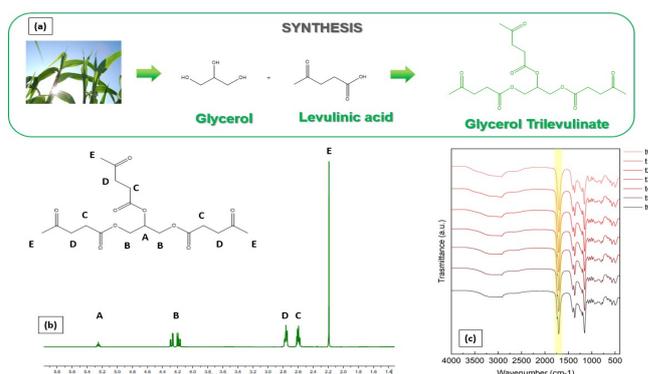


Figure 2 (a) Synthesis of Glycerol Trilevulinate plasticizer ;(b) ¹H-NMR spectra of GT; (c) FT-IR spectra at different reaction time.

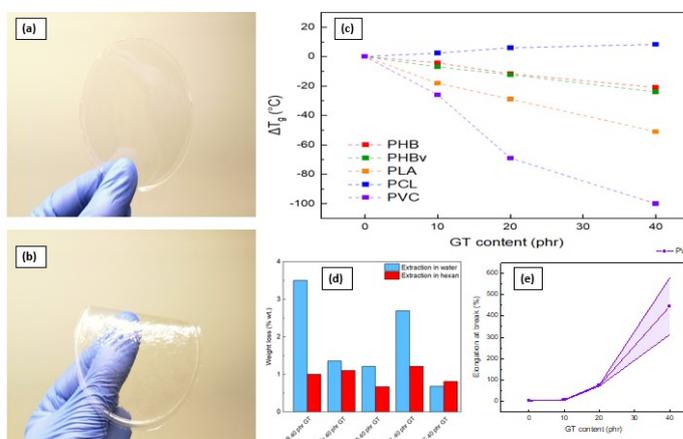


Figure 1. (a) Neat PVC film; (b) PVC film with 40% of GT plasticizer; (c) DSC analysis comparing ΔT_g of the formulations; (d) Migration tests; (e) Tensile strength test.

Poly(lactic acid) and Poly(caprolactone). The additive miscibility in the different polymers have been investigated by migration tests (figure 2e) and SEM imaging. Tensile tests (Figure 2e) and DSC investigations showed a very high plasticization effect of GT in terms of glass transition temperature (T_g), melting temperature (T_m) and crystallinity reduction on all tested polymer (Figure 2c), proving to be a promising and effective alternative plasticizer.

¹ Benjamin, S. et al. Phthalates Impact Human Health: Epidemiological Evidences and Plausible Mechanism of Action. J. Hazard. Mater. 2017, 340, 360-383.

² da Silva, G.P.; Mack, M.; Contiero, J. Glycerol: a promising and abundant carbon source for industrial microbiology. Biotechnol Adv, 2009, 27:30-39

³ Antonetti, C.; Licursi, D.; Fulignati, S.; Valentini, G.; Galletti, A.M.R. New frontiers in the catalytic synthesis of levulinic acid: from sugars to raw and waste biomass as starting feedstock. Catalysts, 2016, 6, 196.

DESIGNING OF HIGHLY FILLED POLYMERIC GELS FOR 3D PRINTING BY DIRECT INK WRITING

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Abstract

In the last few years, 3D printing technologies are getting increasing attention for the advantages they offer with respect to traditional manufacturing, such as rapid prototyping and versatility in complex shapes production. For this reason, 3D printing of traditional materials, such as polymers, is well established and largely studied. Differently, printing techniques of polymers embedding a high fraction of micro- and nanoparticles (e.g. graphene, hydroxyapatite, zeolites) are less analysed and optimized, even though these materials would confer the polymer functional properties of great technological interest (e.g. for electronic devices, tissue engineering, catalysis).¹ Here, the challenge is reaching high particle volumetric fraction, without altering their functionality and even still ensuring the polymer printability. Among others, the Direct Ink Writing (DIW) technique is deemed to be one of the most versatile and suitable for the purpose. DIW consists in the extrusion at room temperature of the polymer-particle mixture through a moving nozzle.² The desired shape is obtained through a layer-by-layer deposition and subsequently consolidated by controlled drying. Even though the advantages of this approach are clear, criteria of materials design printable by DIW are still missing and the mixtures production is still relied on the operator expertise. Printability is generically defined as the ability of a material to be extruded through a nozzle without clogging, with the aim of creating a continuous filament of constant section. The filament has to maintain its shape under the action of capillary forces due to other filaments and the force of gravity.³ These characteristics can be observed in many shear thinning and yield stress-polymers, whose rheological features are suitable for the printing process and, moreover, can be adjusted by a fine tuning of easily controllable parameters, such as concentration or pH. With the aim of defining printability criteria and optimizing the technology, a model system of aqueous sodium alginate solutions and 13X zeolite has been analysed. The mixture composition was varied by changing the zeolite and the polymer concentration, so to highlight each phase contribution. Rheology has been individuated as the main tool to characterize the system. Steady shear tests revealed the non-Newtonian behaviour of the mixtures and their yield stress, while recovery time and materials elasticity were assessed by oscillatory tests. Print trials allow for the correlation of materials behaviour with their printability, in order to develop preliminary empirical criteria and guidelines for their design and printing optimization.

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POLYSTYRENE BIODEGRADATION IN ZOPHOBAS MORIO LARVAE: IN VIVO AND EX-SITU EVALUATION OF MICROBIAL GUTS COMMUNITY ACTIVITYEDOARDO MIRAVALLE¹, SABELA BALBOA², ANA OTERO³, MARCO ZANETTI¹, MASSIMO LAZZARI^{4,5}

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Plastic pollution is one of the major issues of concern in today's society. Due to its high versatility, plastic represents one of the world's most widely used materials, leading to a total production exceeding 360 million tons per year¹. Therefore, it is crucial to find effective recycling and reuse methods to reduce the release of various types of pollutants into the environment resulting from the methods currently used in treating plastic waste². One of the proposed processes, as an alternative to physical and chemical methods, is biodegradation, which has been studied for various types of organisms (e.g. larvae and snails) and microorganisms (e.g. bacteria and fungi). In the former case, however, the degradative capacity in the intestines was attributed to the action of the microorganisms in the guts, which attracted great interest³. Among all the polymers, polystyrene (PS) is one of the most produced and used polymers worldwide, mostly because of its implications in the packaging industry⁴. Its degradation or biodegradation are, consequently, matters of great interest. This study focused on the superworm *Zophobas morio* and its gut bacteria. The ability to live on a sole polymer diet was assessed during a 28-day-period, and parameters like survival rate and plastic consumption were evaluated. PS ingestion and degradation were defined by analysing the frass via ATR-IR, NMR and SEC analysis, obtaining results similar to those reported in the literature. Following the guts of the larvae were retrieved, and the bacteria contained were used to evaluate degradation activity on the surface of PS disks on a novel agar-bacteria-plastic interface. The degradation has been carried out on isolated strains and consortia. Its effects were evaluated via ATR-IR analysis after implementing a specially developed cleaning process without aggressive reagents to allow, during the IR analysis of the PS surface, the observation of peaks in the carbonyl area that can be correlated with degradation, without erroneous attribution. SEM and confocal images have been acquired to understand the degradation process better and gain insight into the bacterial surface colonisation. A two-month enrichment process in a PS rich aqueous media has been performed in different conditions to refine the degrading consortia and follow the consortia's ability to specialise. In conjunction with this process and during the other phases of the study, changes in consortia composition were evaluated by metabarcoding analysis, which revealed the presence of strains not previously reported in the literature. Finally, the enriched consortia were used in a 28-days respirometry test in which the production of CO₂ as evidence of effective mineralisation of the substrate was monitored via GC analysis, and the degradation process on PS was followed by SEC analysis, highlighting the difference in the action of bacteria inside and outside the larvae in the depolymerisation mechanism observed.

¹“Plastics – the Facts 2019,” 2019² R. Geyer, J. R. Jambeck, and K. L. Law, *Sci. Adv.*, vol. 3, no. 7, pp. 25–29, 2017.³ P. Arunrattiyakorn, S. Ponprateep, and N. Kaennonsang, *J. Appl. Microbiol.*, no.132, pp. 2823–2831, 2022.⁴ F. Zhang *et al.*, “Current technologies for plastic waste treatment : A review,” *J. Clean. Prod.*, vol. 282, p. 124523, 2021.

POLYETHYLENE\POLYPROPYLENE BLENDS: STUDY OF THEIR MISCIBILITY USING COMPATIBILIZING AGENTS

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Abstract

The plastic industry is constantly increasing, from 2018 to 2019 the global plastics production grew from 359 to 368 million tonnes. The highest plastic demand comes from the packaging sector, this involves the production of a huge amount of waste every year: in 2018, 17.8 Mt of post-consumer packaging were collected in Europe, corresponding to 60% of the total plastic waste¹.

Several strategies were developed to give value to plastic waste and reduce landfill disposal. Among them, mechanical recycling allows to reintroduce end-life polymers into the production cycle.

The most critical step in mechanical recycling is the separation of plastic waste: it's tricky to separate some polymers, such as low-density polyethylene (LDPE) and polypropylene (PP), because of their similar density.

Furthermore, many polymers are immiscible and this affects the mechanical properties of the blends.

To reduce the interfacial energy between different polymers, compatibilizing agents, such as copolymers, ionomers, reactive polymers and nanoparticles, are usually added to polymeric blends². These additives exhibit portions in their structure with different chemistry, so they can stabilize the interface between incompatible polymers, enhancing stress transfer and improving the mechanical properties of the blends.

In our work, we studied the miscibility of virgin LDPE and virgin PP. The aim of this work is to improve the interfacial adhesion between virgin polymers and produce, in the immediate future, materials with added value, starting from recycled LDPE\PP. We selected these two polymers because they are the most abundant in plastic waste.

LDPE\PP blends were prepared by hot melt extrusion at 190°C. To improve the compatibility between the two polymers suitable compatibilizers were added, such as copolymers, polymers grafted with maleic anhydride and organo-modified nanoclays.

¹ PlasticEurope-Association of Plastics Manufactures, Plastics – the Facts 2020, 2020.

² J. Maris, S. Bourdon, J.-M. Brossard, L. Cauret, L. Fontaine and V. Montembault, Polym. Degrad. Stab., 2018, 147, 245–266.

NEXT-GENERATION COMPOSITE POLYMERIC MEMBRANES FOR SEMI-ORGANIC REDOX FLOW BATTERIES

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Abstract

Increasing focus on renewable energy production and storage is paramount as environmental and materials sustainability issues become more prevalent considerations in current and next-generation technologies. Energy sources, including solar and wind are inherently intermittent; thus, it is desirable to pair renewable energy generation with batteries so that the energy can be stored for optimal use. In this realm, redox flow batteries (RFBs) are promising candidates for large scale energy storage thanks to their long service lifetimes, relatively low capital costs, and independent scaling of energy and power density.¹ The membrane is a pivotal component of RFBs as it determines the performance as well as the economic viability of the batteries.² The present work aimed at the development of polymeric membranes for semi-organic RFBs based on 9,10-anthraquinone-2,6-disulfonic acid disodium salt (AQDS)/bromine (Fig.1). Nafion-based proton exchange membranes (PEMs) are regarded as the benchmark for many RFBs because of their high ionic conductivity and high stability in chemically aggressive environments.³ However, disadvantages, including the exceptionally high cost and crossover of unwanted species (e.g. Br₂/Br⁻ in AQDS/Br₂ RFBs) prevent their use for large-scale energy storage. On the basis of these rationales, we developed composite membranes starting from a micro-porous polymeric substrate on which a polymerizable solution of *N*-vinylpyrrolidone (VP), a complexing agent for bromine species⁴, was deposited. After the deposition, the membrane underwent a polymerization reaction, and the experimental conditions were systematically varied to modulate the amount of incorporated PVP. Ion conductivity and exchange, chemical and mechanical stability, and crossover of unwanted species of the membranes were evaluated by different analytical techniques. A RFB single cell with a composite membrane functionalized with 22 wt% of PVP showed a low-capacity loss, high coulombic efficiency and good ohmic resistance compared to the benchmark Nafion-based PEMs.

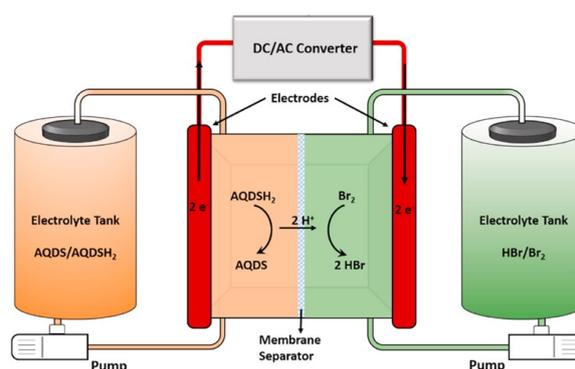


Figure 1: Representation of a semi-organic RFB.⁵

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POLY(CYCLOHEXYL METHACRYLATE-CO-METHYL METHACRYLATE) AS HOST POLYMER MATRICES FOR LUMINESCENT SOLAR CONCENTRATORS

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Abstract

A major challenge in the field of Luminescent Solar Concentrator (LSC) research is to find a highly transparent waveguide and a great fluorophore dispersibility to enhance solar harvesting¹. In commonly used matrices such as poly(methyl methacrylate) (PMMA), less polar repeating units might more effectively stabilize organic fluorophores and allow their use at higher concentrations, thus improving LSCs efficiencies². Here we report the use of methyl methacrylate (MMA) and cyclohexyl methacrylate (CHMA) as comonomers in a polymeric host material for thin-film LSCs. In addition to the two homopolymers, i.e. PMMA and poly(cyclohexyl methacrylate) (PCHMA), composition of 75:25, 50:50 and 25:75 were studied, using Lumogen F Red 305 (LR) as the state-of-the-art fluorophore³ in the 0.4-2 wt% concentration range. The performance of these LSCs was evaluated in terms of internal quantum efficiency (IQE), external quantum efficiency (EQE), fluorophore quantum yield (QY) and electrical efficiency of the device (η_{dev}) when coupled to a silicon photovoltaic cell⁴. Notably, the highest η_{dev} was recorded for the 50:50 P(MMA/CHMA) LSC at 1.6 wt% LR concentration, whereas maximum photon efficiencies were reached by using the 25:75 P(MMA/CHMA) matrix and compared to those gathered from LR/PMMA LSC. The trend of increasing optical and electronic properties of 25:75 P(MMA/CHMA) LSCs throughout the fluorophore concentration range under investigation can be considered promising and paves the way for exploration of these devices at higher LR concentrations, e.g. 2-5 wt%.

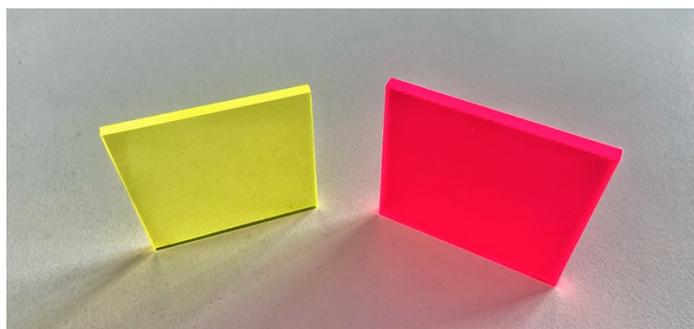


Figure 1. Examples of LSC containing high QY fluorophores

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DEVELOPMENT OF A GELMA/ALGINATE INTERPENETRATING POLYMER NETWORK (IPN) HYDROGEL FOR 3D-BIOPRINTING OF LIVER MODELS

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Abstract

Polymeric hydrogels are gaining great interest in the scientific community, thanks to their attractive properties, including mechanical flexibility, ability to transport small compounds and molecules, ease of functionalization and biocompatibility. These characteristics make them suitable for a wide range of biomedical applications, including tissue engineering, drug delivery, and microfluidics¹. These materials can be exploited for the realization of innovative organotypic *in vitro* models, owing to their physical and biochemical properties mimicking those of the natural extra cellular matrix (ECM). Hydrogel-based 3D-*in vitro* models are receiving considerable attention in the field of toxicity studies, since they represent a route to improve the reliability of conventional cell culture 2D-systems and to overcome the main drawbacks of the animals *in vivo* studies which are time-consuming, expensive and ethically challenging². The aim of this work is to develop a hydrogel for the realization of 3D-*in vitro* models of a liver tissue, based on an interpenetrating polymer network (IPN) constituted by GelMA (Gelatin methacrylated) and alginate, combining the advantageous characteristics of each polymeric component. Alginate is a natural polysaccharide characterized by easy availability and low toxicity, that can be physically crosslinked in the presence of calcium ions. It owns better hydrophilicity and mechanical properties than GelMA, but the lack of appropriate cell binding sites makes its use for 3D-cell encapsulation challenging. GelMA is one of the most popular exploited materials for such application, since it includes the arginine-glycine-aspartic acid (RGD) sequences along the main chain, favouring cell adhesion, migration and proliferation. This material can be photocrosslinked once exposed to UV light in the presence of a photoinitiator, forming a network of covalent bonds, which confer to the final construct structural stability over time. The 3D-bioprinting technique³, which involves the use of bioinks, i.e. the combination of cells and hydrogels, is exploited to develop hepatic constructs, characterized by a high liver-specific function of the tissue. Then, the obtained hydrogel scaffolds can be integrated into fluidic devices for continuous perfusion flow of chemical substances under analysis and to mimic the dynamic conditions to which our organs are subjected *in vivo*. The obtained hydrogels are rheologically characterized to assess their printability and mechanical properties. Morphological analysis is carried out to confirm the obtainment of a porous structure and finally, the printed constructs are subjected to flow conditions into a fluidic device, to verify their structural stability in time. The future perspective is to include hepatic cells inside the IPN hydrogel and print scaffolds to perform toxicity tests of the chemicals extracted from food packaging materials, which can migrate into food and be ingested by human beings, representing a risk for our health.

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**CHEMICAL DEPOLYMERIZATION OF POLYETHYLENE TEREPHTHALATE
BY HYDROLYSIS USING LEWIS-BRØNSTED ACID MIXTURES****MARCO ROLLO¹, GIANLUCA CIANCALEONI², ELISA MARTINELLI²**¹*Department of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 3,
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56126 Pisa (Italy)***Abstract**

The global demand for plastics continues to rise. The number of plastics in circulation is projected to increase from 236 to 417 million ton per year by 2030. Transition to a circular economy through reuse or recycle of plastics is essential to prevent increased accidental or purposeful release of polymeric materials into the environment, and thus curb environmental pollution. Mechanical recycling of waste plastic is an essential tool in an environmentally and economically sustainable economy of plastics, but current mechanical recycling processes are limited by cost, degradation of mechanical properties, and general production of downgrading materials. Chemical recycling is gaining interest, as complementary to traditional recycling methods, especially when it is a selective process capable of returning the polymer to its monomeric feedstocks.¹ Unfortunately, all the protocols require harsh conditions, carrying out the reactions at least at 160 °C. In the present study we propose the use of a series of sustainable Lewis-Brønsted acid mixtures for the chemical depolymerization of post-consumer PET bottles. The effects of process parameters, such as time, temperature, and water content are examined. The maximum conversion of PET and yield for monomer product, terephthalic acid, was observed as 100% and 89% respectively, after one hour at atmospheric pressure and at the reaction temperature of 100 °C.

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COMPUTATIONAL INSIGHTS INTO THE CARBON DIOXIDE-PROMOTED POLYETHYLENE TEREPHTHALATE DEPOLYMERIZATION

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Abstract

Chemical recycling of plastic waste materials is an important tool for the transition to a real circular economy. Indeed, it overcomes some of the problems arising in the mechanical recycling process, as the downgrading of the recycled items. Among the polymers, one of the most common for applications certainly is the polyethylene terephthalate (PET). The large amount of PET produced each year (about 30.5 Mmt in 2019 with the expectation to increase to 35.3 Mmt by 2024)¹ combined to its non-biodegradability in nature, led to waste polymer recycling becoming an urgent issue. Various methods have been proposed and, among them, chemical recycling is the most promising in terms of ‘sustainable development’². In fact, it leads to the formation of raw materials or monomers which allow the further high value added utilization. In the view of environmental protection, the conditions throughout PET depolymerization is performed are crucial, for example the energy consume, catalyst recovery and reuse, ect². In this context, organocatalysis could be a potential solution to make chemical recycling more appealing in the waste treatment process. In the present study, we explore carbon dioxide as a cheap and traceless catalyst to afford PET depolymerization from post-user PET items, as beverage bottles, via aminolysis. Indeed, the CO₂-catalyzed degradation of polymer was already demonstrated to be promising for Nylon-6,6 degradation via transamidation reaction³. In particular, we focus our attention on the reaction mechanism to elucidate both CO₂ and amine roles in the reaction mechanism.

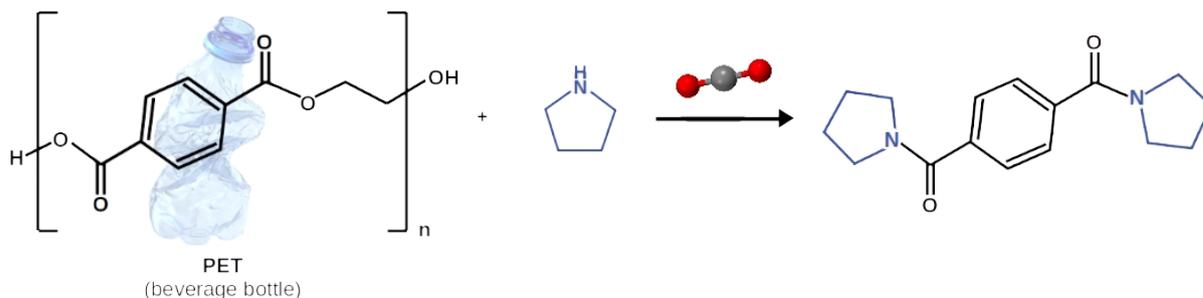


Figure 1: scheme for the CO₂-promoted depolymerization, via aminolysis, of PET from beverage bottle.

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NEW PHOTOSWITCHES BEARING HETEROCYCLES FOR SMART PHOTORESPONSIVE POLYMERS

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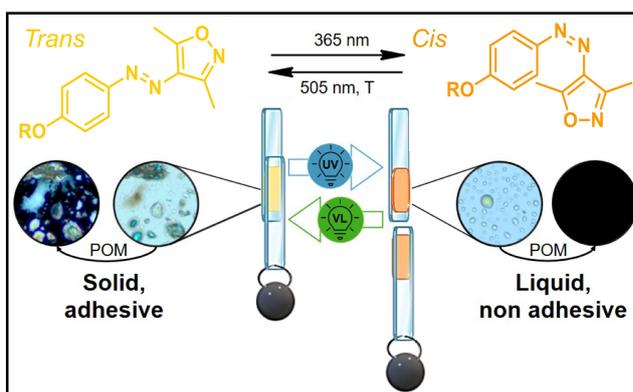
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Abstract

Molecular photoswitches allow a material to change its properties after light irradiation. One of the most used chromophores for this application is the azobenzene, which responds to UV light irradiation with a reversible *trans* to *cis* photoisomerization. Because of the chemical and physical differences between its two isomers. This molecular photoswitch finds several applications in the development of smart photoresponsive materials in different research fields, from adhesive to biomedical one. Among the former field, photoresponsive adhesives allow to use light as a selective stimulus to attach or detach different surfaces in a reversible way. As well as offering the possibility of recycling the adhesive, this is ideal for delicate environments, such as the human body, where the use of high temperature or solvents can be dangerous. For the same reason, in the latter field, the azobenzene has been used as a dye for the development of liquid crystal elastomer (LCE) systems as active materials to assist the muscular cardiac contraction. In both examples photoresponsive polymers show a great potential, but the classical azobenzene has some flaws in terms of light to mechanical energy conversion. Therefore, exploring novel molecules as photoswitches is mandatory to improve material properties and switching behaviour. We describe here the synthesis of new arylazoisoxazoles – azobenzene analogues containing a heterocycle – and their application as adhesives. The presence of such molecules has been recently demonstrated to give an enhanced photoresponsivity comparing to the azobenzene, which means a fast joint detachment under UV exposure and possible recyclability of the materials to rebond new surfaces¹. Here, the arylazoisoxazoles have been put into side chain polymers using the correspondent acrylic monomers. Mechanical tests demonstrate how, in specific cases, it is possible to observe a great enhancement of the adhesion strength passing from low molecular weight to arylazoisoxazoles acrylate polymer. The polymer also shows a drop of more than 70% in the adhesion strength after irradiation with UV light. Such interesting preliminary application also opens for the use of arylazoisoxazolic polymers as new dyes to improve photoresponsive LCEs to be applied in the development of contractile cardiac patches, improving light conversion into mechanical energy. Moreover, the photoswitchable adhesives could provide a safe installation of the patch.



Acknowledgments: The research leading to these results has received funding from MUR under the FISIR program, project FISIR2019_00320 Leonardo.

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POLYMER DISPERSED LIQUID CRYSTALS FOR HIGHLY SECURE CRYPTOGRAPHIC KEYS

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Abstract

Polymer Dispersed Liquid Crystals (PDLCs)¹ are well known inhomogeneous thin polymeric films with randomly dispersed micron-sized nematic liquid crystal (LC) droplets whose applications span from smart windows to tunable displays. PDLCs combine the properties of the polymeric matrix, like optical transparency and flexibility, with the ability of the LCs to orientate themselves and undergo a phase transition when subjected to external stimuli, e.g. electro-magnetic, fields or temperature variation, that then result in change of the optical properties².

In this work, PDLCs have been studied as complex optical systems for cryptographic authentication via Physical Unclonable Functions (PUFs)³. PUFs are physical objects characterized by an intrinsic irreproducible disorder that makes them unclonable and useful for the generation of secure cryptographic keys. Optical PUFs can be interrogated by spatially modulated coherent light intensity profiles, that then diffuses in the disordered medium, and produce an interference pattern named speckle pattern. These constitute a high complex and deterministic responses. After proper image filtering and binarization, the raw image can be transformed in a cryptographic key. We study PDLCs made by a dye-doped liquid crystal formulation for reconfigurable PUFs in which the optical properties can be erased in case of malicious attacks. Different PDLC formulations have been explored to find out the best parameters for the generation of highly complex and secure cryptographic keys that can be safely erased by a simple light illumination.

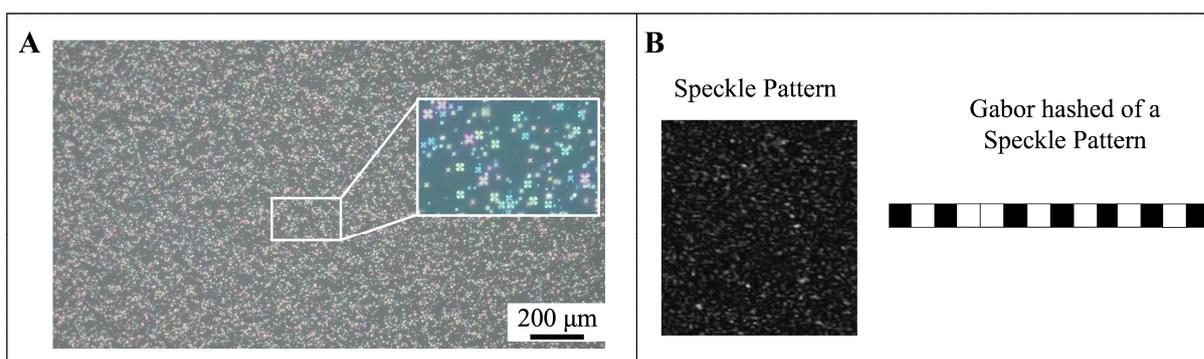


Figure 1. POM image of a PDLC (A) and its magnification. Speckle pattern before and after Gabor filter application (B).

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CONDUCTIVE POLYMERIC NANOCOMPOSITE BASED ON CARBONACEOUS FILLERS FOR INTEGRATED METAL-FREE CABLING AND SENSINGELIO SAROTTO¹, FEDERICO CESANO¹, VALENTINA BRUNELLA¹, ANTONINO VECA²¹*Department of Chemistry, NIS and INSTM Reference Centres, University of Torino, Via P. Giuria 7, 10125 Torino, Italy - Email: elio.sarotto@unito.it*²*CRF, Stellantis South Europe Technical Center, Strada Torino 50, Orbassano, 10043 Torino, Italy***Abstract**

In the last years, the aim to develop new classes of multi-functional materials to reduce component complexity and enhance their recyclability is becoming one of the main driving forces in several industries, first in automotive. In this industrial sector, the use of nanocomposites filled with carbonaceous fillers (such as carbon black) is well consolidated to obtain antistatic and UV resistant polymeric materials. These aspects, merged with the extraordinary electrical properties of carbonaceous graphene-based fillers, such as graphene nanoplatelets (GNP) and carbon nanotubes (CNT), lead to a big interest in the production of a new class of nanocomposites for the automotive industry with both excellent mechanical properties and innovative electrical behaviours¹.

The dispersion of a sufficient amount of carbonaceous nanofillers in an insulating polymeric matrix leads to the formation of a conductive network inside the composite material². When the filler concentration reaches a critical value, the electrical conductivity of the nanocomposite drastically increases by some orders of magnitude. Below this critical value, called the percolation threshold, the electrical properties of the composite are dominated by the insulating polymer matrix and the material acts as an insulator. Above the percolation threshold, the formation of the three-dimensional conductive network leads to a change in the electrical properties of the nanocomposite, and the material acts as a conductor.

Concerning this class of materials, an interesting and promising technology consists in the functionalization by a laser treatment of nanocomposites in which the filler concentration is below the percolation threshold. The interaction between the material and the laser beam leads to the formation of a V-shaped track where the filler concentration is locally above the percolation threshold resulting in a local electrical conductivity of the insulating material³. This innovative type of laser functionalized nanocomposites could pave the way to a new technology for the production of metal-free electrical circuits and sensors with great potential in several application fields. This could revolutionize product design, prototyping and production techniques used nowadays and will lead to several advantages: 1. Weight loss of complex components for automotive and other industries; 2. Reduction of production steps and production materials; 3. Easier recyclability of complex components.

In our research, we used a CO₂ laser with a wavelength of 10640 nm to obtain conductive tracks on polypropylene-based nanocomposites. Three different formulations filled with GNP and graphene oxide (GO) percentages between 2.5 and 4.0 wt% have been tested. We obtained for all the formulations a linear correlation between track length and electrical resistance and resistivity values lower than 2 ohm/sq. This promising result allows us to further optimize this technology by developing new types of nanocomposites using different polymer matrices, including recycled polymers, and different types of carbonaceous fillers, including environmentally friendly fillers like biochar.

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SYNTHESIS AND CHARACTERIZATION OF POLYESTER-URETHANES FROM TOMATO CUTIN FOR APPLICATIONS AS PROTECTIVE AND/OR AESTHETIC COATINGS.

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Abstract

Cutin is the main component of plant cuticles, the outer membrane of the aerial parts of non-woody plants. It is a natural polyester consisting mainly of long-chain fatty acids (C₁₆ and C₁₈) usually ω -functionalized with hydroxyl groups and mid-chain functionalized with oxygen-containing groups (epoxides, hydroxides or vicinal diols) or double bonds^{1,2}. Plant cuticle acts as a gas barrier and thermal regulator as well as a physical barrier that avoids water loss and nutrient leaching, protecting the plant from pests and pathogens as well as mechanical injuries and UV damage^{1,2}. Thanks to these features, cutin has recently gained interest as a possible renewable source for sustainable production of bio-resins. Moreover, cutin monomers (CMs) can be obtained from agro-waste, whose exploitation contributes to the total waste reduction. CMs are actually isolated on industrial scale from tomatoes peels waste by alkaline hydrolysis followed by acidification³. This CM mixture were at first characterized by FT-IR spectroscopy, ¹H and ¹³C-NMR spectroscopy and thermal analyses (TGA and DSC), and then used to prepare olygoesters prepolymers by condensation with 1,4-butandiol (BDO), a commercially available bio related diol. The kinetic of the condensation reaction and the final conversion were determined through ¹H-NMR and titration of -COOH and -OH groups. Several formulations were prepared by varying CMs/BDO ratio, reaction times, temperatures and the catalyst amount. The best prepolymers were finally used to prepare polyesters-urethanes by reaction with an aliphatic diisocyanate. Isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HMDI) were tested and the reaction was studied both in bulk and in methyl ethyl ketone (MEK) as the solvent. The kinetic was followed through FT-IR spectroscopy, and then the resulting polymers were further characterized by ¹H-NMR spectroscopy, thermal analyses (TGA and DSC) and solubility studies in different solvents. The coatings were applied with Mayer bars or by spraying on different substrates, namely aluminium alloy, paper, wood, glass and non-woven cellulose fabrics. Good adhesion was observed on all tested substrates, while the quality of the coatings depended on a combined effect of the coating composition, substrate nature and application method. The coatings exhibiting visually homogenous morphology showed excellent hydrophobicity and barrier to liquid water. Furthermore, EIS and potentiodynamic polarization tests, carried out on Bikar AA2017T4 alloy protected with Cutin/IPDI coating, during 15 days of immersion in simulated acid rain showed very low corrosion rate and highlighted excellent protective properties of the coating. Moreover, the results showed that the barrier effect was improved when the coating thickness was increased from 6 to 21 μ m.

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VISCOELASTIC PROPERTIES AND DEGRADATION OF POLY (BUTYLENE-ADIPATE-TEREPHTHALATE) – CALCIUM-PHOSPHATE GLASS COMPOSITES

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Abstract

The present work aimed to characterize the viscoelastic and degradation properties of biodegradable composite materials based on poly (butylene-adipate-terephthalate) (PBAT) reinforced with calcium-phosphate glass (CPG) microparticles. The composites had been previously realized through a solvent casting technique with five different compositions: 0, 4, 10, 20 and 40 %wt and named PBAT, PBAT+4% CPG, PBAT+10% CPG, PBAT+20% CPG and PBAT+40% CPG, respectively¹.

Characterization of viscoelastic properties was carried out by Dynamic-Mechanical Analysis (DMA) and creep test on injection molded 1BA specimens. From DMA results, a reinforcing effect in the matrix was observed from the increase in storage modulus (E') as a function of filler content. The glass transition temperature (T_g), considered as the peak of the $\text{Tan}\delta$ curves, show a slight decreasing trend, suggesting a good degree of interphase interaction. The creep compliance (J) was measured under constant stress, increasing with the temperature of test for each composite concentration, while at each given temperature it revealed a decrement as a function of the filler content, confirming the reinforcing effect of the CPG addition to the PBAT (Figure 1).

Accelerated weathering was conducted to simulate exposition of composite film samples to environmental conditions, through a combination of UV radiation, heat, and moisture. We obtained enhanced sensitivity to the agents with increasing the filler content, expressed by a more marked colour variation rate and brittleness, mainly attributed to the hydrophilic nature of CPG. The disintegration test was carried out under laboratory-scale composting conditions on film samples. The degree of disintegration (D) increased with the composition of the composites, leading to D values between 38% for PBAT and 79% for PBAT+40% CPG, after three months of test. As an example, Figure 2 represents the PBAT+20% CPG evolution over time. Low-density poly-ethylene (LDPE) was taken as a reference of a non-degradable plastic for both ageing and disintegration tests, confirming the absence of any changes in the chemical structure and in the macroscopical appearance.

Overall, the realization of PBAT-CPG composites allows to enhance and modulate the stiffness of the matrix, according to the filler content, enhancing at the same time the fragmentation behavior. The developed materials can be considered, therefore, as a more sustainable alternative to traditional non-degradable polymers, such as LDPE.

Figure 1 - Creep compliance curves of PBAT-CPG composites

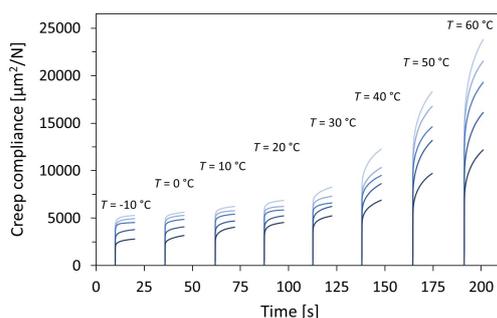
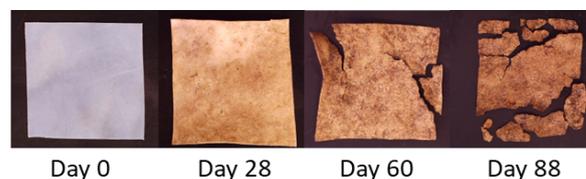


Figure 2 - Degradation of PBAT+20% CPG over time.



HOW TO MIMIC BIOLOGICAL MUSCLES WITH POLYMERS

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Liquid Crystalline Networks (LCNs) are among the best candidates, within smart materials, for artificial muscles development because of their ability to produce mechanical work in response to an external stimulus (light, temperature, etc.).¹

In this communication, we will show the ability of this kind of material to build an artificial heart muscle suitable for tissue engineering. Improving the design and synthesis of new molecules we enhanced the material force developed up to 70 mN/mm² with an illumination power of 1.5 W/mm².² A palette of new cross-linker bearing bulky substituents (dimethyl, trimethyl, phenyl and tert-butyl) in the aromatic cores have been prepared and used for the preparation of LCNs, as shown in Figure 1. Ideally, the introduction of different substituents will decrease the interactions among a LC molecule and its nearest neighbors thus leading to a reduction in the amount of energy to be supplied to obtain the force development. The modification of the crosslinker within the mixture allows to influence the thermal, mechanical and actuation properties of the material. In particular, the crosslinker has the potential to play a major role in influencing the thermal, mechanical and actuation properties of the final material obtained. These new active materials present stimulability and contractility, on the contrary of currently marketed materials for hearth patches and will allow a new approach in the treatment of hearth diseases like acute myocardial infraction.

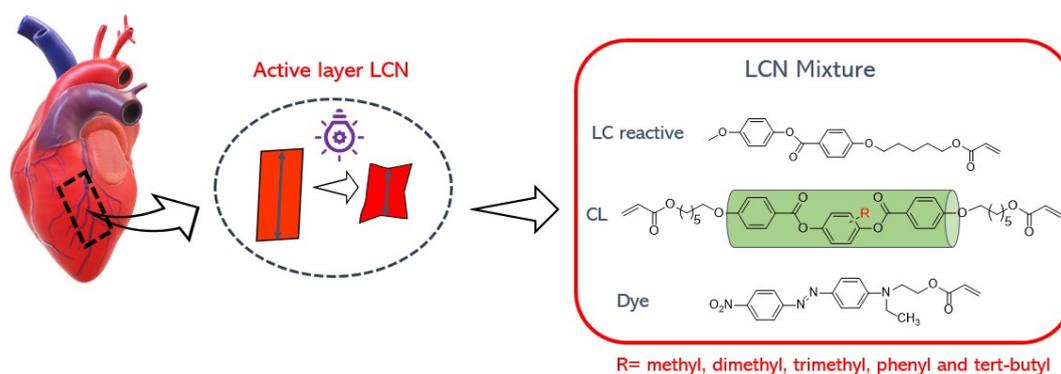


Figure 1: Example of the application of a biomimetic liquid crystalline network for hearth tissue engineering.

Acknowledgments

This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No. 952166 (REPAIR)

¹ Martella, D. *et al*, Opposite Self-Folding Behavior of Polymeric Photoresponsive Actuators Enabled by a Molecular Approach. *Polymers* **2019**, *11*, 1644.

² Ferrantini, C. *et al*, Development of Light-Responsive Liquid Crystalline Elastomers to Assist Cardiac Contraction. *Circulation Research* **2019**, *8*, e44-e54.

POLYMER PHOTONIC CRYSTALS FOR THE ASSESMENT OF FOOD DEGRADATIONANDREA ESCHER¹, HEBA MEGAHD¹, DAVIDE COMORETTO¹, PAOLA LOVA¹¹*Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa (Italy) – Email: andrea.escher@edu.unige.it***Abstract**

Globally, 2.5 billion tons of food are wasted yearly.¹ This also imply the waste of water, land, energy, labour and capital employed for its production, which is responsible for 10% of greenhouse gas emissions. In this context, monitoring the conservation status of fresh food, preventing and mitigating unexpected spoilage, could enormously reduce wastes. For this purpose, colorimetric real-time sensors for low concentrations of food degradation by-products, such as biogenic amines, also suitable for untrained users like the consumers, and compatible with the processing of food packaging, are of great interest.

Among different colorimetric technologies, multilayered photonic crystals (also known as distributed Bragg reflectors, DBRs) made of polymers are attracting more and more attention for their ease of manufacturing, lightweight, and mechanical flexibility, which are inconceivable with widespread inorganic photonic structures.² The color of these structures derives from the interaction between light and their periodic submicrometric refractive index modulation. In these systems, molecular analytes can intercalate within the lattice, modifying its pitch or refractive index, and in turn its color. Therefore, DBRs with their strong color response and ease of production even on large areas are ideal candidates for use in food monitoring even on a large scale.

In this work, we demonstrate not-reversible amine detection with a DBR consisting of alternating thin films of a titania-polyacrylic acid hybrid (TiHy)³ as a high refractive index medium and a blend of polystyrene and polylactic acid (PS:PLA) as low refractive index sensitive medium. In these sensors, the irreversible colorimetric response is ensured by the aminolysis of the PLA, which occurs upon permeation of amines in the structure. PLA was blended with PS to hinder the formation of crystallites with large size, responsible for light scattering in the structure. Indeed, when pristine PLA is employed larger crystallites induce strong light scattering and inhomogeneity in the photonic crystal structure. Last, coupling the active polymer blend with stiff polymer-inorganic hybrid films allows the structure to collapse following the aminolysis of the PLA, thus causing irreversible fading of the structural color. Such irreversible response is essential to prevent any tampering action. These achievements pave the way for real-time monitoring of the conservation status of food along the entire production chain and after purchase by the final consumer.

¹Hamish Forbes, T. Q., Clementine O'Connor *UNEP Food Waste Index Report 2021*; **2021**; p 100.

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POLYPEPTOIDS FOR THE DETERMINISTIC DOPING OF SEMICONDUCTORS

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Abstract

Polymeric materials played a fundamental role in the field of electronics for the fabrication of circuit boards and insulation. To move in the way of nanoelectronics, polymers can also be employed for the scaling down of transistors by modulating the doping process of semiconductors. For this application, the control of the amount and the position of dopant atoms in the semiconductor can be carried out by the use of a polymer containing the dopant atom. Then, the doping process can be performed through a “grafting to” approach. A thin layer of the dopant containing polymer can be deposited onto a silicon wafer surface. Then, the polymer is covalently grafted to the silicon surface by a thermal annealing process. In this way, a dopant layer is obtained. The control of the density of the dopant atoms occurs through the steric hindrance of the dopant containing polymer.

Polymers with a narrow polydispersity index such as polystyrene and poly(methyl methacrylate) with a terminal phosphate moiety have been employed to perform deterministic doping¹. However, during the grafting to reaction, discrimination by molecular weight has been reported so the control of dispersity is still a challenge. Therefore, there is the need of developing novel polymer systems featuring true monodispersity of molecular weight. Polypeptoids are precision polymers endowed with a structure versatility promising for the present application. Polypeptoids can be synthesized by solid-phase submonomer synthesis that allows to control of the unit sequence as well as the molecular weight.

In this work, four polypeptoids with different unit numbers (5-10-14 and 19 units) with a terminal unit containing a phosphorus moiety were synthesized with a dispersity near to one, as determined by MALDI TOF analysis. Then these polypeptoids were tested for the grafting to reaction. The optimized thermal annealing conditions resulted 190°C and 40 s. This procedure is suitable for industrial integration. Finally, the phosphorus dose at the silicon surface was determined by TOF SIMS analysis. An inverse correlation was found between the phosphorus dose and the polypeptoid length.

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ADDITIVE MANUFACTURING OF POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE)-BASED COMPOSITES FOR BONE REGENERATIONGIANNI PECORINI¹, SIMONA BRACCINI¹, FEDERICA CHIELLINI¹, DARIO PUPPI¹¹*Department of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 3, 56126 Pisa (Italy) – Email of the presenting author: gianni.pecorini@phd.unipi.it***Abstract**

Polyhydroxyalkanoates are biopolyesters synthesized by various microorganisms. Thanks to their biodegradability, mechanical properties and processing versatility, they have become unique candidates for research and industrial application [1]. Additive Manufacturing (AM) uses advanced technologies to fabricate parts by joining materials layer-by-layer. Their ability to fabricate 3D objects directly from a digital representation makes them excellent alternatives compared to traditional manufacturing [2]. In this contribution poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) processing in combination with osteoinductive inorganic fillers was investigated by employing computer-aided wet-spinning (CAWS), a solution/suspension-extrusion AM technique. The effect of PHBV blending with poly(D,L-lactide-co-glycolide) (PLGA), an amorphous poly(α -hydroxyacid), on processing and the fabricated prototypes properties was also evaluated to develop optimized scaffolds for bone regeneration.

PHBV, PLGA, and hydroxyapatite (HA) particles were blended as a chloroform suspension and processed by CAWS through extrusion into an ethanol coagulation bath. The fabricated prototypes were characterized by scanning electron microscopy (SEM), contact angle (CA) measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), compression tests, and preliminary *in vitro* cell culture tests.

3D porous prototypes were fabricated by CAWS starting from PHBV/HA and PHBV/PLGA/HA suspensions at different weight ratio. SEM analysis on the obtained structures showed better aligned and smoother fibers for PHBV/PLGA/HA samples, as well as a more defined porosity along z axis and the presence of two distinct polymeric phases resulting, for particular blend compositions, in a microfibrillar morphology of the dispersed phase. CA measurements showed an increase of scaffold wettability by increasing PLGA content in the blend. Thermal analysis showed an increase in the degradation temperature and a decrease of crystallinity after blend formation, while compression tests revealed a comparable modulus for the fabricated prototypes. Scaffolds also sustained *in vitro* proliferation and differentiation of murine preosteoblasts.

The better processability of PHBV/PLGA/HA suspensions compared with PHBV/HA ones was probably due to an increase in viscosity. This aspect can be exploited to obtain a more precise and reproducible fiber deposition and to control scaffold morphological properties like pores dimension and surface roughness, as well as the intrinsic wettability and crystallinity of the resulting material, without affecting sample's mechanical properties.

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2. Puppi D.; Chiellini F. Biodegradable Polymers for Biomedical Additive Manufacturing. *Applied Materials Today* **2020**, *20*, 100700, DOI: 10.1016/j.apmt.2020.100700

**SELF-HEALING AND SHAPE-MEMORY HYDROGELS BY MICELLAR
POLYMERIZATION**

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Abstract

Hydrogels are three-dimensional polymeric network with the capability to absorb a large amount of water or biological fluids. Usually, these materials are made of hydrophilic crosslinked polymer chains able to swell in water and present a soft rubbery consistency similar to living tissues. For this reason, hydrogels are used for biomedical, biotechnology and pharmaceutical applications [1,2]. The crosslinker nature separates hydrogels in two large families namely chemical or physical crosslinked. In the former, crosslinking is obtained by covalent bonding the chains either during the polymerization or in a post polymerization process [3]. In the latter, 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 involves a hydrophilic monomer (acrylamide), a hydrophobic monomer (octadecylacrylate, C18A), a surfactant (sodium dodecyl sulfate), and a salt (sodium chloride). The polymerization was initiated using a redox initiator consisting of ammonium persulfate and sodium metabisulfite. In addition, a multifunctional monomer, divinylbenzene (DVB), was used with the aim of creating branched chains and evaluating their effect on the material characteristics. Three series of samples were prepared by varying the amount of octadecylacrylate and divinylbenzene.

The samples were characterized with thermal (DSC) and rheological analysis, both before and after each purification steps. As the concentration of C18A increases, the amount of water within the hydrogels decreases. In addition, the melting and crystallization enthalpies of the hydrophobic domains increase, and in a parallel fashion an increase in mechanical modulus G' takes place.

Furthermore, as the DVB concentration increases, the water content decreases, and the mechanical modulus G' increases. This effect is probably due to the formation of additional chemical crosslinkings within the polymer network.

The self-healing behavior of these materials was also demonstrated by several rheology measurements and other specific experiment. As the DVB concentration increases, the self-healing efficiency decrease and so does the shape-memory behavior. Heating the materials above T_m , hydrogels could be deformed into different shapes that can be fixed on cooling. Then, heating again above T_m , the original shape is recovered. This effect can be observed only for samples containing more than 20% of hydrophobic monomer.

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DEVELOPMENT OF CELLULOSE-BASED FOOD PACKAGING MATERIALS

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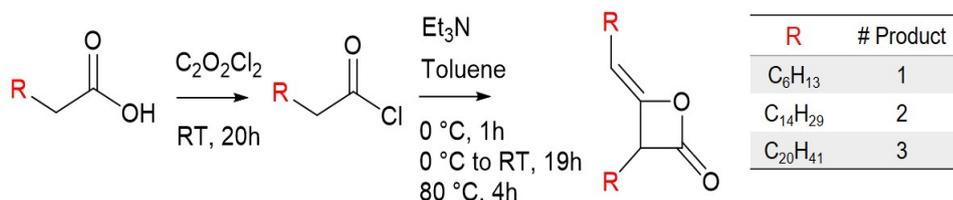
Abstract

Cellulose is the most abundant renewable biopolymer that exists in natural resources and has been used as material for packaging and other applications owing to its peculiar features such as biodegradability, low cost, light-weight, and easy recyclability. However, cellulose cannot be processed by conventional technologies (such as extrusion) and is a hydrophilic matrix that tends to strongly interact with water. Therefore, the development of cellulose-based food packaging is not simple and requires a very thorough study. With the goal of producing hydrophobic and easily recyclable cellulose-based packaging, both the technological aspects of cellulose dry molding and the characteristics of the material to be moulded were studied.

The first phase of the project involved the synthesis of hydrophobic additives formed by a 4-membered β -propiolactone ring system (alkyl ketene dimers, *AKDs*).

The chemical structure of these additives includes a group that allows ester bond formation with cellulose and two alkyl chains to increase the water repellency of the final object.

Therefore, three *AKDs* formed by alkyl chains with different numbers of carbon atoms ($R = C_6, C_{14}$ and C_{20}) were synthesized and tested.



Different *AKDs* synthesized for cellulose hydrophobization

Once the additives were synthesized, the addition of these substances to cellulose was investigated in depth. Two strategies for functionalization of cellulose fibers (β -ketoester production) and two strategies for physical mixing of cellulose fibers with the synthesized hydrophobizing additives were developed.

Among the additive methods developed, the most sustainable one is the addition of the different *AKDs* to cellulose via an aqueous suspension. Since *AKDs* are not stable in emulsion, cationic starch¹ was synthesized as a biodegradable retention aid. Indeed, cationic starch stabilizes the emulsion through the phenomenon of hetero-coagulation and enables the retention of *AKDs* on cellulose fibers.

Product 2 shows the best results in terms of emulsion stability and resistance to hydrolysis at different pHs, as well as being easy to synthesize compared with the high molecular weight *AKD*. Once the best emulsification conditions between the different *AKDs* and cationic starch were found, the emulsions were applied to the fibers by rotary evaporator drying, by which the additive is optimally dispersed among the fibers through gradual heating.

The last phase of the project involved hot pressing of cellulose fibers additivated with different weight percentages of medium molecular weight *AKD*/cationic starch blends. The moulded samples are hydrophobic and suitable for recyclable food packaging applications.

¹Yang, L. et al. Nanocrystalline cellulose-dispersed *AKD* emulsion for enhancing the mechanical and multiple barrier properties of surface-sized paper. *Carbohydrate Polymers* **2016**, 1035-1040.

POLYMERIC ANION EXCHANGE MEMBRANES FOR GREEN HYDROGEN PRODUCTION

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Abstract

Producing hydrogen by using anion exchange membrane (AEM) water electrolysis is a promising approach to address the severe energy crisis facing human society. AEM electrolysis can be integrated with renewable energy sources and utilizes low-cost electrocatalysts and other inexpensive components in stacks. To enable commercially viable hydrogen generation, improvement of the AEM component is imperative,^[1] and the goal of fabricating a membrane, in which the chemical, mechanical and electrochemical requirements are combined and optimized in a synergistic way, still represents a challenging task.^[2,3] The present work was, therefore, aimed at addressing several unique features of AEMs for implementation in an industrially scalable and sustainable energy- production process through a suitable synthetic strategy that involves the post-modification of a commercially available poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) triblock copolymer matrix by grafting vinylbenzyl chloride (VBC). The synthesized SBS-*g*-VBC copolymers were, therefore, used for the fabrication of AEMs by solution casting followed by quaternization reaction with trimethylamine (TMA) for the quantitative conversion of $-\text{CH}_2\text{Cl}$ into $-\text{CH}_2(\text{CH}_3)_3\text{N}^+$ groups. Obtained films were thermally, mechanically and electrochemically characterized. By varying the VBC functionalization degree of the copolymers it was possible to modulate the ionic exchange capacity, conductivity, water uptake and mechanical properties of the membranes derived therefrom. The most promising AEM was selected for testing in electrolytic cells and was found to resist to real operating conditions for more than 2200 hours.

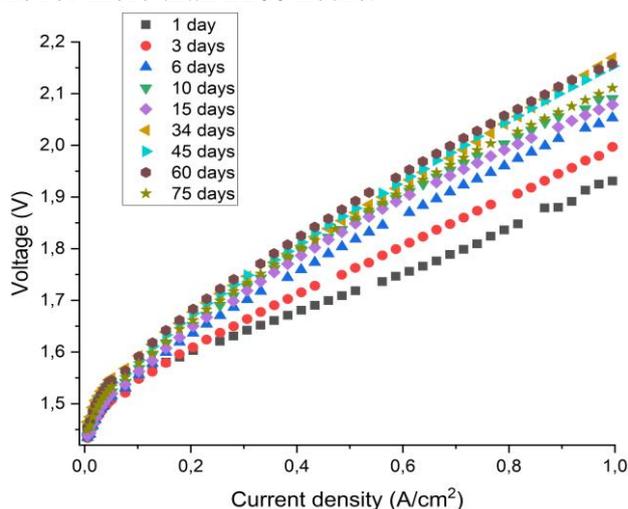


Figure 1. SBS-*g*-VBC based AEM (left) and polarization curves of the AEM as a function of residence time in an electrolytic cell (KOH 1 wt % at 55 °C) (right).

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Highly electron-donor copolymeric ligands as promotor/inhibitor agent in redox nanocatalysis

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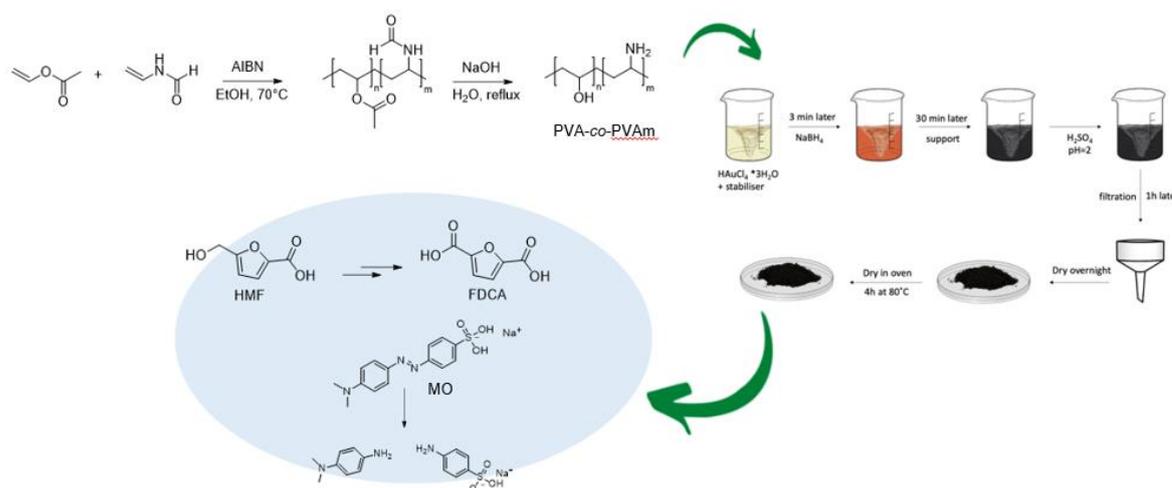
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Abstract

Several researchers have recently highlighted the role of polymeric stabilizers used to prevent metal colloidal nanoparticles aggregation like a tool able to tune the electronic properties of the nanomaterials as well as their size, shape and morphology.^{1,2}

In this optic, the development of customized macromolecules with a controlled molecular weight, composition or the presence of specific functional groups have been studied in order to rationalize their influence on the nanocatalysts in terms of conversion, selectivity and availability of active sites. Moreover, the employment of high electron donor groups (aminic, phosphinic) can be led an increase of electronic density charge on the particles surface and therefore promote or inhibit the catalytic mechanism during the redox reactions.^{3,4}

On this purpose, the effect of PVA-co-PVAm copolymers was investigated focussing on the properties of nanogold supported catalysts employed in two different reaction: hydroxymethyl-furfural (HMF) oxidation and methyl orange (MO) reduction. In particular, a series of copolymers with different composition have been synthesized and used like stabilizers to prepare Au/AC catalysts by sol immobilization approach. The as-prepared materials were tested on the chosen reactions and the study of their mechanism have allowed to determine the peculiar effect derived from the presence of the aminic group on the catalysis route.



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NEW AMPHIPHILIC BLOCK COPOLYMERS AS STABILIZERS FOR LIPID DRUG DELIVERY NANOPARTICLES

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Abstract

One of the main issues to face in nanomedicine is the scarce solubilisation of therapeutic molecules when injected into the organisms, as well as, the selective release to the target site of the disease. In the last years, drug delivery systems (DDS) tried to solve these drawbacks increasing the solubility of the loaded molecules, producing a spatial and temporal controlled release. Lipid assemblies, thanks to their biocompatibility and similarity with the plasma membrane, are considered the most suitable candidates for DDS. In particular, complex lipid assemblies such as cubosomes possess an improved loading capacity and are considered emerging drug delivery vectors¹ for their many fascinating characteristics, like high stability, versatility, tunable morphological characteristics, and a large specific surface area. To date, cubosomes are applied in biomedical applications as a promising platform for the in-vivo delivery of molecules of pharmaceutical and imaging interest².

With this in mind, we have designed a novel class of stimuli-responsive drug delivery systems, using body temperature as a non-invasive stimulus. The new class of drug delivery systems consists of cubosomes of the lipid glycerol-monooleate (GMO) were stabilized by a recently synthesized thermo-responsive polymer poly(N,N-dimethylacrylamide)-b-poly(N-isopropylacrylamide) (PDMA-b-PNIPAM) in place of the conventional Pluronic F127 (PEO-b-PPO-b-PEO). This copolymer contains a thermo-responsive block of PNIPAM which changes its polarity from hydrophilic to hydrophobic in water, when the temperature rises above its lower critical solution temperature³, at a temperature close to physiological conditions. Using a combination of complementary experimental techniques (Dynamic Light Scattering (DLS), Quartz Crystal Microbalance with Dissipation monitoring (QCM-D), Small-Angle X-ray Scattering (SAXS), Cryogenic Electron Microscopy (Cryo-EM)) cubic dispersions stabilized by two block copolymers of DMA-b-NIPAM of Mn = 10.000 g/mol and 20.000 g/mol, respectively, were prepared. Their physicochemical properties were investigated and studied with model membranes, comparing the results with the standard dispersions stabilized by the polymer Pluronic F-127.

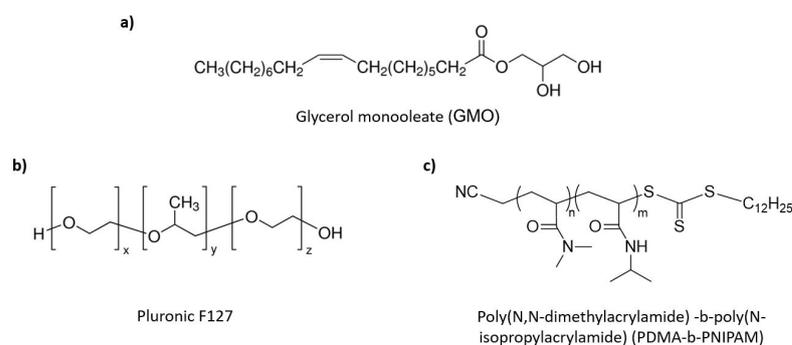


Figure 1. Chemical structures of the lipid glycerol monooleate (GMO) (a) and of the stabilizers Pluronic F127 (b) and poly(N,N-dimethylacrylamide)-b-poly(N-isopropylacrylamide) (PDMA-b-PNIPAM) (c).

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**EFFECT OF NATURAL FIBERS ON DEGRADATION OF POLYLACTIC ACID
BIOCOMPOSITES**LIBERA VITIELLO¹, MARTINA SALZANO DE LUNA¹, SABRINA C. CARROCCIO², GIOVANNI FILIPPONE¹¹*Department of Chemical, Materials and Production Engineering, University of Naples Federico II,
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To mitigate the plastic pollution problem, biopolymers represent one of the most interesting solutions. These “green” plastics have the inherent advantage of being produced from renewable resources and, more important, they can be biodegradable or compostable. The latter point is highly desirable to reduce the environmental footprint. Many plastics are biodegradable, but the time needed to complete the process can be very long¹. The challenge is shortening this time as much as possible while preserving the plastics properties. In the present study, this ambitious goal is pursued exploiting the inherent pro-degradation ability of natural fibers. To reach this goal, biopolymeric matrices susceptible to hydrolysis and hygroscopic vegetal fibers were combined into green composites. The hemicellulose fraction of the fibers acts as water vehicle that triggers the hydrolysis of matrix. The shortened polymer chains can be hence mineralized by microorganisms². To exploit the full potential of the pro-degradative effect of the fibers, the optimal material-related parameters to speed up biodegradation were investigated and the properties of selected biocomposites were assessed. Polylactic acid-based composites filled with different volumetric percentage fibers of hemp shives and kenaf bast were prepared using a batch mixer. Degradation phenomena were investigated by rheological analysis to evaluate degradation over time of the biocomposites in the molten state. The results showed that the complex viscosity progressively decreases while testing. The reduction is more pronounced for the composite, meaning that the fibers promote matrix degradation. From a chemical point of view, in the temperature range considered, hydrolytic degradation can be considered the predominant mechanism³. Therefore, the hydroxyl groups of natural fibers trigger the matrix degradation. To study biodegradation in the solid state, hydrolytic degradation in vivo was carried out. The hydrolytic degradation tests were performed by immersing the samples in 50 mL of natural water at 45°C for 7 weeks. The biodegradation rate was estimated by evaluating changes in the viscoelastic properties of the samples using dynamic mechanical thermal analysis. The glass and rubbery modulus, which represent the mechanical behavior above and below the glass transition temperature of the samples, showed a decrease with soaking time. The loss in the mechanical performance indicates an advance in PLA degradation which resulted relevant in samples with high volumetric fiber contents. The results confirm that natural fibers can be exploited to accelerate the degradation of hydrolysable polymeric matrices.

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THE ROLE OF POLYMERIC HYDROGELS FOR BIOLOGICAL TISSUE CLEARING

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Abstract

Polyacrylamide gels have been used in many different fields: from biological laboratories, as a medium for electrophoresis application for protein separation to industries for papermaking and fossil fuel production.

An unconventional use of these polymers is to clarify biological tissue clearing. In the last years, new clearing approaches based on tissue transformation have been developed to reconstruct entire organs, avoiding tissue slicing. In my project; I used CLARITY method¹ to make mouse brain transparent. The basic idea behind CLARITY is to transform a biological tissue, in our case brain, into a hydrogel–tissue hybrid. The hydrogel, which is mainly composed of acrylamide monomers, has the function of stabilizing dispersed proteins and nucleic acid by covalent bonds. This technique allows to reconstruct whole-brain maps of activated neurons during the many phases of aversive memory to address specific treatment for patients affected by post-traumatic stress disorders.



¹ Chung et al. *Nature* 2013

SHAPING GELATIN-BASED HYDROGELS: FROM THE CROSS-LINKING MECHANISM TO THE PREPARATION OF MICROPARTICLES FOR BIOMEDICAL APPLICATIONS

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Abstract

Gelatin is a biopolymer derived from the denaturation of collagen which is endowed with many attractive features such as biocompatibility, biodegradability, non-immunogenicity, availability, and versatility¹. This polymer has found numerous applications in food, cosmetics and in the biomedical field, but often requires a cross-linking treatment to improve its thermal stability in physiological conditions.

In this contribution an overview about different gelatin-based materials developed in our group will be given, focusing on materials targeted for biomedical applications.

First, different strategies for cross-linking gelatin will be presented, showing how different chemical cross-linking agents, namely glutaraldehyde and glycerinaldehyde, impact hydrogels properties². Different cross-linking conditions were tested, and the hydrogels were investigated in terms of physico-chemical properties, morphology, nanoscale structure, mechanical and diffusional properties.

Then, the possibility of using gelatin to prepare porous microparticles will be described³. An oil-in-water-in-oil emulsion method was used to this purpose, modifying the synthetic parameters such as gelatin/surfactant ratio and the stirring speed to tune their size and porosity. The effect on the structural properties, including surface and inner porosities, was assessed by multiple microscopy techniques (optical, electron, and confocal Raman). Selected samples were then cross-linked, and their swelling properties and stability against dissolution were evaluated, while the influence of the cross-linking at the nanoscale was studied by scattering of X-rays. Depending on the preparation protocol, we obtained particles with different shapes and porosities, demonstrating the possibility to design microparticles with tunable features that are promising for the use as micro-scaffolds for cells growth.

Gelatin microparticles were also used as templating agents for the creation of macro-porosities in magnesium phosphate-based cements (MPCs)⁴. These materials, which are promising as bone void fillers in orthopedic applications, are not endowed with hundreds of μm -sized pores, which would be important to promote cells permeation and the growth of new tissue. To overcome this issue, gelatin microparticles prepared with a water-in-oil emulsion method were included in cement formulations. Upon incubation in physiological conditions, the microparticles dissolve, resulting in a macroporous MPC. Moreover, gelatin microparticles were loaded with alendronate (a drug commonly used as anti-osteoporotic agent) in order to achieve a local delivery action during their dissolution, endowing the obtained material with functional properties.

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**MAIN CHAIN AZOBENZENE POLYMERS:
DOES SEQUENCE CONTROL ENABLE CONTROL OF DEGRADATION?**

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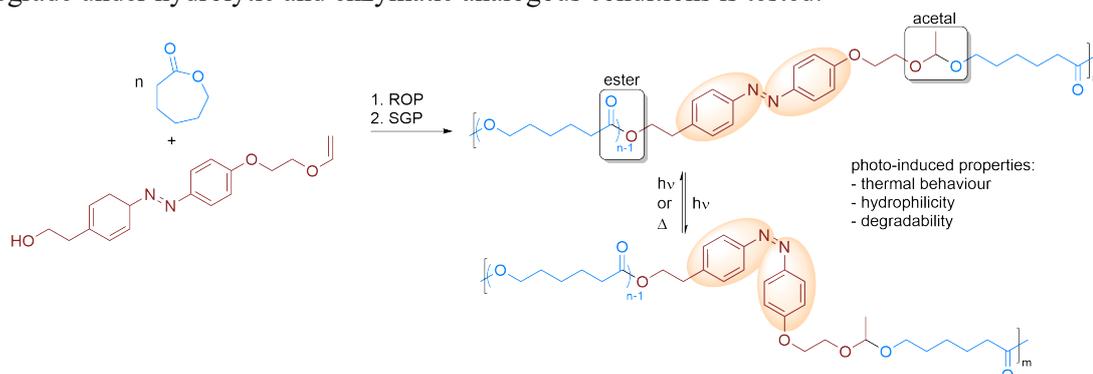
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Abstract

Polymer degradation is one essential feature that will enable the circular economy of polymeric materials.¹ The mere presence of degradable functions (e.g. ester groups) within the polymer backbone, however, does not automatically lead to a material with desired degradation behaviour. Degradation of polylactide, for instance, leads to a loss of material properties within weeks (service life), whereas the total erosion of the material takes years. An elegant solution that could equal the service life and the time required for the total erosion of the polymeric material is a triggered degradation.

To develop a polymer that's degradation could be triggered by UV light irradiation, herein, the synthesis of a main chain azobenzene polymer is described. A polymerization technique² that allows for sequence control is used to incorporate light-responsive azobenzene groups into the main-chain of a polymer. The azobenzene groups are separated by polycaprolactone (PCL) blocks of selectable length and are linked by degradable acetal groups.³ This synthetic approach is not limited to the chosen monomers, thus, polymers with other azobenzene derivatives and polyesters could be synthesized as well. Upon irradiation the polymer with UV light, the azobenzene groups isomerize from trans to cis. The influence of different PCL block lengths and the possible effect of isomerisation on the thermal behaviour of the polymers are investigated. Furthermore, the ability of these polymers to degrade under hydrolytic and enzymatic analogous conditions is tested.



Scheme 1: Ring-opening polymerization (ROP) of caprolactone and subsequent step-growth polymerization (SGP) yields a main-chain azobenzene polymer.

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Ring-Opening Polymerization Catalyzed by New NSSN-type Group IV Metal Complexes

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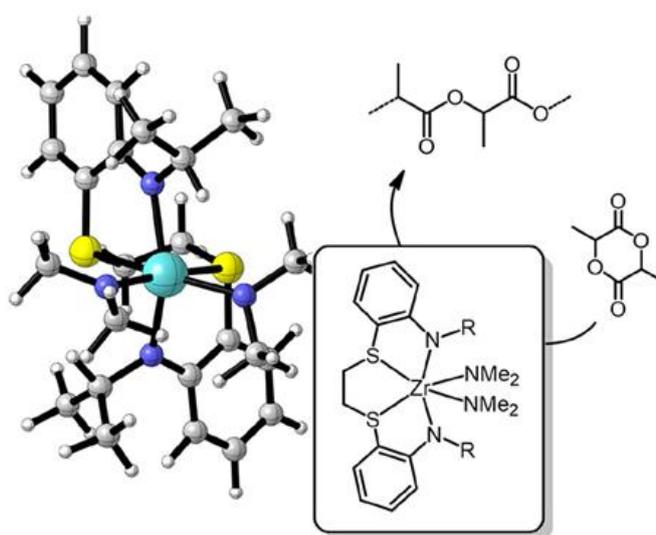
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Abstract

The aliphatic polyesters can be considered an interesting alternative to conventional polymer of petroleum origin. The ring-opening polymerization (ROP) of cyclic esters allows obtaining aliphatic polyesters using mild reaction conditions and avoids the formation of small molecule byproducts. ROP using metal catalysts turns out to be particularly efficient as it allows obtaining controlled molecular masses. Group 4 metal complexes are particularly interesting as they show: low toxicity, high activity, good control over polymerization process and stability even in the presence of protic impurities.¹ In this work, a new class of zirconium and hafnium complexes coordinate by linear dianionic tetradentate NSSN ligands is reported.



The ligands feature two amide functions coupled with two thioether groups linked by a central flexible ethane bridge and two lateral rigid phenylene bridges and differ for the substituent on the aniline nitrogen atoms, i.e. isopropyl, cyclohexyl or mesityl substituents. The synthesis of ligands start by reacting of 2-aminothiophenol with 1,2-dibromoethane to afford the NSSN ligands without substituents on the aniline nitrogen atoms. Subsequently, the aniline function was alkylated through a reductive amination with acetone or cyclohexanone, or palladium-catalyzed cross coupling reaction with mesityl bromide. The corresponding Zr and Hf complexes were obtained through a transamination reaction between the neutral ligands and Zr(NMe₂)₄ or Hf(NMe₂)₄.² They were characterized by NMR spectroscopy and X-ray diffraction analysis (except complex with mesityl group). In all the cases, a distorted octahedral coordination geometry around the metal atoms was observed. All the complexes adopt a pseudo C₂-symmetrical configuration with two *cis*-arranged dimethyl-amine groups. The catalytic performances of complexes in the ring-opening polymerization of cyclic esters, such as L-Lactide, were investigated. The zirconium complex with isopropyl group resulted the most active: its polymerization activity was superior to those generally displayed by zirconium complexes featuring OSSO ligands and well compare with that of the most active group IV complexes operating in toluene solution.³

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