XXVI Convegno Nazionale

ASSOCIAZIONE ITALIANA di SCIENZA e TECNOLOGIA delle MACROMOLECOLE



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Politecnico di Torino

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Il PROGRAMMA

Plenary lecture
Keynote lecture

Polimeri da fonti rinnovabili e degradabili, riciclo
Materiali polimerici ibridi e (nano)compositi: sintesi, caratterizzazione e applicazioni
Processabilitá e stampa 3D di materiali polimerici
Chimica e fisica dei polimeri

DOMENICA 6 SETTEMBRE

Politecnico di Torino – Corso Duca degli Abruzzi 24

18:00		Registrazione
19:00		Welcome party

LUNEDÌ 7 SETTEMBRE

Polo Biotecnologico dell'Università di Torino (Via Nizza 52)

8:30		Registrazione
9:00		**Apertura lavori - Sala Keplero**
		Chairperson: R. Bongiovanni
9:10	**PL1**	**Y. Leterrier** (Ecole Polytechnique Fédérale de Lausanne) Robust superhydrophobic composite surfaces
10:00	**KN1**	**A. Dodero** (University of Fribourg) Block copolymer self-assembly in emulsions: from structural-color microparticles to multifunctional and reprogrammable photonics
10:30		*Coffee break*

PARALLEL SESSIONS

		Sala Keplero		**Sala Leonardo**
		Chairperson: M. Salzano de Luna		*Chairperson: R. Simonutti*
11:00	**O1.1**	**A. Barbato** (Università di Salerno) Development of active biodegradable PLA/PBSA films containing blueberry waste antioxidants extracted using nades as green solvents	**O3.1**	**A. Bardelli** (Università di Genova) From marine plastic litter to 3D printing: optimising blended polyolefin formulations for additive manufacturing
11:15	**O1.2**	**B. Brugnoli** (Università di Roma – La Sapienza) Multifunctional eugenol-based nanogels through copolymer design: antioxidant activity, intrinsic fluorescence, and drug encapsulation	**O3.2**	**R. Di Girolamo** (Università di Napoli Federico II) In situ stereocomplex formation during melt extrusion: an efficient nucleating strategy for crystallization of high-molecular weight PLA
11:30	**O1.3**	**A. D'Ilorio** (Università di Ferrara) Solvent-free grafting of pbs oligomers onto cellulose nanofibers for enhanced biocomposite compatibility	**O3.3**	**A. Sorze** (Università di Trento) Effect of natural fillers as substitutes for glass fibers in polyamide 6 composites for large-format additive manufacturing
11:45	**O1.4**	**M.R. Acocella** (Università di Salerno) Mechanochemical polymer-to-polymer recycling of polylactic acid	**O3.4**	**E. Togliatti** (Università di Parma) Influence of graphene on the electrical and mechanical properties of SLS-printed PA11
12:00	**O1.5**	**F. Bisio** (Università del Piemonte Orientale) (Meth)-acrylated tannic acid as a bio-based adhesion promoter for EB-curable coatings	**O3.5**	**D. Rigotti** (Università di Trento) Fused filament fabrication of TPU/PCM composites for thermally active wearable sport applications
12:15	**O1.6**	**G. Damonte** (Università di Genova) Environmentally friendly upcycling of PHA-based copolymers into branched multifunctional oligomers	**O3.6**	**A. Caccini** (Politecnico di Milano) Extending rubber fracture characterisation methods to layer adhesion assessment in 3D-printed TPU
12:30		Lunch time		

LUNEDÌ 7 SETTEMBRE (cont.)

		Sala Keplero		
		Chairperson: K. Sparnacci		
14:30	**KN2**	**V. Ambrogi** (Università di Napoli Federico II) Rethinking epoxy thermosets: from dynamic networks to circular materials		
		SESSIONI PARALLELE		
		Sala Keplero		**Sala Leonardo**
		Chairperson: P. Stagnaro		*Chairperson: C. Marano*
15:00	**O1.7**	**M. Calosi** (Università di Ferrara) Amorphous blends of PLA and PHA for waterborne coatings and foam applications	**O2.1**	**A. Bifulco** (Università di Napoli Federico II) Transparent and self-extinguishing silica-epoxy nanocomposites based on Novolac resin
15:15	**O1.8**	**R. Chiarcos** (Università del Piemonte Orientale) Investigation into the potential of poly(β-amino ester)-based vitrimers	**O2.2**	**L. Broggio** (Università di Trento) Solvent-free processing of high β-phase poly(vinylidene fluoride) films for energy conversion applications
15:30	**O1.9**	**S. Alfano** (Università di Roma – La Sapienza) Formulation and characterization of polyhydroxyalkanoate blends with waste protein fibers for packaging application	**O2.3**	**E. Buratti** (Università di Ferrara) Hybrid microgels based on PNIPAM and natural proteins: from molecular interactions to biomaterial applications
15:45	**O1.10**	**A. Giovagnoli** (Università di Bologna) Development and industrial processing of cellulose-based materials for rigid packaging applications	**O2.4**	**M.T. Letizia** (Istituto Universitario di Studi Superiori Pavia) Towards sustainable electrical cable insulation: design of a novel polyethylene-based composite system
16:00	**O1.11**	**D. Gaikwad** (Università Milano Bicocca) Use of fruit peels for the development of bio-based hydrogels	**O2.5**	**C. Ciarlantini** (Università di Roma – La Sapienza) Cyclodextrin-grafted chitosan scaffolds for enhanced curcumin delivery
16:15	**O1.12**	**G. Filippone** (Università di Napoli Federico II) Effect of processing pressure on the interfacial shear strength in short fiber biocomposites: implications for manufacturing	**O2.6**	**B. Bertoncini** (Università di Pisa) Long vs. short chain covalent functionalization in the preparation of mechanochromic polymers
16:30		*Coffee break*		
18:00		*Torino Tour – Ritrovo in Piazza San Carlo, di fronte al monumento*		

MARTEDÌ 8 SETTEMBRE

Polo Biotecnologico dell'Università di Torino (Via Nizza 52)

Sala Keplero

Chairperson: G. Malucelli

9:00	**PL2**	**D. Beneventi** (University Grenoble Alpes) Cellulose fibres and derivatives: from traditional papermaking to advanced additive manufacturing
9:50	**KN3**	**S. Losio** (Istituto di Scienze e Tecnologie Chimiche) Cyclic olefin based copolymers via transition metal catalysis: bridging synthesis and functional application
10:20		*Coffee break*

SESSIONI PARALLELE

		Sala Keplero		**Sala Leonardo**
		Chairperson: A. Dorigato		*Chairperson: A. Pucci*
10:50	**O2.7**	**A. Bianucci** (Politecnico di Milano) Effect of silane coupling agent content on strain-induced cavitation in silica-filled SBR	**O4.1**	**C. Cecone** (Università di Torino) Electrospun membranes obtained from plant proteins and maltodextrins for the treatment of gadolinium-contaminated wastewater
11:05	**O2.8**	**S. Gabellini** (Università di Bologna) Synthesis and nanostructuration of DPP-based fluorescent polyesters for bioimaging	**O4.2**	**M. Turriani** (Università di Pisa) From amphiphilic random copolymers to functional nano-chelators: a new strategy for radionuclides sequestration
11:20	**O2.9**	**C. Imparato** (Università di Napoli Federico II) Silica-based nanostructured mixed oxides via sol-gel for the enhancement of fire resistance and recyclability of epoxy resins	**O4.3**	**L. Tosato** (Università di Bologna) A novel melamine-free waterborne intumescent coating for fire protection of wood
11:35	**O2.10**	**L. Gianoglio** (Università di Torino) Electrospun maltodextrin-derived carbon fibers: a sustainable platform for gold-based catalysts	**O4.4**	**J.A. Talamo Ruiz** (Politecnico di Torino) Electrospinning and solution blow spinning of water-based polymer solutions for the sustainable manufacturing of nanofibrous mats
11:50	**O2.11**	**A. Liguori** (Università di Bologna) Multifunctional and sustainable vitrimer systems	**O4.5**	**M. Scoti** (Università di Napoli Federico II) Tacticity-independent crystallization as a design strategy for chemically recyclable semicrystalline polymers
12:05	**O2.12**	**A. Nicosia** (Università di Catania) Functional polymers for the optical detection of amines: from bio-inspired to natural sensing units	**O4.6**	**G. Pignatiello** (Università di Napoli Federico II) Structure-property relationships in biopolymeric cryogels produced by freeze-casting
12:20	**O2.13**	**M. Righetti** (Università di Torino) Intercalated sodium bentonite in thermoplasticized corn starch: tuning oxygen barrier and mechanical performance for flexible food packaging applications	**O4.7**	**F. Olla** (Politecnico di Milano) Pressure-induced crystallization and polymorphic transitions of polybutene-1: high-pressure PVT study
12:35	**O2.14**	**F. Passoni** (Politecnico di Milano) Study of the high-pressure H_2 exposure effect on the mechanical behaviour of nbr based compounds	**O4.8**	**E. Guazzelli** (Università di Pisa) HEMIN-based amphiphilic random copolymers as biomimetic and recyclable catalysts for ARGET-ATRP in water
13:00		Lunch time		

MARTEDÌ 8 SETTEMBRE (cont.)

	Sala Keplero			
	Chairperson: P. Bracco			
14:30	**KN4**	**C. Zagni** (Università di Catania) Functionalized polymeric materials: versatile macromolecular platforms for pharmaceutical and environmental applications		
	SESSIONI PARALLELE			
		Sala Keplero		**Sala Leonardo**
		Chairperson: P. Russo		*Chairperson: D. Caretti*
15:00	**O1.13**	**M. Colombo** (Politecnico di Milano) Structural control and amyloid reinforcement of waste-derived protein films	**O2.15**	**L. Simonini** (Università di Trento) Development and characterization of sandwich composites with thermal management and mechanical properties
15:15	**O1.14**	**V. La Matta** (Università di Napoli Federico II) Prospective life cycle assessment of tyre manufacturing: evaluating industrial decarbonisation pathways	**O2.16**	**R. Medri** (Università di Bologna) Eco-friendly dye–porphyrin copolymer for organic solar cells: from ternary donor to interfacial layer
15:30	**O1.15**	**N. Ferrentino** (Università di Salerno) From thiol-ene chemistry to bio-based polymeric networks: multifunctional limonene-derived materials	**O2.17**	**A. Riccioni** (Politecnico di Torino) Furanized cellulose nanocrystals for the preparation of diels-alder rubber composites
15:45	**O1.16**	**C. Di Bernardo** (Politecnico di Torino) Emerging concepts for sustainable biocomposites	**O2.18**	**R. Rossi** (Università di Firenze) Smart polymeric architectures based on photoswitches: from adhesives to responsive nanocarriers
16:00	**O1.17**	**A. Longo** (IPCB-CNR) Tuning PLLA Crystallization Kinetics via Reactive Extrusion Branching Strategies	**O2.19**	**P. Stagnaro** (SCITEC-CNR) Engineered polymer-based composites for radiative cooling systems
16:15		*Coffee break*		
16:30	**O1.18**	**M. Mollo** (Politecnico di Torino) Designing vanillin-based dynamic networks for the development of sustainable thermosets for future generation composites	**O2.20**	**L. Vitiello** (IPCB-CNR) Enhanced hydrolytic degradation of pla green composites by nanometric zno covalently bound on natural fibres via ALD
16:45	**O1.19**	**E. Pellegrino** (Politecnico di Torino) Melt-processing of dialcohol cellulose fibres/starch blends: processing strategies, structure and properties	**O2.21**	**V. Spinoso** (Università di Firenze) Capacitive sensor based on porous liquid crystalline gel
17:00	**O1.20**	**V. Giglio** (IPCB-CNR) Beyond biodegradability: comparative lc-ms profiling of plastic additive release from fossil-based and biodegradable agricultural mulch films into soil	**O2.22**	**A. Pucci** (Università di Pisa) Pyrolysis-derived telechelic polypropylene as a mechanochromic probe for visualizing stress redistribution and cavitation in polyolefin-based materials
17:15	**O1.21**	**C. Invigorito** (Anton Paar) Multiscale polymer analysis: correlating chemical structure, thermal behavior, and rheological response through complementary analytical techniques		
17:30		*Assemblea dei Soci*		
18:00		*Sessione Poster*		
20:30		Cena di gala @OGR Officine Grandi Riparazioni, Corso Castelfidardo, 22		

MERCOLEDÌ 9 SETTEMBRE

Polo Biotecnologico dell'Università di Torino (Via Nizza 52)

Sala Keplero

Chairperson: M. Zanetti

9:00	**PL3**	**A. Figoli** (Istituto per la Tecnologia delle Membrane - CNR) Innovative polymerised tailored membranes for gas and liquid applications
9:50	**KN5**	**D. Martella** (Università di Firenze) 3D printing meets liquid crystal polymers: responsive materials across different scales and applications
10:20		*Coffee break*

SESSIONI PARALLELE

		Sala Keplero		Sala Leonardo
		Chairperson: M. Messori		*Chairperson: M. Castellano*
10:50	**O1.21**	**D.H. Lamparelli** (Università di Salerno) When molecular imperfection works: sustainable polyester copolymers with industrial potential	**O2.23**	**P. Rizzo** (Università di Salerno) From hydrophobic to high-performance water filled polymeric films: a new paradigm in water purification materials
11:05	**O1.22**	**P. Russo** (IPCB-CNR) Natural antioxidant effect of hazelnut shell powder in PBS biocomposites under accelerated UV aging	**O2.24**	**S. Scurti** (Università di Bologna) Missive bottle-brush copolymers for soft opto-electronic via orthogonal polymerization
11:20	**O1.23**	**C. Noè** (Politecnico di Torino) Bio-based and antifungal by design: UV-cured eso/essential oil composites for next-generation active packaging	**O2.25**	**A. Dorigato** (Università di Trento) eEvaluation of the self-healing behaviour of multifunctional thermoplastic composite laminates
11:35	**O1.24**	**C. Pellecchia** (Università di Salerno) Engineering circular polyesters through molecular architecture: from thermoplastic elastomers to dynamic covalent networks	**O2.26**	**G. Proietto Salanitri** (Università di Bologna) Functional polymer hybrid hydrogels for multi-adsorption of oppositely charged emergent pollutants
11:50	**O1.25**	**R. Sergi** (Università di Roma – La Sapienza) Eugenol-derived polymeric networks as eco-friendly and circular wet-strength agents for high-performance paper products	**O2.27**	**C. Parmeggiani** (Università di Firenze) Shape-changing polymeric microparticles based on liquid crystal emulsions
12:05	**O1.26**	**F. Cano** (Università di Torino) Mechanical recycling of multi coupled material body seals based on thermoplastic elastomers in the automotive industry	**O2.28**	**R. Simonutti** (Università di Milano Bicocca) Fabrication of porous microparticles by RAFT polymerization
12:20			**O2.29**	**A. Fusari** (Politecnico di Milano) Investigating bacteria-driven alginate hydrogel matrix degradation: a rheological framework to discriminate between crosslinker depletion and backbone cleavage
13.00		Lunch time		

MERCOLEDì 9 SETTEMBRE (cont)

	Sala Keplero	
	Chairperson: G. Filippone	
14:00	**KN6**	**M. Bertoldo** (Università di Ferrara) Polyesters in water: from dispersion strategies to functional applications
14:30	**KN7**	**D. Natali** (Ecole Polytechnique Fédérale de Lausanne) *Macrogiovani 2026 Winner* 4D-Printable shape morphing double network granular elastomers (DNGEs)
15:00		Conclusioni e saluti finali
15:30		Coffee break

LISTA DEI *la* POSTERS

POSTER

Polimeri da fonti rinnovabili e degradabili, riciclo	
P1.1	**B. Cavallo** (Università di Torino) Development of cellulose fibers recovery strategy from siliconized papers
P1.2	**M. Ceraulo (Università di Palermo)** PBAT/grape pomace biocomposite for film blowing applications
P1.3	**S. Coiai (ICCOM-CNR)** Antioxidant and UVv-blocking poly(butylene succinate) films via nitroxide radical coupling functionalization
P1.4	**E. Di Francesco (Università di Genova)** Thermal method to recover glass fibers from epoxy resin composites
P1.5	**M. Di Maro (STEMS-CNR)** Influence of fast pyrolysis bio-oil-derived phenolic-rich fraction on PLLA UV stability
P1.6	**G. Fredi (Università di Trento)** Polyethylene glycol-assisted film stacking of polylactide/bacterial cellulose nanocomposites for sustainable food packaging
P1.7	**L. Gianoglio (Università di Torino)** Biopol4Soil- Bioderived polymeric granules and non-woven fabrics for sustainable agriculture:biodegradability and phytotoxicity evaluation
P1.8	**C. Meo** (Università di Ferrara) Characterization of hydrolyzed polyesters from agro-waste: effect of extraction conditions on composition
P1.9	**M.C. Mistretta (Università di Palermo)** Influence of glochids and xompatibilizer on the rheological, mechanical and biodegradation behaviour of PBAT and PLA biocomposites
P1.10	**P. Scarfato** (Università di Salerno) Circular valorization of post-consumer polyurethane foams through mechanical recycling and sustainable composite design
P1.11	**R. Simonutti** (Università di Milano Bicocca) Itaconic Acid: a sustainable platform alternative to acrylic acid in radical polymerization
P1.12	**S: Zeynalova** (Politecnico di Torino) Biobased vitrimers using eutectic hardener systems

Materiali polimerici ibridi e (nano)compositi: sintesi, caratterizzazione e applicazioni	
P2.1	**E. Caianiello** (IPCB-CNR) Graphene oxide functionalization of bacterial cellulose: effects on the structure and adsorption performance
P2.2	**F. Cicogna** (ICCOM-CNR) Residual antioxidant activity of winery by-product biofillers in LDPE and HDPE composites
P2.3	**L. Conzatti** (SCITEC-CNR) Upcycling hazelnut by-Products into functional elastomeric composites for sustainable sports surfaces
P2.4	**R. D'Auria** (IPCB-CNR) Development of lignin-containing biodegradable polymer blends for fishing net applications
P2.5	**D. Errico** (Università di Ferrara) Preparation and characterization of thermoresponsive films obtained from hybrid PNIPAM/silk fibroin systems
P2.6	**T. Landovsaky** (Institute of Physics of the Czech Academy of Sciences) Stabilization of magnetic nanoparticles in liquid crystalline polymers via tailor-made ligands
P2.7	**V. Fiore** (Università di Palermo) Development of PBSA-based biocomposites reinforced with ceiba speciosa natural fibres
P2.8	**G. Malucelli** (Politecnico di Torino) Physics-informed machine learning for predicting optical transmittance and haze in transparent wood
P2.9	**G. Malucelli** (Politecnico di Torino) Preparation and characterization of UV-LED curable bio-based coatings containing polymeric carbon dots
P2.10	**G. Malucelli** (Politecnico di Torino) Sustainable transparent wood based on bio-based isobornyl acrylate/methacrylate matrices
P2.11	**M. Morreale** (Università di Enna "Kore") Microplastics release from pp-based blends and nanocomposites
P2.12	**P. Stagnaro** (SCITEC-CNR) Sustainable routes to lead-free flexible piezoelectric polymer-ceramic films for energy harvesting

Processabilitá e stampa 3D di materiali polimerici	
P3.1	**R. Arrigo** (Politecnico di Torino) Processing as a design tool for tailoring microstructure and properties in complex polymer systems

Chimica e fisica dei polimeri	
P4.1	**A. Bandini** (Università di Pisa) Fluorine-free proton exchange membranes: synthesis and characterization of sulfonated PPO-PBI networks for pemwes
P4.2	**A. Frache** (Politecnico di Torino) Towards circular flame-retarded polypropylene: fire performance after recycling and aging
P4.3	**S. Pragliola** (Università di Salerno) Design of carbazole-functionalized poly(triphenylamine)s for VISIBLE-driven water remediation

Il COMITATO SCIENTIFICO



Sabrina Carola Carroccio

IPCB-CNR Catania



Silvia Vicini

UNIGE



Katia Sparnacci

UPO



Riccardo Chiarcos

UPO



Alberto Fina

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UNITO

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Chiara Gualandi



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UPO

La SEGRETERIA ORGANIZZATIVA



Diego Antonioli



Patrizia Barraco



Andrea Batistini



Maria Graziella Viola

Ecco i

PLENARY SPEAKERS



Ives Leterrier

EPFL Zurigo
Svizzera



Davide Beneventi

CNRS Grenoble
Francia



Alberto Figoli

ITM-CNR
Italia

PLENARY SPEAKERS

Plenary Lectures

ROBUST SUPERHYDROPHOBIC COMPOSITE SURFACES

Yves Leterrier

Laboratory for Processing of Advanced Composites (LPAC)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
CH-1015 Lausanne, Switzerland
e-mail: yves.leterrier@epfl.ch

The presentation is an overview of the activities carried out at the EPFL to produce robust bioinspired polymer composite surfaces [1]. Focus is on integrative synthetic strategies based on photopolymerization to achieve superior property combination such as self-cleaning, antireflectivity and wear-resistance. Hybrid organic-inorganic nanocomposites are produced using acrylate, epoxy and organosilane precursors with surface-treated silica nanoparticles and microfibrillated cellulose via a dual cure photopolymerization and thermal condensation process [2]. The dynamics of network formation are investigated using photo-hyphenated methods such as photo-rheology and photo-calorimetry. The optimization of the dual cure sequence, with the right timing of the photo-exposure vs. condensation leads to an improved printability and nanoscale shape fidelity owing to a reduced viscosity, and a superior hardness, up to several 100 MPa with a high loading of preformed particles. The addition of a reactive surfactant into the hybrid formulation further enables to control the surface energy of the composite via an enthalpy gradient migration from the bulk to the composite-air interface [3]. The subsequent replication of the surface of lotus leaves and rose petals with hierarchical roughness leads to superhydrophobic surfaces that are wear-resistant [4,5]. Ongoing work investigates photo-reversible chemistries to add self-repair and reshaping performance to the property portfolio.

1. González Lazo M.A., Katrantzis I., Dalle Vacche S., Karasu F., Leterrier Y., A Facile in Situ and UV Printing Process for Bioinspired Self-Cleaning Surfaces, Materials, 9, 738 (2016). DOI 10.3390/ ma9090738.
2. Poothanari M.A., Schreier A., Missoum K., Bras J., Leterrier Y., Photo-Cured Nanocellulose Composites: Recent Advances, ACS Sustainable Chem. Eng. 10, 3131−3149 (2022). DOI 10.1021/ acssuschemeng.1c07631.
3. Wasser L., Dalle Vacche S., Karasu F., Müller L., Castellino M., Vitale A., Bongiovanni R., Leterrier Y., Bio-Inspired Fluorine Free Self-Cleaning Polymer Coatings, Coatings, 8, 436 (2018). DOI 10.3390/coatings8120436.
4. Cully P., Karasu F., Müller L., Jauzein T., Leterrier Y., Self-Cleaning and Wear-Resistant Polymer Nanocomposite Surfaces, Surf. Coat. Technol., 348, 111–120 (2018). DOI 10.1016/j.surfcoat.2018.05.040.
5. Balkan A., Sola E., Karasu F., Leterrier Y., Photo-Curable Thiol-Ene / Nanocellulose Elastomeric Composites for Bio-Inspired and Fluorine-Free Superhydrophobic Surfaces, ACS Appl. Mater. Interfaces, 16, 61144−61156 (2024). DOI 10.1021/acsami.4c16445.

CELLULOSE FIBRES AND DERIVATIVES: FROM TRADITIONAL PAPERMAKING TO ADVANCED ADDITIVE MANUFACTURING

Davide Beneventi

LGP2, Grenoble Institute of Technology, CNRS, University Grenoble Alpes, Grenoble, France
e-mail: davide.beneventi@pagora.grenoble-inp.fr

Cellulose and its derivatives have long been base raw materials in the paper, board, and textile industries, with more limited but well-established roles as functional additives in battery manufacturing, coatings, and food processing.

Over the past fifteen years, the emergence of cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs) has substantially broadened the accessible propertyies space of these materials. Namely, from high-strength natural fibres to film-forming soluble derivatives, with microfibrillated cellulose and nanocelluloses occupying an intermediate space of tunable mechanical and physicochemical characteristics.

A key enabler for additive manufacturing has been the specific rheological behaviour of nanocellulose-based hydrogels: shear-thinning under nozzle flow and rapid structural recovery upon deposition. This has overcome the historically poor processability of native cellulosic fibres, paving the way to cold-extrusion 3D printing of cellulose pastes, hydrogels, and composite inks.

Application domains span a surprisingly broad range. Indeed, beyond the most cited example of tissue engineering scaffolds, the literature reports CNF hydrogels for stimuli-responsive drug delivery, conductive nanocellulose composites for flexible pressure sensors and wearable electronics, electrodes for enzymatic biofuel cells and electrochemical biosensors, as well as structural components with high thermomechanical performance from thermoset biocomposite pastes. The biodegradability, non-toxicity, and renewability of nanocelluloses make them particularly attractive across all these contexts.

This contribution provides an overview of how cellulose, in its various forms, has been formulated into hydrogels and composite pastes for the additive manufacturing of functional devices and structural objects, and of where this rapidly evolving field currently stands.

INNOVATIVE POLYMERISED TAILORED MEMBRANES FOR GAS AND LIQUID APPLICATIONS

A. Figoli

Institute on Membrane Technology “Enrico Drioli” – National Research Council of Italy,
Via P. Bucci 17c, 87050, Rende (CS), Italy

e-mail: alberto.figoli@cnr.it

Membrane technology is applied with success in many industrial fields and in some of them, as desalination and wastewater treatment, it can be considered a dominant technology.
Recently, innovative polymerizable functionalized membranes have been developed and the possibility of tailoring them allowed to use for a wider number applications.
Three case studies on innovative polymerized membranes in water treatment, gas separation and water electrolysis for producing green hydrogen will be reported and discussed in details, showing the potentiality and the versatility of this innovative approach [1-4]. Moreover, several factors, as the operating parameters and the membrane functionalities materials, influencing the performance of the membrane process will be discussed and future prospects will be also highlighted.

References

1. F. Galiano, A step forward to a more efficient wastewater treatment by membrane surface modification via polymerizable bicontinuous microemulsion, Journal of Membrane Science, 482 (2015) 103
2. A. Figoli et al. Bicontinuous microemulsion polymerized coating for water treatment, WO/2015/044335A2, 2015.
3. A. Figoli et al. Membranes containing polymerized ionic liquid for use in gas separation WO/2019/171409, 2019.
4. F. Galiano et al. Phosphonium ionic liquid-polyacrylate copolymer membranes for improved CO2 separations, Journal of Membrane Science 635 (2021) 119479
5. E. Fontananova et al. CytroCell@PIL: A New Citrus Nanocellulose-Polymeric Ionic Liquid Composite for Enhanced Anion Exchange Membranes, Chemical Engineering Journal Advances 25 (2026) 101007

I
KEYNOTES

BLOCK COPOLYMER SELF-ASSEMBLY IN EMULSIONS: FROM STRUCTURAL-COLOR MICROPARTICLES TO MULTIFUNCTIONAL AND REPROGRAMMABLE PHOTONICS

A. Dodero[1,2]

[1] Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700, Fribourg, Switzerland
[2] National Center of Competence in Research (NCCR) Bio-Inspired Materials, Chemin des Verdiers 4, 1700, Fribourg, Switzerland
e-mail: andrea.dodero@unifr.ch

Controlling structural color through scalable, precise, and multifunctional materials design remains a central challenge in the development of next-generation photonic materials. Here, we present a versatile approach based on the confined self-assembly of block copolymers (BCPs) within emulsion droplets, enabling the fabrication of photonic microparticles with highly ordered internal nanostructures and vivid structural colors. By exploiting supramolecular additives and low-molecular-weight swelling agents, the photonic bandgap can be tuned across the visible spectrum through controlled variations in domain periodicity and refractive-index contrast. This strategy enables broad spectral control while preserving the structural integrity of the particles and their compatibility with scalable emulsification processes. Building on this materials platform, the photonic microparticles can be translated into practical water-based structural-color coatings by dispersing them in polymeric binders and combining them with broadband absorbers. The resulting formulations generate vivid structural colors and can be deposited on a variety of substrates relevant to packaging, textiles, cosmetics, and other coating technologies.

Beyond coloration, the nanostructured BCP framework provides a programmable host matrix for the selective incorporation of functional nanomaterials. Quantum dots, plasmonic nanoparticles, and magnetic nanoparticles can be localized within specific polymer domains, producing hybrid microparticles that combine Bragg reflection with photoluminescent, plasmonic, or magnetic functionalities. In this way, optical properties arising from the periodic BCP structure can be coupled with additional responses originating from the incorporated nanomaterials. The emulsion-based processing strategy also allows the construction of more complex hierarchical particle architectures. In particular, double-emulsion templates can be used to generate core-shell microparticles in which a structurally colored BCP shell surrounds a functional liquid or solid core.

Control over droplet deformation and particle morphology further enables the fabrication of anisotropic rod-like photonic microparticles with orientation-dependent optical properties. When magnetic nanoparticles are incorporated, these anisotropic particles can be aligned by external magnetic fields, enabling control of their optical response through particle orientation. Their incorporation into thermoresponsive polymer gels provides an additional route towards reprogrammable photonic materials. In the gel state, the particles are immobilized within the polymer network, preserving their orientation and the corresponding optical state. Upon transition to the sol state, particle mobility is restored, allowing the microparticles to be reoriented under an applied magnetic field. Subsequent gelation fixes the newly programmed orientation, enabling repeated switching between mobile and immobilized states and the reconfiguration of the material's macroscopic optical response.

Overall, confined BCP self-assembly provides a scalable, modular route to structurally colored, multifunctional microparticles. The ability to control internal periodicity, refractive-index contrast, nanoparticle localization, particle shape, hierarchical compartmentalization, and field-induced orientation enables the development of static, responsive, and reprogrammable photonic materials. These capabilities offer opportunities for applications in sensing, optical tagging, anti-counterfeiting, adaptive coatings, display technologies, and wearable photonic devices.

RETHINKING EPOXY THERMOSETS: FROM DYNAMIC NETWORKS TO CIRCULAR MATERIALS

V. Ambrogi

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio 80, 80131, Napoli, Italia
e-mail: ambrogi@unina.it

Epoxy thermosets are crucial in high-performance applications owing to their outstanding mechanical properties, thermal stability, and chemical resistance. However, their permanently crosslinked networks poses significant challenges for repair, recycling, and end-of-life management, making them one of the most critical materials in the transition toward a circular economy.
I will discuss the different strategies currently being explored to improve the sustainability of epoxy thermosets. These include the development of vitrimeric epoxy networks as a sustainable-by-design approach, the conversion of conventional thermosets into vitrimer-like ones through mechanochemistry, and the use of solvolysis to recover valuable chemicals by upcycling end-of-life materials. The fundamental principles behind these strategies will be highlighted by discussing representative examples from recent research, and addressing the opportunities and environmental challenges associated with their implementation. Together, they demonstrate how advances in polymer chemistry and technology are opening new perspectives for enhancing the sustainability of epoxy thermosets without compromising the performance that makes these materials essential in demanding applications.

CYCLIC OLEFIN BASED COPOLYMERS VIA TRANSITION METAL CATALYSIS: BRIDGING SYNTHESIS AND FUNCTIONAL APPLICATION

S. Losio

[1] Istituto di Scienze e Tecnologie Chimiche "G. Natta" (SCITEC-CNR), via A. Corti 12, 20133, Milano, Italia
e-mail: simona.losio@cnr.it

Cyclic olefin copolymers (COCs) are thermoplastic materials composed of a cyclic olefin - typically norbornene - and ethylene, generally synthesized via metallocene catalysts [1]. COC exhibit low water absorption, excellent electrical insulation, biological inertness, and UV transparency, making them suitable for advanced biomedical, membrane, and optical applications.
Several commercial COC families exist, differing in monomer structures and polymerization methods. In general, COCs are produced by chain copolymerization of cyclic monomers such norbornene or tetracyclododecane with ethylene. For instance, TOPAS Advanced Polymers (formerly Ticona) manufactures TOPAS COCs from norbornene and ethylene, whereas Mitsui Chemicals utilizes tetracyclododecane to produce APEL COCs. Notably, norbornene monomer synthesis is complex and poses significant engineering safety challenges, which historically led to market monopolies and high manufacturing costs.
While early commercial developments relied on Ziegler–Natta systems, the advent of metallocene and half-sandwich complexes - such as constrained geometry type or non-bridged titanocene-, activated by methylaluminoxane (MAO), revolutionized the field by enabling precise control over polymer microstructure, composition, and transparency [2]. Recent research has expanded beyond traditional formulations to focus on the copolymerization or terpolymerizations of cyclic olefins with propylene, higher α-olefins, functionalized cyclic olefins, reactive dienes to tailor thermal, chemical, and mechanical performances [3].
Understanding the relationships between catalyst design and polymer properties provides key insights into both academic research and industrial applications, facilitating the development and commercialization of advanced COCs with tailored properties [4].

References:
[1] Tritto, I.; Boggioni, L.; Ferro, D. R. *Coord. Chem. Rev.* **2006**, *250*, 212–241.
[2] Wang, W.; Qu, S.; Li, X.; Chen, J.; Guo, Z.; Sun, W.-H. *Coord. Chem. Rev.* **2023**, *494*, 215351.
[3] Losio, S.; Boggioni, L.; Vignali, A.; Bertini, F.; Nishiyama, A.; Nomura, K.; Tritto, I. *Polym. Chem.* **2025**, *16*, 3709–3719.
[4] Losio, S.; Tritto, I.; Boggioni, L.; Mancini, G., Luciano, G., Tofani, L.; Viglianisi, C.; Menichetti, S., Sacchi, M.C.; Stagnaro, P. *Polym. Degrad. Stab.* **2017**, *144*, 167-175.
[5] Fredi, G.; Mallegni, N.; Dorigato, A.; Milazzo, M. *Adv. Funct. Mater.* **2026**, *36*, e75610.

FUNCTIONALIZED POLYMERIC MATERIALS: VERSATILE MACROMOLECULAR PLATFORMS FOR PHARMACEUTICAL AND ENVIRONMENTAL APPLICATIONS

Chiara Zagni

Dept. of Drug and Health Sciences, Università di Catania, V.le A. Doria 6, 95125, Catania, Italy

The design of functionalized polymeric materials provides versatile macromolecular platforms capable of addressing critical challenges in both the pharmaceutical and environmental sectors. In pharmaceutical applications, three-dimensional porous networks serve as biocompatible containers for controlled drug delivery and as active heterogeneous supports for metal catalysts (e.g., Pd complexes) in the catalytic synthesis of Active Pharmaceutical Ingredients (APIs). Concurrently, for environmental mitigation, amino acid-functionalized hydrogels enable selective CO_2 capture, while surface-charge and hydrophobicity modulation drive the efficient removal of organic contaminants and heavy metals during water remediation, highlighting the immense structural potential of these customizable architectures.

3D PRINTING MEETS LIQUID CRYSTAL POLYMERS: RESPONSIVE MATERIALS ACROSS DIFFERENT SCALES AND APPLICATIONS

C. Parmeggiani[1,2], S. Nocentini[2], D. S. Wiersma[3], D. Martella[1,2]

[1] Department of Chemistry "Ugo Schiff", University of Forence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy
[2] European Laboratory for Non-Linear Spectroscopy (LENS), Via Carrara 1, 50019 Sesto Fiorentino, Italy
e-mail: daniele.martella@unifi.it

The use of light in polymer science offers unique opportunities, spanning from fabrication of smart materials by photopolymerization, to their actuation for different applications. By combining shape-changing liquid crystalline networks (LCNs) with advanced 3D printing technologies, complex architectures with stimuli-responsive properties can be produced. LCNs are crosslinked polymer networks prepared from reactive mesogens that efficiently convert external stimuli, such as light, into mechanical motion. Their chemical composition can be tailored to tune mechanical properties and optimize force generation during actuation. In this contribution, we demonstrate their integration with additive manufacturing techniques to fabricate a variety of functional devices, including light-driven actuators, structurally colored responsive structures, and photonic components.

Polyesters in Water: From Dispersion Strategies to Functional Applications

Matteo Calosi[1], Andrea D'Ilorio[1], Elena Buratti[2], Monica Bertoldo[1]

[1] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari, 46, 44121 Ferrara, Italy
e-mail: andrea.monica.bertoldo@unife.it
[2] Department of Environmental and Prevention Sciences, University of Ferrara, C.so Ercole I D'Este, 32, 44122 Ferrara, Italy

Aqueous dispersions of biopolyesters have long been used in drug delivery, typically in highly diluted formulations. At higher solid contents, however, they open new opportunities as sustainable waterborne materials for films, coatings, and functional composites. Our group has developed stable biopolyester dispersions with solid contents up to 40%, suitable for paper coatings that provide water and oil resistance while preserving biodegradability and recyclability. These systems can also be blended with water-soluble polymers such as polyvinyl alcohol, combined with fillers such as graphene oxide for sensor applications, or used to incorporate thermolabile bioactive molecules, including osteogenic peptides in PLA films. Beyond PLA, our work explores different polyesters, including PLGA obtained from CO_2-derived building blocks, PHA as a biodegradable polymer in diverse environments, and mixed PHA/PLA emulsions to tailor properties and expand applications.

4D-Printable Shape Morphing Double Network Granular Elastomers (DNGEs)

DANIELE NATALI[1], ESTHER AMSTAD[1].

[1]*Institute of Materials, Soft Materials Laboratory (SMaL), École Polytechnique Fédérale de Lausanne (EPFL, Switzerland)*
email: daniele.natali@epfl.ch

The growing relevance of soft robotics within materials science has, in the recent years, driven increasing interest in the development of soft, yet load-bearing and responsive materials that can be processed into customized shapes. Double network granular elastomers (DNGEs), composed of crosslinked microparticles interconnected through a second interpenetrated elastomeric network combine toughness with load-bearing properties and extrudability.[1] To prepare DNGEs, the microparticles are swollen in the precursors' solution of the second network before being centrifuged to increase packing densiy of the microparticles to a point where they are named jamming (*Figure 1a*). In the jammed state, the swollen microparticles are shear-thinning, exhibit a low yield point and fast shape recovery, assets ideal for (DIW)-based 3D printing (*Figure 1b*). The mechanical properties of DNGEs can be tuned with the composition of the DNGE. In this talk, I will introduce smart DNGEs that exhibit a thermo-sensitive shape-morphing behaviour. This is achieved by formulating DNGEs from crystallizable monomers that are crosslinked through a photo-induced thiol-ene reaction. The crystallization of polymeric domains are exploited for the fixation of different temporary shapes, while the original shape of samples is recovered by heating above the material's melting transition (*Figure 1c*). Semicrystalline domains thus consent to combine the enhancement of the mechanical properties with the obtainment of thermo-sensitive shape-memory properties, introducing a novel elastomeric material suitable for load-bearing applications and capable to generate active force upon heating (*Figure 1d*). Mechanical properties of the DNGEs are optimized by regulating the amount of crosslinker in the microparticles and in the second network. Leveraging multi-material DIW printing, I will showcase DNGEs with locally varying compositions that deform in pre-defined ways. I foresee shape-memory DNGEs, to open up new possibilities in 4D-printing load-bearing smart materials well-suited, for example for soft robotics.

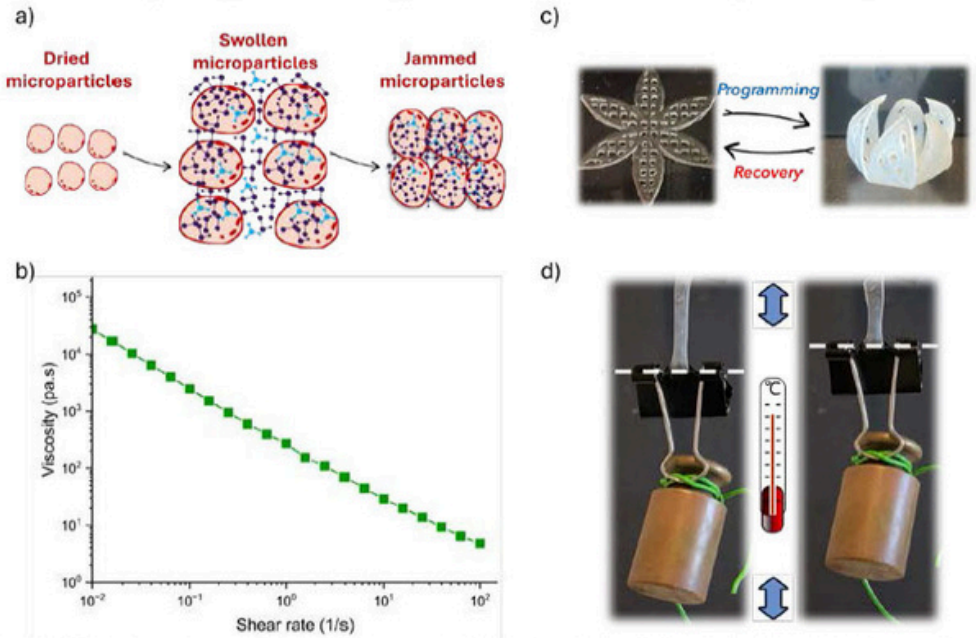


Figure 1. a) steps for the preparation of the shear-thinning ink: first the microparticles are swelled in the solution of second network precursors before being jammed; b) flow curve of the ink showing shear-thinning behavior; c) shape-memory properties of 3D-printed DNGEs; d) load-bearing and active force demonstration of shape-morphing DNGEs: the materials can be programmed to bear and lift loads when activated through heating.

References:

[1] E. Baur, B. Tiberghien, E. Amstad. Advanced Materials. 3D Printing of Double Network Granular Elastomers with Locally Varying Mechanical Properties, *36, 2313189*, 2024.

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DEVELOPMENT OF ACTIVE BIODEGRADABLE PLA/PBSA FILMS CONTAINING BLUEBERRY WASTE ANTIOXIDANTS EXTRACTED USING NADES AS GREEN SOLVENTS

A. Barbato[1], A. Apicella[1], F. Alchera[2], L. Incarnato[1]

[1] Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy
[2] Department of Chemistry, University of Turin, Via Pietro Giuria 5, 10125, Turin (TO), Italy
e-mail: abarbato@unisa.it

Introduction

The development of sustainable food packaging requires materials able to reduce environmental impact while maintaining the protective functions needed to preserve food quality. Biodegradable polyesters such as polylactic acid (PLA) and poly(butylene succinate-co-adipate) (PBSA) are promising candidates for flexible packaging, although their limited functionality and barrier performance may restrict their use for oxidation-sensitive foods [1]. In this framework, active coatings incorporating natural antioxidants recovered from agro-food by-products represent a circular strategy to improve packaging performance. Blueberry peels are particularly attractive because they are rich in polyphenols and anthocyanins [2]. Their extraction by Natural Deep Eutectic Solvents (NADES) offers a greener alternative to conventional organic solvents, combining low volatility, reduced toxicity and the ability to stabilize bioactive molecules [3]. This work aimed to develop PLA-coated PBSA/PLA biodegradable films containing blueberry-peel antioxidants extracted by NADES and to assess their suitability as active food-packaging materials [4].

Results and discussion

The blueberry peel extract was obtained using a natural solvent composed of NADES (lactic acid:glucose) with the addition of glycerol and water, which serve to regulate the physical composition of the solvent and improve its extraction capacity [5]. The final solvent mixture, hereinafter referred to as NBE, composed of (lactic acid:glucose):glycerol:H_2O in a ratio of 50:20:30 % v/v, was produced and characterized. UV–Vis analysis showed the typical absorption bands of phenolic compounds at 270–280 nm and anthocyanins at around 520 nm. The extract exhibited a high total phenolic content, equal to 1657 mg phenols/100 g, together with strong radical-scavenging activity, showing 88.5% DPPH inhibition and 98.4% ABTS inhibition.

Different coating solutions of amorphous PLA Luminy® LX975 (Total Corbion PLA; density: 1.24 g cm^{-3}; glass transition temperature: 60 °C; melting temperature: 130 °C; 88% L-isomer) were prepared in acetone by incorporating NBE at concentrations ranging from 5 to 20% (v/v), with Span 80 added as a surfactant at 1% (w/w). The coating formulation was stabilized and optimized in order to ensure a homogeneous dispersion of the antioxidant extract within the PLA matrix. However, the formulation containing 20% v/v NBE showed gelation phenomena, likely related to extract aggregation, which negatively affected its processability. For this reason, only the formulations containing 5 and 10% NBE were selected for film preparation.

The active structures were produced by applying the heat-sealable PLA coating, either neat or loaded with 5 and 10% NBE, onto a biodegradable PBSA/PLA 80/20 substrate. This substrate was selected due to its good transparency and balanced mechanical and barrier properties, which make it suitable for the target application in fresh-cut fruit packaging.

FTIR analysis confirmed the presence of the extract in the coating and suggested interactions between hydroxyl groups from the phenolic/NADES phase and PLA carbonyl groups. The incorporation of NBE increased the polarity of the coating surface and modified the optical response of the films, reducing light transmittance because of the naturally pigmented antioxidant phase. Nevertheless, the films retained suitable mechanical behaviour and sealing performance for flexible packaging applications. In particular, the PLA coating improved heat-seal strength, and the NBE-loaded coatings maintained comparable sealability values with respect to the neat PLA-coated film.

Release tests in food simulants confirmed the ability of the NBE-loaded films to act as antioxidant carriers in both aqueous and fatty food environments. The antioxidant activity at the release plateau increased with the extract

concentration and was markedly higher in ethanol 95% than in ethanol 10%, highlighting a greater availability of blueberry polyphenols in less polar media. The BS_PLA+10%NBE film showed the highest Trolox-equivalent antioxidant capacity, reaching 4.00 µmol TR by DPPH and 32.50 µmol TR by ABTS in ethanol 10%, and 22.83 µmol TR by DPPH and 51.25 µmol TR by ABTS in ethanol 95%. Lower values were observed for BS_PLA+5%NBE, confirming the loading-dependent antioxidant response. Overall, the higher ABTS values suggest a broader radical-scavenging capacity of the released compounds, supporting the potential of these films for active packaging of oxidation-sensitive foods.

The release profiles were described using the Korsmeyer-Peppas model for the initial stage and the Weibull model for the later phase. The lower-loaded films showed faster release, whereas the 10 wt% NBE systems displayed a slower and more controlled release, probably due to stronger interactions and partial clustering of the NADES/extract phase within the PLA coating. These results indicate that the active response can be tuned by adjusting the NBE concentration and the coating formulation.

Conclusions

The combination of a PBSA/PLA biodegradable substrate, a heat-sealable PLA coating and NADES blueberry-peel extract is a promising route to obtain active antioxidant food-packaging films from renewable and waste-derived resources. The developed materials combine biodegradability, sealability, controlled antioxidant release and valorization of agro-food residues. Shelf-life validation on fresh-cut apple is currently ongoing and will be used to verify the effectiveness of the most promising formulation under real refrigerated-storage conditions.

Acknowledgements

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References

[1] A. Apicella, A. Barbato, E. Garofalo, L. Incarnato, P. Scarfato, Polymers, 14, 935 (2022).
[2] T. Piechowiak, B. Skora, K. Grzelak-Blaszczyk et al., Food Analytical Methods, 14, 2317-2327 (2021).
[3] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R.L. Reis, A.R.C. Duarte, ACS Sustainable Chemistry & Engineering, 2, 1063-1071 (2014).
[4] J.R. Westlake, M.W. Tran, Y. Jiang, X. Zhang, A.D. Burrows, M. Xie, ACS Food Science & Technology, 2, 1166-1183 (2022).
[5] F.S. Bragagnolo, M.M. Strieder, R.S. Pizani, L.M. De Souza Mesquita, M. González-Miquel, M.A. Rostagno, TrAC Trends in Analytical Chemistry, 175, 117726 (2024).

MULTIFUNCTIONAL EUGENOL-BASED NANOGELS THROUGH COPOLYMER DESIGN: ANTIOXIDANT ACTIVITY, INTRINSIC FLUORESCENCE, AND DRUG ENCAPSULATION

Benedetta Brugnoli[1], Alessia Mariano[2,3], Valerio La Gambina[1], Daniel Salzarulo[1], Mauro Giustini[1], Luisa M. Migneco[1], Antonella Piozzi[1], Anna Scotto d'Abusco[2], Alessandra Del Giudice[1], Luciano Galantini[1], Karin Schillén[4], Claudia Vuotto[5], Jonathan D. Hirst[6], Dmitry Karlov[6], Vincenzo Taresco[6], Iolanda Francolini[1]

[1] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 00185, Rome, Italy

[2] Department of Biochemical Sciences, Sapienza University of Rome, Rome, Italy

[3] BeSSA Department, Wellbeing, Health and Environmental Sustainability, Sapienza University of Rome, Via delle Fontanelle snc, Rieti, Italy

[4] Department of Chemistry, Lund University, P.O. Box 124, Lund SE-22100, Sweden

[5] Saint Camillus International University of Health Sciences, Via di Sant'Alessandro, 8, 00131, Rome, Italy

[6] School of Chemistry, University of Nottingham, University Park, NG7 2RD, Nottingham, United Kingdom
e-mail: benedetta.brugnoli@uniroma1.it

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Introduction

Phenolic compounds are attractive building blocks for functional materials due to their rigidity, chemical versatility, and intrinsic bioactivity [1]. Integrating these phenolic motifs into polymeric nanosystems translates their bioactivity into nanostructures while introducing crucial structural and interfacial functionalities for drug delivery [2]. While conventional nanogels (NGs) offer high biocompatibility and tunable crosslinked networks, they often suffer from limited affinity for hydrophobic active pharmaceutical ingredients (APIs). Amphiphilic nanogels overcome this limitation, providing a versatile platform that improves loading capacity and colloidal stability for both water-soluble and poorly soluble APIs [3]. Furthermore, increasing attention has shifted toward multifunctional nanocarriers incorporating intrinsically bioactive moieties. Among these, eugenol (4-allyl-2-methoxyphenol) has attracted significant interest due to its versatile chemical structure and inherent antioxidant, antimicrobial, and anti-inflammatory properties.

In this work, amphiphilic nanogels were synthesized via dispersion copolymerization of a eugenol-based methacrylate monomer (EUMA) [4] and hydroxyethyl methacrylate (HEMA). Preservation of the phenolic moiety of eugenol enables a single-motif design in which intrinsic antioxidant activity is embedded directly into the polymer backbone.

The physicochemical properties of the obtained NGs were evaluated by dynamic light scattering, with particular attention to particle size and colloidal stability. Their spectroscopic properties were also investigated by UV-vis and fluorescence spectroscopy. The therapeutic potential of these NGs was assessed using usnic acid, a hydrophobic compound with anticancer and antimicrobial activity, as a model drug. In particular, the study investigates whether the amphiphilic nanogel structure can improve usnic acid aqueous solubility, modulate its cytotoxicity, and preserve its antibacterial activity. Overall, this work aims to establish eugenol-based nanogels as bio-based platforms for multifunctional and self-reporting drug delivery systems.

Results and discussion

This study presents a single-motif design strategy to synthesize multifunctional, bioactive nanogels by copolymerizing 2-hydroxyethyl methacrylate (HEMA) with a eugenol-derived methacrylate monomer (EUMA) crossliked by bis-acrylamide.

Dynamic light scattering (DLS) confirmed that the morphological properties are easily modulated by the copolymer design. Specifically, the inclusion of EUMA progressively altered the size and surface properties, yielding tunable diameters

and negative zeta potential (ZP) (Table 1). NGs also showed good colloidal stability up to 9 months.

Table 1: Hydrodynamic diameter, PDI and zeta potential of NGs

Sample	Size (nm)	PDI	ZP (mV)
pHEMA	80±1	0.08±0.01	-18.7±0.5
pHEMA:EUMA$_{90:10}$	214±1	0.20±0.01	-22.7±0.2
pHEMA:EUMA$_{80:20}$	157±1	0.07±0.01	-18.4±0.7
pHEMA:EUMA$_{70:30}$	133±3	0.13±0.02	-31.1±0.3

Fluorescence spectroscopy revealed that pHEMA:EUMA exhibited intrinsic fluorescence (Figure 1A-B). This behavior proved to be pH-responsive, showing significant variations between acidic (pH 2) and alkaline conditions (pH 7 and 10). These results make EUMA-based NGs attractive candidates for tracking application in biological environments. Computational analysis also suggested that the emission in the visible region (420 nm) may originate from extended conjugation generated by partial autoxidation and subsequent coupling of eugenol units within the nanogel network.

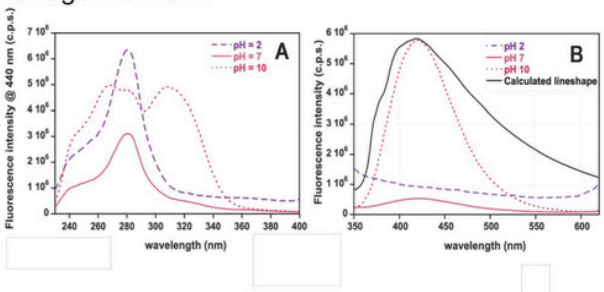


Figure 1. Excitation spectra monitored at 440 nm (A) and emission spectra excited at 320 nm (B) of pHEMA:EUMA 70:30 NGs at different pH values. The black curve in (B) resulted from computational simulation study.

EUMA-based nanogels also demonstrated good antioxidant properties, which improved with the EUMA content (Figure 2A).
When loading Usnic Acid (UA), a potent but poorly water-soluble anticancer and antimicrobial agent, pHEMA:EUMA 70:30 formulation achieved a superior Encapsulation Efficiency (EE) of 91% and Loading Capacity (LC) of 14%, compared to pure pHEMA (EE = 37%, LC = 7%). We believe this finding is related to the EUMA-based NG amphiphiphilicity obtained by copolymer design.
The UA-loaded formulations showed potent antimicrobial efficacy against *Staphylococcus aureus* strains (Figure 2B).

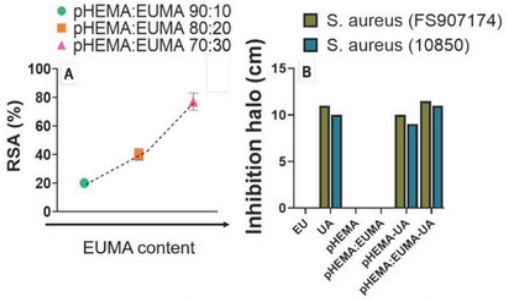


Figure 2. Radical Scavenging Activity (RSA%) of EUMA-based NGs (A) and inhibition halo of unloaded and loaded NGs on Staphylococcus aureus strains (B).

Overall, these findings highlight that eugenol-based copolymer engineering represents a highly efficient strategy to produce multi-functional biomaterials with fluorescent and antioxidant properties, as well as therapeutic delivery.

Conclusions

In conclusion, EUMA integration in pHEMA nanogels plays a pivotal role in engineering multifunctional pHEMA-based nanogels by enhancing colloidal stability and increasing hydrophobic drug encapsulation. EUMA incorporation successfully induces an intrinsic, pH-modulated visible fluorescence originating from the partial oxidation and coupling of eugenol units, enabling label-free tracking. Crucially, UA-loaded formulations showed antimicrobial efficacy against *Staphylococcus aureus*.
This single-motif design establishes eugenol-based nanogels as versatile, biobased platforms combining efficient therapeutic delivery, inherent phytochemical bioactivity, and self-reporting imaging.

References

[1] H. Lee, B. P. Lee, P. B. Messersmith, *Nature*, vol. 448, 338–341 (2007).
[2] M. A. Rahim, S. L. Kristufek, S. Pan, J. J. Richardson, F. Caruso, *Angew. Chem. Int. Ed.*, vol. 58, 1904–1927 (2019)
[3] K. S. Soni, S. S. Desale, T. K. Bronich, *J. Control. Release*, vol. 240, 109–126 (2016).
[4] M. Di Consiglio, E. Sturabotti, B. Brugnoli, A. Piozzi, L.M. Migneco, I. Francolini, *Polym. Chem.*, vol. 14, 432–443 (2023).

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SOLVENT-FREE GRAFTING OF PBS OLIGOMERS ONTO CELLULOSE NANOFIBERS FOR ENHANCED BIOCOMPOSITE COMPATIBILITY

Andrea D'Iorio[1], Simone Fantinel[1], Elena Buratti[2], Giulia Ronconi[3], Lucia Gioiella[4], Giuseppe Proietto Salanitri[5], Monica Bertoldo[1].

[1] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari, 46, 44121 Ferrara, Italy
e-mail: andrea.diorio@unife.it

[2] Department of Environmental and Prevention Sciences, University of Ferrara, Via L. Borsari 46, Ferrara 44121, Italy

[3] Department of Engineering, University of Ferrara, Via Saragat 1, 44122 Ferrara, Italy

[4] Department of Chemical, Materials and Production Engineering (INSTM Consortium – UdR Naples), University of Naples Federico II, Piazzale Tecchio 80, Naples 80125, Italy

[5] Institute for Polymers, Composites and Biomaterials CNR-IPCB, Via Paolo Gaifami 18, 95126 Catania, Italy

Introduction

Growing interest in sustainable materials has driven the development of biodegradable composites. Among reinforcing agents, cellulose nanofibers (CNFs) are attractive due to their abundance, renewability, and biodegradability, although their compatibility with hydrophobic polymers remains limited[1]. To address this issue, CNFs were chemically modified through a three-step process: 1) oxidation of cellulose fibers; 2) mechanical extraction of CNFs; 3) solvent-free grafting of poly(butylene succinate) (PBS) oligomers onto the cellulose molecular chains. While the first two steps are extensively reported in the literature[2–4], the present work aims to investigate the possibility of improving the compatibility and then the dispersion degree of the resulting CNFs in PBS matrices through a green, solvent-free polymer grafting approach. The modified CNFs are intended for the development of fully biodegradable PBS-based composites with improved interfacial adhesion and performance.

Results and discussion

Cellulose fibers from Whatman filter paper were oxidized using the TEMPO/NaBr/NaOCl system, as previously reported by Saito et al[2], introducing sodium carboxylate groups on the cellulose chains with a degree of substitution of 0.15, which is consistent with previous literature reports[5]. The presence of anionically charged groups facilitates the mechanical extraction of cellulose nanofibers (CNFs) by high-pressure homogenization[3]. Successful nanofibrillation was confirmed by optical and scanning electron microscopy (SEM) analyses (Figure 1).

To improve compatibility with PBS, solvent-free in situ polycondensation of succinic acid and 1,4-butanediol was used to graft PBS oligomers onto CNFs, exploiting the functional groups introduced at the end of the oxidation process, as well as the OH group naturally occurring on cellulose. Various parameters were tested, and the best reaction conditions identified are the following: cellulose loading of 25 wt%; 1 mol% zinc acetate; reaction temperature of 140°C; and 48h under vacuum.

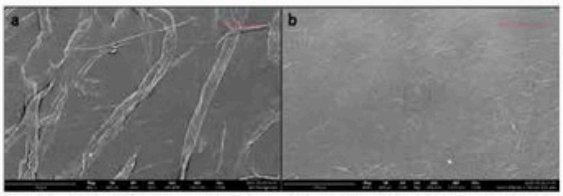


Figure 1: SEM images of the starting cellulose fibers (a) and the extracted CNFs (b).

At the end of each reaction test, ATR-FTIR analysis confirmed successful polymer grafting onto CNFs through an ester C=O peak at ~1727 cm^{-1} and increased intensity of the signals between 3000 and 2925 cm^{-1}, associated with the vibrational modes of aliphatic –CH– groups (Figure 2).

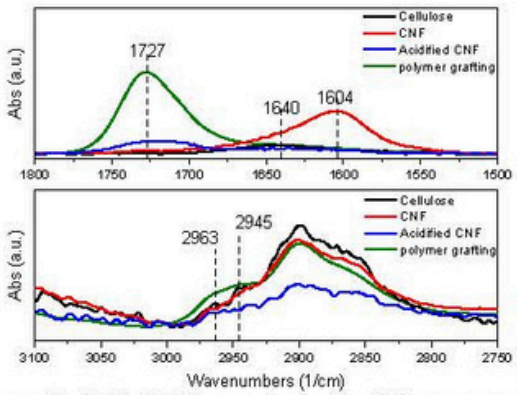


Figure 2: ATR-FTIR spectra of cellulose samples before and after polymer grafting in the 1800-1500 cm^{-1} (top) and 3100-2750 cm^{-1} (bottom) spectral region.

After identifying the optimal reaction conditions, the process was scaled up using a rotary evaporation system. Three polymerization experiments were performed using acidified CNFs (CNF-*g*-PBS), cellulose fibers (CF-*g*-PBS), or no cellulose (PBS-neat). Table 1 summarizes the weight percentage (wt%) of the Soxhlet-extracted solid residue and the number-average molecular weight ($\bar{M}_n$) of the soluble fraction determined by GPC analyses.

Table 1: Soxhlet-insoluble residue (wt%) and number-average molecular weight (Mn) of the soluble fraction for CNF-g-PBS, CF-g-PBS, and PBS-neat samples

Samples	Cellulose loading (wt%)	Solid residue (wt%)	$\bar{M}_n$ (Da)
CNF-*g*-PBS	25	31	4053
CNF-*g*-PBS	25	17	4118
PBS-neat	0	0	5645

For CNF-*g*-PBS, the Soxhlet-extracted solid residue reached 31 wt%, exceeding the theoretical cellulose content (25 wt%) and suggesting successful grafting. For the CF-*g*-PBS sample, the actual cellulose content fed is lower than the theoretical one, probably due to the lower homogeneity of the fiber dispersion. The data obtained from GPC analysis clearly show that the addition of cellulose to the system results in a reduction in the molecular weight of the PBS produced via polycondensation compared to the cellulose-free reference test (neat PBS). This result can be attributed to the presence of additional hydroxyl groups arising from cellulose, which add to those provided by the butanediols. As a consequence, the overall OH/COOH ratio may deviate from the ideal value of 1, limiting chain growth in step-growth polymerization and reducing the attainable average molecular weight. ATR-FTIR analysis confirmed results consistent with those previously obtained (Figure 2).

DSC analysis (Table 2) shows that all analysed PBS samples consisted of semicrystalline materials despite the relatively low average molecular weight. Cold crystallization temperature (T_{cc}), melting temperature (T_m), and crystallization temperature (T_c) varied in a small range and are generally lower for the soluble fractions than for the grafted ones.

Further characterization of the extracted residues by HR-MAS ^{1}H-NMR revealed the characteristic signals of PBS in both CNF-g-PBS and CF-g-PBS samples, indicating the effective association of PBS chains with cellulose, either through covalent grafting or strong interfacial interactions (Figure 3).

Table 2: DSC data for PBS-neat, the DCM-soluble fractions (ext.), and purified CNF-g-PBS and CF-g-PBS samples

Sample	T_{cc} (°C)	T_m (°C)	T_c (°C)
CNF-g-PBS_ext	86	112	64
CNF-g-PBS	98	117	74
CF-g-PBS_ext	93	114	72
CF-g-PBS	98	113	78
PBS-neat	99	114	81

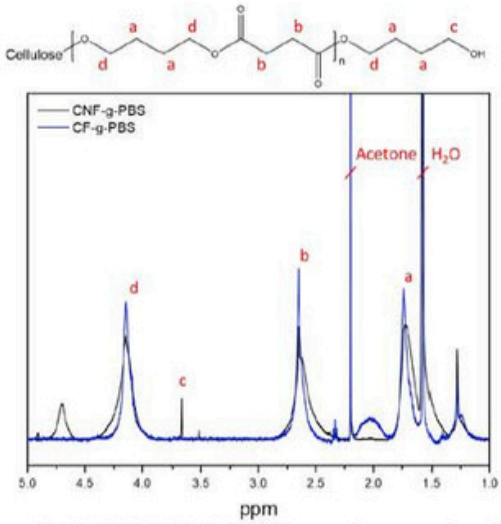


Figure 3: ^{1}H-NMR HR-MAS spectra acquired for the samples CNF-g-PBS and CF-g-PBS.

Conclusions

This study confirms the successful grafting of PBS onto CNFs through a solvent-free and low-impact process. The scalability of the method further supports its potential for the development of sustainable CNF–PBS composite materials.

References

[1] P. V. Kelly, S. Shams Es-haghi, M. E. Lamm, K. Copenhaver, S. Ozcan, D. J. Gardner, W. M. Gramlich, *ACS Appl. Polym. Mate.*, 5, 3661–3676 (2023).

[2] T. Saito, S. Kimura, Y. Nishiyama, A. Isogai, Biomacromolecules. 8, 2485–2491 (2007).

[3] A. Isogai, T. Saito, H. Fukuzumi, *Nanoscale*, 3, 71–85, (2011).

[4] J. L. Sanchez-Salvador, C. Campano, P. Lopez-Exposito, Q. Tarrés, P. Mutjé, M. Delgado-Aguilar, M. C. Monte, A. Blanco, *Nanomaterials*, 11, 2077 (2021).

[5] T. Saito, Y. Nishiyama, J. L. Putaux, M. Vignon, A. Isogai, *Biomacromolecules*, 7, 1687–1691 (2006).

Acknowledgments

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MECHANOCHEMICAL POLYMER-TO-POLYMER RECYCLING OF POLYLACTIC ACID

A.Kiani,[1] A. Di Martino, [1] F. Santulli, [1] M. Carratù,[1] M. Mazzeo,[1] M.Rosaria Acocella[1]
e-mail: m.acocella@unisa.it

Introduction

The widespread use of polymeric materials has generated significant environmental concerns, driving the search for sustainable alternatives and efficient end-of-life management strategies. Among biodegradable polymers, polylactic acid (PLA) has emerged as one of the most promising materials due to its bio-based origin, compostability, and extensive use in packaging, disposable products, and biomedical applications[1]. However, PLA degradation remains slow under natural environmental conditions, highlighting the need for effective recycling technologies. Chemical recycling offers important advantages over conventional mechanical recycling by converting polymers into monomers or oligomers that can be reprocessed into high-quality materials, although the following step of repolymerization requires some resources in terms of solvents, catalysts, and elevated energy input.[2] An alternative and potentially more sustainable strategy could involve the mechanochemical degradation of PLA.

Although mechanochemical depolymerization of PLA has already been reported in the literature,[3] previous approaches typically relied on a large excess of methanol, promoting alcoholysis and leading predominantly to the formation of monomeric species methyl lactate derivatives. In contrast, the strategy presented here is designed to selectively generate reactive PLA oligomers through radical-induced depolymerization under limited alcohol conditions. These oligomers can subsequently undergo in situ mechanochemical repolymerization, avoiding complete depolymerization to monomers and enabling a more efficient closed-loop recycling process. By systematically varying milling parameters, controlled radical-induced depolymerization was achieved, producing reactive PLA oligomers. Remarkably, further adjustment of the milling conditions enabled the in situ repolymerization of these oligomers, restoring molecular weights close to those of the original polymer without the use of solvents, catalysts, additional monomers, or chemical reagents. This approach transforms a known limitation of incomplete depolymerization into an advantage, providing an efficient route for the regeneration of PLA from heterogeneous waste streams.

Results and discussion

Depolymerization

A mechanochemical depolymerization procedure was developed using a low-molecular-weight PLA (PLA-LMW, Mn = 19.5 kDa) as a model substrate before extending the method to post-consumer high-molecular-weight PLA waste. Ball milling alone induced gradual polymer degradation, reducing the molecular weight from 19.5 kDa to 7.7 kDa after 4 h. The addition of small amounts of alcohol (methanol or ethanol) significantly accelerated depolymerization, reducing Mn to as low as 6.5 kDa after only 2 h. The effect was mainly attributed to alcohol-induced swelling of the polymer matrix, which enhances chain mobility and facilitates mechanically driven chain scission. Molecular weight reduction was strongly influenced by milling parameters. An optimal milling speed of 300 rpm was identified, while lower speeds (100 rpm) generated insufficient energy for efficient degradation and higher speeds (500 rpm) led to broader molecular weight distributions without improving depolymerization efficiency.

MALDI FT-ICR analysis revealed hydroxyl-terminated oligomers and the absence of methoxide end groups, demonstrating that transesterification reactions were negligible under the selected conditions. Instead, the results support a radical-induced fragmentation mechanism involving random cleavage of ester bonds. Further evidence of the radical pathway was obtained by performing the mechanochemical degradation in the presence of a radical scavenger, tert-butylcatechol, which effectively suppressed the degradation process even after 4 h of milling

The influence of the initial polymer molecular weight was also investigated. Very low molecular weight PLA oligomers (Mn = 4.4 kDa) did not undergo further degradation, indicating the existence of a limiting molecular weight (Mlim) below which mechanochemical depolymerization becomes ineffective. Conversely, high-molecular-weight post-consumer PLA (Mn = 60.5 kDa)

exhibited partial degradation, generating bimodal molecular weight distributions consisting of a residual high-molecular-weight fraction and a low-molecular-weight fraction close to Mlim. The addition of methanol enhanced degradation of the high-molecular-weight fraction but did not eliminate the bimodal character.

Table 1: Influence of solvent and ball milling parameters on PLA-LM$_W$ and PLA-HMw degradation

Entry	Time (h)	Milling speed (rpm)	Alcohol (ml)	Mn b (kDa)	Đ b
1	2	300	-	13.2	2.4
2	4	300	-	7.7	4.6
3	2	300	MeOH (0.1)	12.6	1.9
4	2	300	MeOH (0.3)	6.5	2.1
5	1	300	MeOH (0.3)	9.0	2.2
6	2	500	MeOH (0.3)	10.4	2.8
7	2	300	-	62.8	1.6
				3.05	2.0
8	2	300	MeOH (0.6)	53.7	1.9
				3.80	1.3

Repolymerization

Mechanochemical treatment of high-molecular-weight PLA (PLA-HM$_W$) initially produced a bimodal molecular weight distribution, consisting of a low-molecular-weight fraction near the limiting molecular weight (Mlim) and a second fraction close to the original polymer molecular weight. This behavior supports a degradation mechanism dominated by radical fragmentation rather than alcoholysis-driven transesterification.
Unexpectedly, extending the milling time from 2 to 4 hours transformed the bimodal distribution into a single molecular weight distribution centered at 45.5 kDa. This result suggests that, alongside depolymerization, radical recombination reactions occur during prolonged milling, allowing fragmented chains to reconnect and form larger polymer species. To verify this hypothesis, the same experiment was performed on PLA-LM$_W$. After an initial reduction in molecular weight from 19.5 to 6.5 kDa after 2 h of milling, prolonging the treatment to 4 h increased Mn to 9.8 kDa while maintaining a monomodal distribution. This confirms that chain growth through radical recombination takes place under the applied mechanochemical conditions.
Further evidence was obtained by adding lactide after the initial depolymerization stage and continuing milling for an additional 2 h. In both PLA-LM$_W$ and PLA-HM$_W$, the molecular weight increased significantly, reaching 13.2 kDa and 50.6 kDa, respectively, values approaching those of the starting materials. These results demonstrate that lactide can be incorporated into the growing chains, promoting mechanochemical chain extension.

Table 2. *Re-polymerization of PLA-LMW and PLA-HMW oligomers.*

Entry	PLA	Time (h)	Milling speed (rpm)	MeOH (ml)	bMn (kDa)	bĐ
1	PLA-HMW	2	300	0.6	53.7	1.9
					3.80	1.3
2	PLA-HMW	4	300	0.6	45.5	2.2
3	PLA-LMW	2	300	0.3	6.5	2.1
4	PLA-LMW	4	300	0.3	9.8	2.6
c5	PLA-HMW	4	300	0.6	50.6	2.2
c6	PLA-LMW	4	300	0.3	13.2	5.3

Conclusions

This work demonstrates a solvent-free and catalyst-free mechanochemical recycling strategy for PLA based on radical-induced depolymerization into oligomers followed by in situ repolymerization. Both low- and high-molecular-weight PLA were successfully processed, with MALDI FT-ICR analysis confirming a radical degradation mechanism rather than transesterification. The degradation efficiency depended on the initial molecular weight, while prolonged milling promoted radical recombination and chain extension, enabling recovery of molecular weights close to the original polymer. By avoiding complete depolymerization to monomers and the need for conventional repolymerization processes, this approach offers an efficient, sustainable, and potentially closed-loop route for PLA recycling.

References

[1] C. Jehanno, J.W. Alty, M. Roosen, S. De Meester, A.P. Dove, E.Y. Chen, F.A. Leibfarth, H. Sardon, *Nature*, 603 803-814 (2022)
[2] D.S. Rajendran, S. Venkataraman, S.K. Jha, D. Chakrabarty, V.V. Kumar, *Food Sci Biotechnol*, 33 1759-1788 (2024)
[3] H.W. Lee, K. Yoo, L. Borchardt, J.G. Kim, Green Chemistry, 26 2087-2093 (2024)

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(Meth)-acrylated tanni acid as a bio-based adhesion promoter for EB-curable coatings

F.Bisio[1], K.Sparnacci[1], G.Mirone[2], S.Pasquin[2], A.Nicorelli[2]

[1] Dipartimento di Scienze ed Innovazione Tecnologica, Universita` degli Studi del Piemonte Orientale "A. Avogadro" via Michel 11, 15121 Alessandria, Italy
e-mail: katia.sparnacci@uniupo.it

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[2] METLAC SpA, Strada Provinciale ex strada statale 35 Bis Dei Giovi 53 , 15062 Bosco Marengo, AL, Italy

Introduction

Polymeric coatings protect substrates while enhancing surface performance. Driven by sustainability, the industry has increasingly adopted solvent-free radiation curing technologies such as ultraviolet (UV) and electron beam (EB) curing. Compared to UV, EB curing offers deeper penetration and eliminates the need for photoinitiators, thereby mitigating migration risks in food-contact metal packaging [1]. Because robust adhesion is critical to preventing delamination and corrosion, bio-based adhesion promoters are drawing significant research interest. Tannic acid is highly promising due to its polyphenolic structure, which interacts effectively with metal surfaces; however, its integration into acrylic networks requires chemical functionalization. In this work, tannic acid was partially acrylated via reaction with glycidyl methacrylate to tune polarity and introduce reactive groups capable of covalently integrating during EB curing. Three TA–GMx derivatives with varying degrees of functionalization were synthesized, incorporated at multiple loadings into a commercial, partially bio-based EB-curable acrylic formulation, and evaluated for adhesion, flexibility, and corrosion resistance. [2]

Results and discussion

Three TA–GMx additives with varying degrees of acrylation were synthesized via the reaction of tannic acid with glycidyl methacrylate (**Figure 1**).

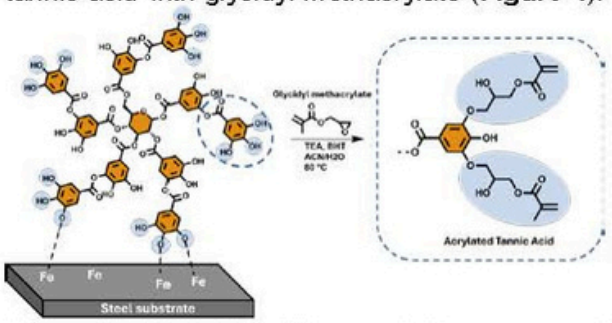


Figure 1. Schematic of the acrylation process of tannic acid with glycidyl methacrylate

Successful functionalization was confirmed by ^{1}H NMR and FTIR analyses (**Figure 2**), which revealed the disappearance of epoxide signals alongside the emergence of characteristic methacrylate peaks [3]. The degree of functionalization was precisely controlled by adjusting the tannic acid/GMA molar ratio.

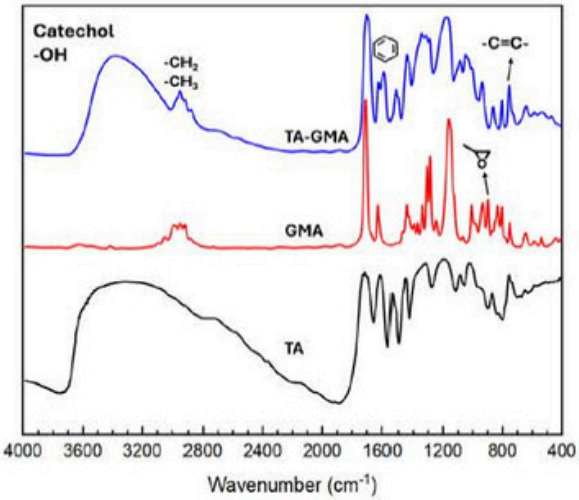


Figure 2. ATR FT-IR spectra of TA, GMA and TA-GM15.

Initial incorporation of TA–GMx into the reference EB-curable formulation resulted in poor miscibility, particularly for the less acrylated derivatives, due to a polarity mismatch between the hydrophilic tannic acid derivatives and the predominantly non-polar resin matrix. To address this issue, two polar comonomers were introduced, namely Cyclic Trimethylolpropane Formal Acrylate (CTFA) and Tetrahydrofurfuryl Acrylate (THFA). Both comonomers significantly enhanced additive solubility, yielding stable formulations at 1 and 3 wt% TA–GMx loadings.

DMTA analysis indicated that the additives influenced the crosslinked network as a function of both the degree of acrylation and

concentration. At a 1 wt% loading, increasing the degree of acrylation from TA–GM5 to TA–GM20 enhanced the crosslink density, with TA–GM20 yielding the highest value due to its greater number of polymerizable methacrylate groups. However, increasing the overall loading from 1 to 3 wt% reduced the crosslink density. This decrease is likely because residual phenolic groups acted as radical scavengers, partially inhibiting EB polymerization. Consequently, the additives establish a competing balance between introducing additional crosslinking sites and causing potential polymerization inhibition.

Adhesion testing focused on the derivative TA–GM15, which exhibited the optimal overall performance. While the reference formulation showed negligible adhesion to the tested metal substrates, TA–GM15 significantly enhanced adhesion, particularly within the IBOA/CTFA blend. The best results were achieved at 1 wt%, demonstrating excellent adhesion across oxidized electrolytic tinplate (ETP ox), Cr-free tinplate (CFPA), and low-tin steel (LTS) substrates. This improvement was attributed to hydrogen bonding and metal coordination between the catechol/hydroxyl groups of tannic acid and the metal oxide surface. Conversely, higher additive loadings slightly reduced adhesion, likely due to microphase separation or interfacial stress.

Wedge bend tests confirmed that TA–GM15 also improved flexibility and adhesion under deformation. The IBOA/CTFA formulation containing 1 wt% additive exceeded the 85% intact-film threshold across all substrates, reaching up to 92.5%. Furthermore, corrosion tests on Cr-free tinplate revealed that TA–GM15 markedly suppressed delamination. The optimized EB-cured formulation (IBOA/CTFA with 1 wt% TA–GM15) achieved a level of corrosion resistance comparable to that of a commercial solvent-based coating, confirming the potential of these sustainable additives for metal packaging applications [2].

Conclusions

Partially acrylated tannic acid derivatives (TA–GMx) were validated as bio-based adhesion promoters for EB-curable coatings in metal packaging. Tannic acid was functionalized with glycidyl methacrylate, while polar comonomers such as CTFA or THFA were required to ensure miscibility in the industrial formulation. The additives significantly enhanced adhesion, post-deformation flexibility, and corrosion resistance on all evaluated metal substrates. The optimal performance was achieved at a 1 wt% loading, which successfully balanced metal-surface interactions with efficient polymer network formation. Ultimately, the optimized IBOA/CTFA system incorporating 1 wt% of the modified additive performed comparably to a conventional solvent-based coating, highlighting its viability for sustainable EB curing in food packaging applications.

References

[1] A. Lestido-Cardama, J. Bustos, Comprehensive Reviews in Food Science and Food Safety, 21, 3558–3611 (2022)
[2] F. Bisio, K. Sparnacci, J Coat Technol Res (2026)
[3] R. Sesia, M. Sangermano, Progress in Organic Coatings, Vol 189 (2024)

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ENVIRONMENTALLY FRIENDLY UPCYCLING OF PHA-BASED COPOLYMERS INTO BRANCHED MULTIFUNCTIONAL OLIGOMERS

G. Damonte[1], M. Cozzani[1], A. Fortunato[1], A. Pellis[1], G. M. Guebitz[2,3], O. Monticelli[1]
[1]Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy
[2]Institute of Environmental Biotechnology, Department of Agricultural Sciences, BOKU University, Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria
[3]Austrian Centre of Industrial Biotechnology, Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria
e-mail: giacomo.damonte@edu.unige.it

Introduction

Polyhydroxyalkanoates (PHAs) are considered a sustainable alternative to oil-based plastics due to their biodegradability and low carbon footprint [1]. Among these, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) represents a promising alternative to poly(3-hydroxybutyrate) (PHB), due to its improved ductility and thermal stability, and wider processability window [2]. However, to expand the application of this promising polymer and make its use sustainable and scalable, recycling strategies need to be implemented. With this rationale, an alcoholysis process for PHBH was developed using bio-based reagents that could allow the formation of branched compounds with a high number of functional end groups, under solventless conditions and without the need for further purification steps. For this purpose, a polyalcohol as well as a catalyst from renewable resources, namely pentaerythritol (PE) and zinc stearate ($Zn(St)_2$), were used to promote transesterification reactions between the hydroxyl groups of PE and the ester bonds of PHBH with the formation of branched oligomers with hydroxyl end groups. Notably, the use of the above catalyst, which is also non-toxic and biocompatible, is a novelty in the alcoholysis reaction of PHA-based materials [3]. The developed oligomers were subsequently used as additives in the formulations of PHBH-based porous films through phase inversion using water as coagulant and Cyrene® as solvent, owing to their natural compatibility with the PHBH matrix and the potential ability to make the porous material also highly functional [4]. The influence of oligomers prepared using different amounts of PE on film properties, including morphology, thermal and mechanical properties, porosity, and water uptake, was investigated. In addition, the retention capacity of the films was evaluated by using an organic compound, namely pararosaniline hydrochloride (PR), a cationic triarylmethane dye which mimics the behavior of amino-containing drugs and organic pollutants, and palladium chloride ($PdCl_2$) as a source of an inorganic cation. The latter study also aimed to prove the possibility of using the developed films as adsorbers for the recovery of homogeneous catalysts. Moreover, to further expand the applications of the developed systems, the catalytic activity of the Pd-loaded PHBH-based films was also evaluated after the reduction of the adsorbed Pd ions to form Pd metal clusters. Finally, the susceptibility of the modified films to enzymatic hydrolysis was evaluated through degradation tests using *Humicola insolens* cutinase (HiC) in different concentrations and media.

Results and discussion

The alcoholysis reaction of PHBH with different amounts of PE (2, 5, and 10 wt.%) in the presence of $Zn(St)_2$ (2% wt.%) led to the direct formation of branched hydroxyl-terminated oligomers in one step and under solventless conditions, as determined by FTIR, ^{1}H-NMR, and GPC measurements. During this process, a dramatic reduction in the number-average molecular weight of the starting polymer was observed, decreasing from about 127000 g/mol for neat PHBH to values as low as 1350 g/mol for the systems prepared using 10 wt.% of PE. Moreover, the obtained oligomers exhibited progressively lower glass transition temperatures, decreasing from −2 °C for PHBH to −16 °C for the sample having the lowest molecular weight, confirming the strong influence of branching and reduced molecular weight on chain mobility. The obtained oligomers were subsequently employed, without purification, as additives in PHBH-based porous films prepared through phase inversion using water as a coagulation bath and Cyrene® as a biobased solvent. Specifically, the incorporation of the recycled oligomers (20 wt.%) within the high-molecular weight PHBH matrix (80 wt.%) enabled the formation of films with sponge-like morphologies, increasing the average pore size from 0.73 µm, measured for neat PHBH films, up to about 1 µm for modified systems. The functionalized porous films also displayed dramatically enhanced water uptake, increasing from about 10% for neat PHBH up to 218% for the

sample prepared using the lower molecular weight additives. The retention capability of the developed systems towards pararosaniline hydrochloride (PR), used as a model cationic compound, increased from 87 µg/g for neat PHBH films up to 390 µg/g for the most effective system, highlighting the beneficial effect of the multifunctional oligomers on adsorption properties. Furthermore, Pd-loaded porous films, tested in the hydrogenation reaction of a model compound, i.e., trans-stilbene, exhibited catalytic activity comparable to commercial Pd/C with 10 wt.% Pd loading, demonstrating the possibility of employing the developed materials as functional catalytic supports. Finally, enzymatic hydrolysis tests performed at 37 °C using HiC solutions prepared using different enzyme concentrations (1 or 5 µm) and media conditions (water or KPO buffer) highlighted the strong influence of upcycled oligomers on this property. While neat PHBH films reached about 74% degradation after 10 days of immersion in HiC 5 µM in KPO, the films containing the lowest molecular weight oligomers underwent complete degradation under the same conditions. RP-HPLC-MS analyses on the obtained supernatants, performed in positive ion mode, revealed the formation of monomeric and oligomeric species arising from the enzymatic depolymerization of PHBH chains, including 3-hydroxybutyric (3-HBA)-based monomers, dimers, and trimers. Simultaneously, RP-HPLC-RI monitoring of 3-HBA formation showed a good correlation with the measured mass loss during enzymatic hydrolysis, with increasing concentrations over time depending on the effectiveness of the enzymatic medium. These results demonstrate for the first time the complete depolymerization of PHBH-based materials within days using HiC under mild conditions. Moreover, the degradation profile could be tuned by varying the branched oligomer structure or the enzymatic hydrolysis conditions, highlighting the potential of these systems for future chemo-enzymatic recycling approaches.

Conclusions

In this work, a sustainable alcoholysis process for the production of multifunctional PHBH oligomers using non-toxic reagents and solventless conditions was successfully developed. The resulting upcycled branched products were effectively valorized as functional additives for the manufacture of highly porous PHBH-based films with enhanced adsorption and degradation properties. Moreover, the direct applicability of the obtained oligomers without requiring additional purification steps further improves the sustainability and scalability of the proposed upcycling strategy. The developed approach represents a promising route for the environmentally friendly upcycling of PHBH into highly tunable multifunctional additives, with potential application in high-molecular weight polymer systems and extension to other PHA-based systems or polyesters.

References

[1] F. Muneer, I. Rasul, F. Azeem, M. H. Siddique, M. Zubair, H. Nadeem, *Journal of Polymers and the Environment*, *28*(9), 2301–2323 (2020).
[2] F. M. Lamberti, L. A. Román-Ramírez, J. Wood, *Journal of Polymers and the Environment*, *28*(10), 2551–2571 (2020).
[3] M. Melchiorre, M. E. Cucciolito, M. Di Serio, F. Ruffo, O. Tarallo, M. Trifuoggi, R. Esposito, *ACS Sustainable Chemistry & Engineering*, *9*(17), 6001–6011 (2021).
[4] T. Marino, F. Galiano, A. Molino, A. Figoli, *Journal of Membrane Science*, *580*, 224–234 (2019)

AMORPHOUS BLENDS OF PLA AND PHA FOR WATERBORNE COATINGS AND FOAM APPLICATIONS

M. Calosi[1], A.D'Iorio[1], C. Raouf[1,2], M. Lahcini[2], M. Dippold[3], H. Ruckdäschel[3], E. Buratti[4], M. Bertoldo[1]

[1] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, via Borsari 46, 44121 Ferrara, Italy

[2] IMED-Lab, Faculty of Sciences and Techniques, Cadi Ayyad University, Avenue Abdelkrim Elkhattabi, B.P. 549, 40000 Marrakech, Morocco

[3] Department of Polymer Engineering, University of Bayreuth, Universitätsstraße 30, 95447, Bayreuth, Germany

[4] Department of Environmental and Prevention Sciences, University of Ferrara, via Borsari 46, 44121 Ferrara, Italy

Introduction

Poly (lactic acid) (PLA) is the most widely used bio-based and biodegradable polymer due to its versatility and relatively low cost. It is particularly promising as a replacement for traditional non-biodegradable polymers in the packaging world, in sectors such as films, paper coatings or foamed materials. However, PLA is only readily biodegradable in a thermophilic industrial composting environment, while in home composting (lower temperatures) or in soil biodegradation is far slower and in freshwater and seawater environments nearly absent.

The environmental biodegradability of PLA can be enhanced by blending with more degradable polymers.[1] This can be explained by an increase in exposed surface, by the easier formation of biofilms on these surfaces and by an increase in water permeation within the material. A good choice for such a blend partner for PLA are polyhydroxyalkanoates (PHAs), which are also bio-based and biodegradable aliphatic polyesters, but offer superior environmental biodegradability. The currently low production capacity and high costs of PHAs, associated with their direct production by microorganisms has limited their adoption as commercial materials. The use of PHAs as blend partners of PLA can lead to a material with lower costs compared to PHA and enhanced biodegradability compared to PLA. A commercial amorphous copolymer of 3- and 4-hydroxybutyrate (P34HB), specifically commercialized as a modifier for other polymers was chosen as the blend partner for PLA.[2]

In this work we report the blending of this P34HB with amorphous PLA grades to obtain fully amorphous PLA/PHA blends. Two different blending techniques were used: melt compounding and waterborne dispersion followed by coating or film casting. In both cases, miscibility and interfacial interactions, as well as any processing-induced degradation were assessed.

The waterborne blend was used to produce both free-standing films and paper coatings. The stability of the waterborne dispersions was assessed and their film-forming capabilities and the quality of the paper coatings were assessed, while the melt-blended product was used to produce foams by batch foaming with supercritical CO_2, studying the effect of temperature and pressure on foam density and cellular morphology to optimize the process.

Finally, we quantified the biodegradation of foam and film samples, mostly under home-composting conditions, by combining respirometry, mass loss, SEM, GPC, and NMR to track morphological and molecular changes and relate them to blend composition and sample morphology.

Results and discussion

Waterborne dispersions of PLA and PHA, as well as the pure polymers, were obtained by adapting a method previously used for PLA alone[3] by which the polymer(s) were dissolved in ethyl acetate, mixed with an aqueous solution containing a PEG-PLA-PEG copolymer surfactant, homogeneized by ultrasonication and the organic phase was then removed by evaporation. The dispersions were stable at all tested compositions (10-30-50-70-90% PHA content as well as the pure polymers) and had a 200-300 nm particles size and ~-40 mV Z-potential. Solids content was ~15% and further concentration of the dispersion increased this up to 35% without coagulation. Film-forming testing revealed that, while PLA dispersions had a minimum film forming temperature of ~50°C and only formed continuous films above this, PHA and blend dispersions with at least 50% PHA content were capable of filming at room temperature with good particle coalescence (Figure 1). Paper

coating tests were carried out by bar coating and concentrated dispersions of PLA/PHA blends were successfully applied on top of the paper substrate without the need for thickening agents.

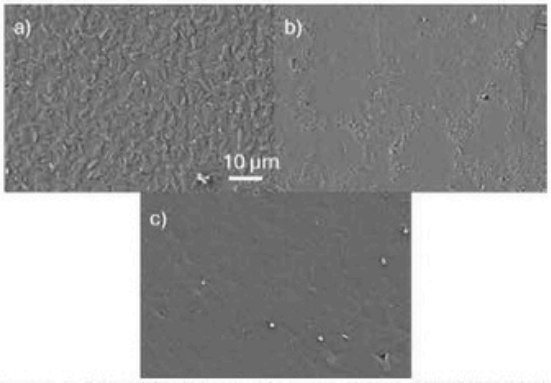


Figure 1 SEM images of films cast at 25 °C from waterborne dispersions of a) PLA b) a 50/50 PLA/PHA mixture c) PHA.

For melt blending, PLA and PHA were compounded at 185 °C. Viscosity measurements and SEC analysis indicated some thermal degradation of the PHA component at the mixing temperature, leading to a reduction in its molecular weight. The obtained blend granules were batch foamed via pressure drop method using supercritical CO_2 and the foaming was successful at obtaining low density foams (< 80 g/L) for blends with at most 30% PHA content. Foam densities and morphologies were dependent on foaming pressure and temperature. The lowest density was obtained for all blend compositions at 50 °C and 90 bar and had a closed-cell morphology and 40-80 µm of cell size. Using both blending techniques, the two phases were immiscible and two distinct glass transitions, as well as separate phases by TEM were observed.

The biodegradation properties of PLA/PHA blends was studied for films cast from waterborne dispersions and for low-density foams. The main studied condition was in simulated home-composting at 30°C, a temperature at which it was confirmed that PLA in both forms is scarcely degradable (ultimate biodegradation < 20%). When the films were tested (Figure 2a), a strong increase in the biodegradation rate of the blends was noticed compared to PLA, even with a PHA content as low as 10%. Importantly, the biodegradation of the blends was not the average of the two components but was closer to the one of the faster degrading PHA, indicating an acceleration of the biodegradation rate of the PLA component. 30% PHA content was found to be sufficient to obtain home compostable materials (ultimate biodegradation >80%). By contrast, the blend foams degraded slower than the films at the same blend ratios (Figure 2b), likely due to their closed-cell nature reducing the exposed surface, although the degradation of the PLA component was still found to be enhanced. Disintegration in simulated a marine setting was also studied for the foams and a limited degradation, selective for the PHA fraction with the PLA fraction being left untouched was instead observed in this case.

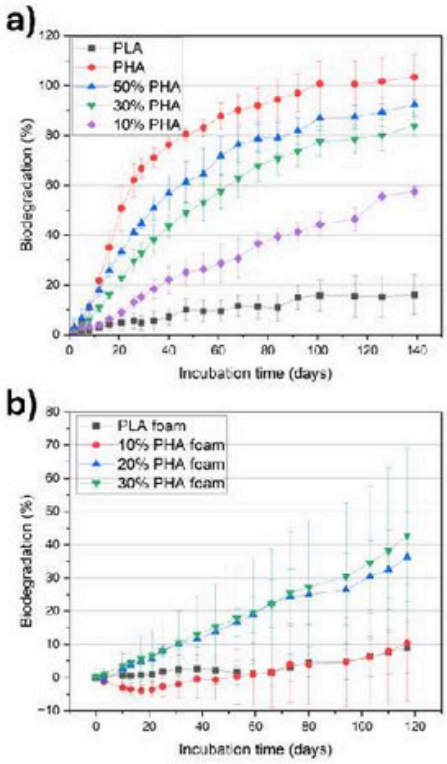


Figure 2. Respirometric biodegradation data the compostability at 30 °C of PLA, PHA or their blends at various blend ratios in the form of a) films cast from waterborne dispersions of b) low-density foams.

Conclusions

This work demonstrates that amorphous blends of PLA and PHA obtained through both waterborne dispersion and melt-compounding techniques are suitable for waterborne coatings and low-density foams and the environmental biodegradability of the resulting materials is increased compared to PLA, though to a lesser extent in foam form compared to film.

References

[1] Easton, Z. et al, Macromolecular Chemistry and Physics. 2023, 224 (6), 2200421.
[2] Han, G. et al, Polymer Testing, 2023, 126, 108155.
[3] M. Calosi et al, Progress in Organic Coatings, 2024, *193*, 108541.

Acknowledgments

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INVESTIGATION INTO THE POTENTIAL OF POLY(B-AMINO ESTER)-BASED VITRIMERS

Riccardo Chiarcos[1], Mattia Lippelli[1], Diego Antonioli[1], Michele Laus[1]

[1] Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale (UPO), Viale T. Michel 11, 15121, Alessandria, Italia
e-mail: riccardo.chiarcos@uniupo.it

Introduction

Vitrimers are an emerging class of polymer networks containing dynamic covalent bonds [1]. In the presence of appropriate stimuli, typically temperature changes, these bonds alter their relative position allowing the material to flow. This is the way these crosslinked networks can be reprocessed as thermoplastic polymers. Among the various types of vitrimers, one of the most promising system consists of poly(β-amino ester)s networks synthesized by the Aza-Michael reaction of acrylate and amine monomers [2]. Both bifunctional and trifunctional acrylate monomers were used in the works reported in literature[2], [3]. Bifunctional acrylates generally provide easily reprocessable materials with Tgs ranging from -50 to 70 °C. On the other hand, poly(β-amino ester)s networks based on trifunctional acrylates have higher Tgs but cannot be reprocessed at temperatures lower than 180 °C. In this work, a detailed study was carried out using formulations in which the amount of bifunctional and trifunctional acrylates was progressively varied. The final goal is to have a complete perspective on how the thermal and mechanical properties of the vitrimer vary as the percentage of the components varies.

Results and discussion

Poly(β-amino ester)s-based vitrimers were synthesized using bisphenol A glycerolate (1 glycerol/phenol) diacrylate (BPADA) and 1,4-butanediol diacrylate (BDA) as the bifunctional acrylates, pentaerythritol triacrylate (PTA) as the trifunctional acrylate and 4,4'-methylenebis(cyclohexylamine) (MCBA) as the amine. The percentages of BPADA and PTA were varied across the different formulations. All the synthesis were carried out with an acrylate/amine groups ratio of 2/1 at the temperature of 100 °C for 24 h.

The Tg of the material progressively increases as the percentage of PTA increases, as shown in Figure 1.

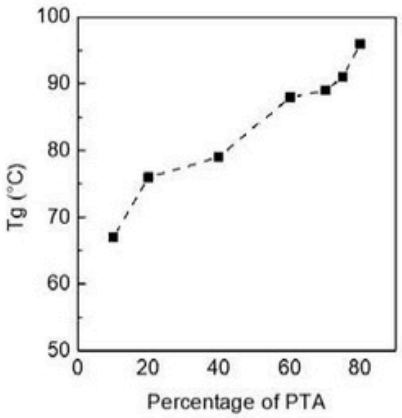


Figure 1. Tg of the vitrimers as a function of the PTA percentage.

The capability of the material to flow was investigated by stress-relaxation measurements. The derived relaxation times are reported in Figure 2 as a function of the PTA percentage. It results that increasing the amount of the trifunctional acrylate leads to an increase of the relaxation time, especially at temperatures lower than 160 °C.

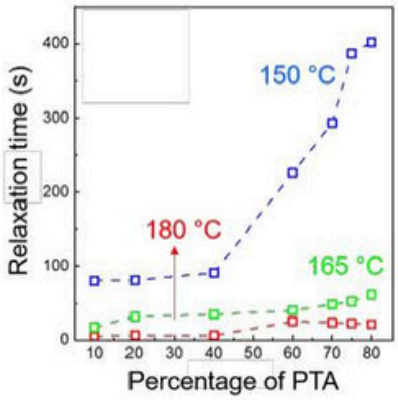


Figure 2. Relaxation time of the vitrimers as a function of the PTA percentage and temperature.

Consistently, the vitrimers with the lowest amount of PTA can be reprocessed in a hot press at 150 °C in 30 min, whereas temperatures higher than

180 °C are necessary for the vitrimers with high percentage of PTA.
Finally, having established that vitrimers based on bifunctional acrylates are much easier to reprocess, they were used as the basis for a new hybrid system. Poly(β-amino ester)s-based oligomers were synthesized starting from bifunctional acrylates and an amine in solution with a methacrylic monomer. In this reaction step, the methacrylic monomer does not participate in the reaction due to its lower reactivity and acts as a solvent. The obtained viscous liquid, which can be molded or coated, was then cured by thermally initiating the radical polymerization of the methacrylic monomer with some free acrylate groups contained in the poly(β-amino ester)s-based oligomers. Rigid materials with promising thermal and mechanical properties were obtained.

Conclusions

Poly(β-amino ester)s-based vitrimers were syntheisized starting from a mixture of bifunctional and trifunctional acrylate monomers and an amine. It was demonstrated that increasing the amount of the trifunctional monomer increases the Tg of the final material but significantly decreases the reprocessing capability by increasing the relaxation time of the vitrimer. Furthermore, poly(β-amino ester)s-based oligomers based on bifunctional acrylates were integrated in an innovative hybrid system thermally cured through the radical polymerization of the oligomers with a methacrylic monomer.

References

[1] C.J. Kloxin, C.N. Bowman, *Chem. Soc. Rev.*, vol. 42, 7161-7173 (2013)
[2] C. Taplan, M. Guerre, F.E. Du Prez, *J. Am. Chem. Soc.*, vol. 143, 9140-9150 (2021)
[3] S.S. Kashyap, K. Borah, J. Shivam, S. Kumar, S. Sarmah, M.K. Bera, P. Basak, R. Narayan, *ACS Appl. Polym. Mater.*, vol. 6, 3894-3908 (2024)

FORMULATION AND CHARACTERIZATION OF POLYHYDROXYALKANOATE BLENDS WITH WASTE PROTEIN FIBERS FOR PACKAGING APPLICATION

S. Alfano[1], G. Tittaferrante[1], A. Martinelli[1], A. Piozzi[1], L. Galantini[1], R. Mezzenga[2], I. Francolini[1]

[1] Dept. of Chemistry, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00185, Roma, Italy
[2] Dept. of Health Sciences & Technology, ETH Zurich, Schmelzbergstrasse 9, 8092, Zurich, Switzerland
e-mail: sara.alfano@uniroma1.it

Introduction

Agri-food waste valorization plays a key role in the transition toward a circular economy, as it enables residual biomass to be converted into valuable resources through different technological approaches. These residues represent an abundant and renewable source of valuable compounds, including polysaccharides, proteins, lipids, and other bioactive molecules, which can be recovered and reintroduced into new production chains. Beyond the extraction of individual components, agri-food waste can also serve as a low-cost feedstock for microbial fermentation processes aimed at producing bio-based polymers.

Among these, polyhydroxyalkanoates (PHAs) have attracted increasing interest as biodegradable and biocompatible polyesters synthesized by microorganisms under specific growth conditions [1]. Their renewable origin, processability, and potential biodegradability make them promising candidates for replacing conventional petroleum-based plastics, particularly in packaging applications.

In this context, waste protein fibers (WPF) have gained attention as a groundbreaking class of high-aspect-ratio building blocks for bioplastic reinforcement. Formed through the controlled denaturation and hierarchical self-assembly of industrial protein by-products, these nanostructures possess an extensive supramolecular hydrogen-bonding network that confers exceptional mechanical stiffness and intrinsic toughness [2,3].

Integrating WPFs into PHA matrices offers a unique opportunity to design fully renewable, high-performance bio-blends. Nevertheless, combining highly hydrophilic protein networks with a hydrophobic polyester matrix introduces critical thermodynamic compatibility challenges, resulting in poor interfacial adhesion, phase aggregation, and drying-induced shrinkage.

To overcome these barriers, targeted compatibilization strategies are required to tailor the interphase between WPFs and PHA, promoting stronger molecular interactions, improved stress transfer, and a more homogeneous phase morphology. These strategies may include the chemical or enzymatic modification of WPFs, the use of compatibilizers or coupling agents, and reactive blending approaches. In parallel, plasticization and controlled processing conditions can mitigate shrinkage and aggregation by enhancing chain mobility and dispersion stability, ultimately enabling the development of dimensionally stable, mechanically robust, and fully bio-derived composite systems.

This work investigates the synthesis and application of sulfonated PHBH (PHBH-SO_3) [4] as a compatibilizer for PHA/WPFs (Waste Protein Fibers) blends. Specifically, different PHBH-SO_3 contents were incorporated while maintaining a fixed PHA/WPF ratio, to assess the effect of compatibilizer concentration on phase adhesion, dispersion quality, and overall blend performance. In parallel, blends containing different WPF loadings were prepared at a constant compatibilizer content, allowing the influence of protein fiber concentration on morphology, dimensional stability, and thermo-mechanical behavior to be systematically evaluated.

Finally, films were obtained by exploring two processing techniques, namely solvent casting and compression molding, to identify the most suitable route for achieving homogeneous and dimensionally stable PHA/WPFs bio-blend films.

Results and discussion

The integration of PHBH and WPFs was systematically evaluated, firstly identifying 25 wt% PHBH-SO_3 as the optimal compatibilizer content for effective fibril incorporation and homogeneous components distribution. FTIR analysis confirmed that WPFs were successfully incorporated into

the polymer matrix, with chemical signals varying consistently according to the fibril loading.

Subsequent experiments were conducted by maintaining constant PHBH-SO_3 content while varying the PHBH: WPFs weight ratios

The results from film characterisation, including shrinkage, material loss, yield, and surface morphology, are presented in Figure 1.

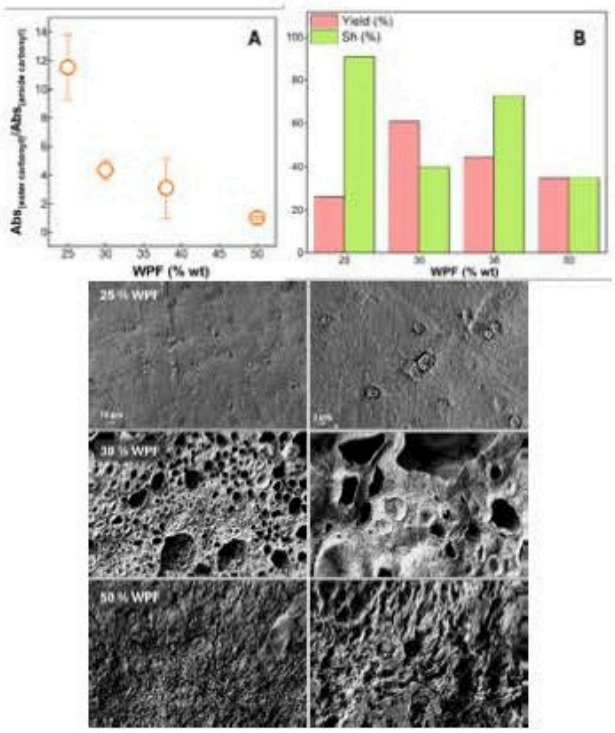


Figure 1. Characterisation of PHBH/WPF films with fixed PHBH5-SO_3 content (25 %wt) and different PHBH: WPF ratios 2:1 (25% WPF), 1.5:1 (30% WPF), 1:1 (38% WPF), and 0.5:1 (50% WPF). a) Ester and amide carbonyl intensity ratio as a function of WPF %wt; b) Shrinkage (Sh factor) and material loss (Yield) variation related to WPF (%wt). Morphological characterization of film with different PHBH: WPF ratio. Micrographs at 1k x (left column) and 5k x (right column) magnification.

Optimized film characteristics, including minimal shrinkage and high material yield, were obtained at intermediate WPF contents. SEM analysis corroborated this, revealing that optimal loading yields homogeneous surfaces, whereas deviations lead to phase separation and void formation. Furthermore, DSC and POM analysis highlighted the role of WPF as a nucleating agent: the incorporation of fibrils effectively promotes PHBH crystallization and significantly reduces spherulite size, indicating a high nucleation density and superior microstructural homogeneity.

While emulsion casting served as a fundamental method for morphological characterization, it often resulted in localized drying stresses. Preliminary tests on the compression moulding of dried emulsion-derived blends proved superior, yielding free-standing, transparent films with improved surface uniformity and mechanical integrity.
Static contact angle and water response measurements confirmed that the tested formulation at different polymer/WPF ratios remains almost hydrophobic, despite minor variations, suggesting potential use in non-water-soluble packaging.
Water contact angle measurements were conducted to confirm that the tested formulations remain hydrophobic across all polymer/WPF ratios, suggesting potential use in non-water-soluble packaging. Mechanical and viscoelastic properties are currently under evaluation.
By minimizing residual stress from solvent evaporation, this emulsion-based compression moulding strategy offers a robust pathway for producing high-performance, biodegradable PHBH/WPF materials.

Conclusions

Sulfonated PHBH effectively compatibilizes hydrophilic WPFs with hydrophobic PHBH, enabling homogeneous composite formation. WPFs incorporation further improves structural integrity by promoting refined matrix crystallization. Compression moulding of emulsion-derived powders emerges as a superior, scalable processing route compared to solvent casting, offering enhanced film quality. This strategy provides a robust foundation for the fabrication of sustainable, high-performance biocomposites.

References

[1] G. Salvatori, S. Alfano, *Industrial and Engineering Chemistry Research*,62, 17400–17407 (2023)
[2] S. R. Goswami, *ACS Sustainable Chemistry and Engineering*, 13, 8068-8077 (2025)
[3] J. Adamcik, R. Mezzenga, *Macromolecules*,45, 1137-1150 (2011)
[4] S. Alfano, *ACS Applied Bio Materials*,13, 6109-6120 (2025)

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DEVELOPMENT AND INDUSTRIAL PROCESSING OF CELLULOSE-BASED MATERIALS FOR RIGID PACKAGING APPLICATIONS

A.Giovagnoli[1], L. Menegaldo[2], F. Bonvicini[2], D. Caretti[1], G. Mazzotti[3]

[1] Dept. of Industrial Chemistry "Toso Montanari", University of Bologna, Via P. Gobetti 85, 40129, Bologna, Italy
[2] Dept. of Pharmacy and Biotechnology, University of Bologna, Via Massarenti 9, 40138, Bologna, Italy
[3] SACMI S.C., Via Selice 17/A, 40026, Imola, Italy

e-mail: angelica.giovagnoli2@unibo.it

Introduction

Increasing environmental concerns related to conventional fossil-based plastics have strongly stimulated research into bio-based materials and natural polymers as sustainable alternatives for packaging applications [1]. Many industrial and academic researches are nowadays focused on enhancing the functional properties of these materials such as mechanical strength, barrier performance, and thermal stability through blending, preparation of biocomposites, and surface modifications, in order to make them more competitive than possible with conventional plastics in packaging applications [2]. In this PhD project, the molecular design optimization of flavonoid-derived compounds with high apolar behaviour led to the development of fully cellulose-based rigid closures for beverage applications shaped by Sacmi's Dry Compression Moulding methodology. The work started from laboratory scale research in which bio-based compounds have been synthesized and deeply characterised in order to investigate their structural nature, curing and thermal properties. The compounds synthesized, have been applied onto fibrous cellulose substrates and consequently moulded by an hydraulic manual hot-press that simulates the Sacmi's dry compression moulding. Finally, the obtained disc-shaped moulded objects have been deeply characterised to investigate their mechanical, thermal, structural, biodegradability, leaching tenedency and active properties. The most performing cellulosic treated substrates have been chosen to be moulded by the automated Sacmi's machinery in order to obtain three-dimensional shaped objects with high degree of detail like bottle caps and necks. Their structural integrity after different liquids uptake test has been investigated by thomography and their closure performance was verified by sealing performance tests.

Results and discussion

^{1}H-NMR and FT-IR spectroscopic analyses on synthesized compounds confirmed the achievement of the designed structures.

Both the flavonoid-derived compounds, once applied onto cellulosic substrates highlighted values of WCA higher up to 130° and Cobb values lower than 20 g/m^2 on disc-shaped dry moulded samples. Young's Modulus values up to 2300 MPa, obtained from the tensile tests, confirmed that the final materials resulted compatible with rigid packaging applications while thermal analysis (TGA) demonstrated that the presence of the additives onto the cellulosic substrate didn't affect the degradation temperature of the final material that remained close to the one of pure cellulose. Moreover, thermal analyses and ^{1}H-NMR confirmed that the temperature set for the moulding process didn't induce degradation of the additive and, of the final material. The processability of the treated cellulose was confirmed by the moulding step into automated industrial machinery for the production of dry-compressed bottle caps and necks. Their good barrier effect was confirmed by low uptake values (lower by 10%) of water and polar liquids commonly used for beverage as reported in Figure 1.

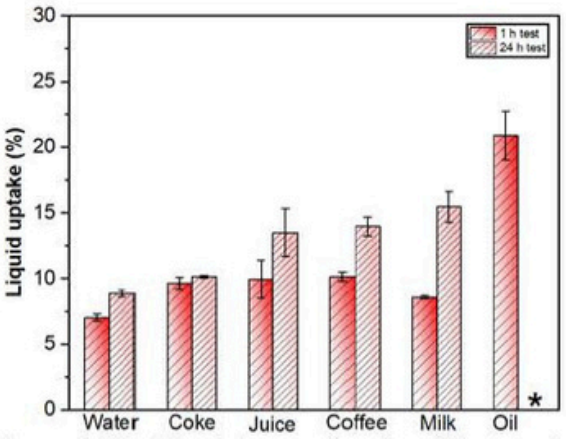


Figure 1. Liquid uptake results after 1 hour and 24 hours test.

Thomographic images demonstered a good structural integrity of the moulded object even after the liquid uptake except for fatty liquids like oil and milk. Releasing test, confirmed the low tenedency of the additive, due to its high apolarity, to migrate from the cellulosic substrate to an acqueos matrix, reaching leaching values lower that 10 mg/dm^2. The fluorescent properties of the compound under a 390 nm UV lamp were exploited to follow the additive's distribution whithin the fibers before and after the moulding process, verifying that the used temperature and pressure conditions favour its homogeneous spread onto the cellulosic matrix. Biodegradability assay confirmed good tendency of the material to degrade under controlled soil composition as confirmed from gravimetric evaluation and SEM images acquisition that has shown a severely disrupted and fragmented morphology of the fibers after three months.

DPPH assays highlighted the high antioxidant activity (Figure 2) of the final treated material that achieved values up to 95% of scavenging activity whene 2% w/w of additive was applied to cellulose substrates.

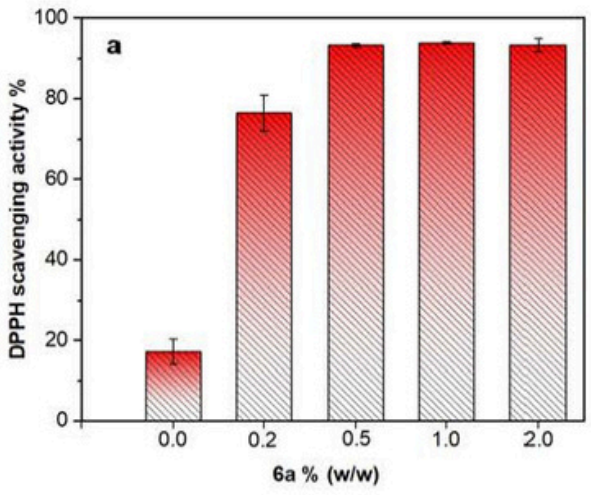


Figure 2. Results of scaveninging activity versus % of additive.

Biological assays have proven at three different temperatures the anti-biofilm activity against *Staphilococcus Aureus'* bacterial strain, giving the best results for 37°C conditions; providing an interesting and promising property for beverage shelf-life and safety improvement.

Conclusions

Very promising results about sustainable cellulose-based rigid packaging have been developed in terms of polar liquid barrier properties without any use of fossil-based plastics. The good biodegradability of the final materials underlined the sustainable nature and end-of-life of the final material. The most promising compound synthesized in this research project, highlighted active properties, opening the door to the development of smart packaging systems. The high yeld of the synthesis and the low production of by-products to be purified is a good compromise for a possible future scalability of additive's production.

The good processability of the cellulosic treated material into the automated machinery is a promising step for the moulding scalability in an industrial continuous process.

Overall, a sustainable, active, biodegradable new cellulosic material with high liquid water barrier performances has been developed, demonstrating the importance of research in the field of innovative sustainable materials to be used in packaging for a greener future.

References

[1] I. Sazdovsky et al., *Polymers*, vol. 17, 1629, (2025)

[2] K. Olonisaki et al., *Green Chem.*, vol. 27, 11656, (2025)

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USE OF FRUIT PEELS FOR THE DEVELOPMENT OF BIO-BASED HYDROGELS

D. Gaikwad, M. Mauri, U. Edlund, R. Simonutti

[3] Dept. of Fibre and Polymer Technology , Royal Institute of Technology KTH, Teknikringen 56, 10044 Stockholm, Sweden
[4] Dipartimento di Scienza dei Materiali;Università di Milano – Bicocca;Via Cozzi 55, Milano, Italy

Email:d.gaikwad@campus.unimib.it

Introduction

Food waste represents a growing environmental burden, especially because discarded peels are rich in organic matter, and biodegradable components. https://doi.org/10.1016/j.foodchem.2016.12.093 (1) , However, these residues are also valuable sources of natural biopolymers such as cellulose, hemicellulose, pectin, lignin, starch, and aliphatic polyesters https://www.mdpi.com/2077-0375/15/12/354 (2) .Converting such waste into functional materials offers a sustainable route to address both biomass waste management and water contamination. Bio-based hydrogels have gained attention as promising adsorbents because of their high-water uptake, porous three-dimensional networks, tunable swelling behavior, and abundance of reactive functional groups. hydrogels.https://doi.org/10.1016/j.eurpolymj.2015.04.017 (3). These functional groups can interact with pollutant molecules through hydrogen bonding, electrostatic interactions, and surface adsorption mechanisms.

The novelty of this work relies in the use of kiwi/apple peels that are further hydrolyzed and exploited as precursors for gel formation by free radical polymerization of HEMA and PEGMA crosslinked by N, N-methylene-bis(acrylamide) (MBA) following the seminal paper by Baglioni and coworkers https://pubs.acs.org/doi/10.1021/la3048664 (4) andhttps://patents.google.com/patent/EP4463593A1/en (5). This gel (Fig.1a) inhibits rapid swelling leading to maximum adsorption within the first few hours where the gel structure is stable.

Here, as drug models, we test Diclofenac Sodium (DCF) and Norfloxacin (NOR) that are common pollutants found in pharmaceutical water waste. DCF is one of the non-steroidal anti-inflammatory drugs (NSAID) and NOR is a fluoroquinolone antibiotic drug. We also test the adsorption properties of Methylene blue; a common dye used in textile as well as biomedical research.

Results and discussion

The pore structure of the gel was characterized by recording FE-SEM images on the freeze-dried samples. Images reveal a clean, porous structure for the kiwi-based hydrogel with flawless visibility of interconnected networks. Pore sizes appear irregular; the walls of larger pores present small holes. In the case of green apple-based hydrogel, a completely different landscape appears, with small thread-like structures showing connectivity proving crosslinking of the material forming 3-dimensional structure Figure 1c. The kiwi-based hydrogels exhibited clear methylene blue (MB) dye-removal capability [Fig 1d], as confirmed by UV–Vis-spectroscopy. At low MB concentration, particularly 2 μM, the hydrogels removed almost all of the dye from the solution, indicating a high adsorption efficiency under dilute conditions. In contrast, at higher MB concentrations, the relative removal efficiency decreased, suggesting progressive saturation of the available adsorption sites within the hydrogel network. Calibration curves constructed for MB solutions in the concentration range of 2–20 μM under different pH conditions, namely pH 3 and pH 5, showed excellent linearity with correlation coefficients of R2 = 0.994–0.999. This confirms the applicability of the Beer–Lambert law within the selected concentration range. After adsorption for around 28 hours, the measured absorbance values of the residual MB solutions were below the lower limit of the calibration range, indicating that the remaining MB concentration was negligible. These results suggest nearly complete removal of MB from an aqueous solution under the tested low-concentration conditions, including both pH 3 and pH 5 environments.

For Green apple peel-based hydrogel, the drug removal efficiency was calculated where the maximum adsorption for DCF is noticed at 25 mg L^{-1} with q_e = 0.216 mg g^{-1} and q_e=0.023 mg g^{-1} for NOR at 11 mg L^{-1} with maximum removal efficiency at 79.6% and 20.57% respectively. Further the adsorption kinetics were evaluated

on working solutions, obtained by diluting the stock solutions of each drug molecule to the required concentrations in the range of (2,5,10,11,12,20,25 mg/L) using pseudo-first order and pseudo-second order are plotted for both DCF and NOR.
The adsorption kinetics for DCF are well fitted using pseudo-second order as seen in the (table 1) which shows linearity R^2 closer to 1. However, the 10 and 20 mg L^{-1} fits gave negative intercepts, resulting in negative k_2 values, which are not physically meaningful whereas we also observe that at higher concentration of the solution the gel is more stable with respect to time showing higher intake of drug molecules. The 25 mg L^{-1}condition gave the most reliable pseudo-second-order fit, with positive k_2 = 4.2178 g mg^{-1} min^{-1} and R^2 = 0.9986. The 5 mg L^{-1}sample showed a weaker fit, with R^2 = 0.8877, suggesting less stable kinetic behavior at low concentration.
The adsorption behavior for NOR showed low and irregular adsorption behavior across the tested concentrations. The pseudo-second-order kinetic model only gave a moderate fit at 10 mg L^{-1} (R^2 = 0.7557) and poor fits at 11 and 12 mg L^{-1} (R^2 = 0.3565 and 0.1316). Therefore, NOR adsorption does not strongly follow pseudo-second-order kinetics under these experimental conditions.in table 2.

Conclusions

n conclusion, hydrogels formed by using kiwi peels as bio- based material exhibited strong rapid swelling and effective Methylene Blue adsorption. The calibration curve allowed accurate quantification of dye removal. Kiwi based hydrogels show potential for dye removal and environmental applications.
For green apple peel based hydrogel, during pseudo order calculations it was observed that DCF shows stronger adsorption behavior compared with NOR suggesting greater affinity between DCF molecules and the hydrogel adsorption sites. The pseudo -second-order adsorption model provides better fitting for DCF as evaluated R^2 values are closer between experimental equilibrium adsorption ($q_{e,exp.}$) and calculated equilibrium ($q_{e,cal.}$)adsorption. For NOR, the adsorption data showed comparatively weaker fitting toward the pseudo-second-order model as the experimental equilibrium adsorption ($q_{e,exp.}$) kept fluctuating with respect to time.
Furthermore, this material can be enhanced more by trying to use bio-based crosslinkers and monomers. This work not only suggests solution for one but two environmental solutions which are using bio-based material developed from fruit peels leading to reduction of generated agricultural waste but also solutions for water treatment to trap pollutants from waste water.

References

[1] J. Banerjee, R. Singh, R. Vijayaraghavan, D. MacFarlane, A. F. Patti, A. Arora, Food Chemistry, vol. 225, 10–22 (2017).
[2] Y. Yuan, F. Wang, Y. Yu, Z. Qin, H. Xi, C. Wu, Membranes, vol. 15, Article 354 (2025).
[3] M. R. Guilherme, F. A. Aouada, A. R. Fajardo, A. F. Martins, A. T. Paulino, M. F. T. Davi, A. F. Rubira, E. C. Muniz, European Polymer Journal, vol. 72, 365–385 (2015).
[4] J. A. L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Langmuir, vol. 29, 2746–2755 (2013).
[5] R. Mink, R. Simonutti, M. Mauri, Leather-like material from plant-based wastes, process of manufacturing and use of said leather-like material, European Patent EP4463593A1, European Patent Office (2024).

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Molecule	C_0 (mg L^{-1})	qe,exp (m g g^{-1})	qe,cal (m g g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
DCF	5	0.01257	0.01369	8.7804	0.8877
DCF	10	0.05213	0.04691	-1.9463	0.9992
DCF	20	0.13766	0.12038	-0.5381	0.9992
DCF	25	0.21654	0.21789	4.2178	0.9986
NOR	10	0.02125	0.02218	5.2957	0.7557
NOR	11	0.02262	0.07656	0.0539	0.3565
NOR	12	0.02256	0.05015	0.1347	0.1316

Table. 1. Pseudo-second-order for DCF and NOR adsorption

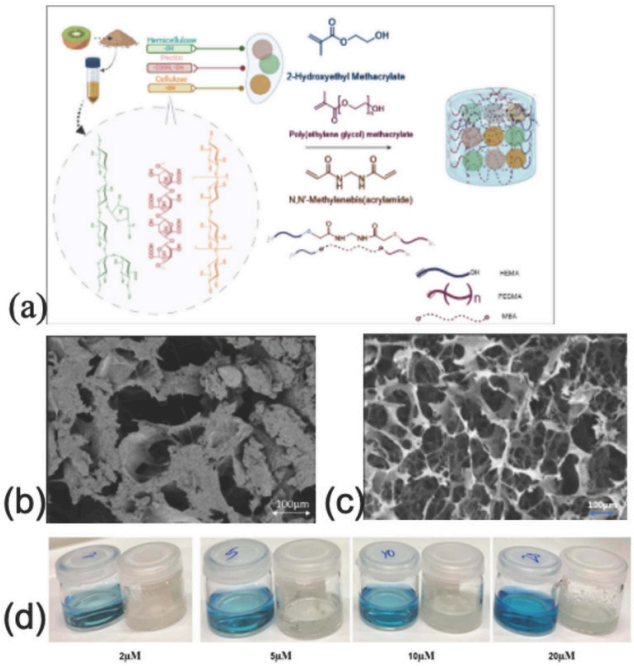


Fig. 1. (a) Illustration showing gel formation process; (b) SEM image of Kiwi- hydrogel; (c) SEM image of Apple-hydrogel; (d) Image showing dye removal

N. Victoria dos Santos[1], L. Gioiella[1], V. Ambrogi[1], M. Salzano de Luna[1], G. Filippone[1]

[1] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale (DICMaPI), Università di Napoli Federico II, p. le Tecchio 80, 50125, Napoli, Italia

e-mail: gfilippo@unina.it

Introduction

Thermoplastic short-fiber biocomposites, obtained by reinforcing bioderived or biodegradable polymer matrices with natural fibers, are receiving increasing attention as more sustainable alternatives to conventional petroleum-based composites. Their interest is related to the ease of thermoplastic processing, the use of renewable raw materials, and the possibility of more favorable end-of-life routes, such as recyclability and biodegradability [1–3].

Despite these advantages, their broader use is still limited by the efficiency of stress transfer at the fiber–matrix interface, which has a direct impact on the mechanical performance of the composite. This interaction is commonly described through the interfacial shear strength, τ_y, a key parameter that determines how effectively the load is transferred from the matrix to the fibers and, consequently, the critical fiber length required for reinforcement [4,5].

Several micromechanical techniques can be used to evaluate τ_y, including fragmentation, microdroplet, and pull-out tests. However, each of these methods presents specific limitations, particularly when natural fibers are involved [6]. One critical aspect of pull-out testing is that specimens are often prepared without applying a controlled pressure. This differs from real thermoplastic composite processing, where pressure is always present and can strongly affect the contact between fibers and matrix. This is especially relevant for natural fibers, whose rough and porous surfaces may allow the polymer matrix to penetrate surface irregularities when pressure is applied. For this reason, the present study investigates the effect of processing pressure on the interfacial shear strength of PLA–hemp biocomposites by means of pull-out testing.

Materials and methods

PLA Ingeo™ 4060D was used as the polymer matrix, while untreated hemp fibers were used as reinforcement. Fibers were cut below 1 cm, dried together with PLA, and melt-compounded in a twin-screw extruder at 180 °C to obtain PLA/hemp pellets. The pellets were then injection molded into ISO 527-2 type 1-BA specimens for tensile testing.

Pull-out specimens were prepared by compression molding PLA strips with aligned hemp fiber bundles at 180 °C under different pressures: 0.05, 20, and 43 bar. Pull-out tests were conducted at room temperature using a universal testing machine (Tensometer 2020, Alpha Technologies) with a 500 N load cell. Specimens were clamped using a support that secured the matrix without compressing it, and fibers were pulled at 0.6 mm/min. The apparent interfacial shear strength was calculated from the maximum force (F_{max}) using Eq. 1:

$$\tau_y = \frac{F_{max}}{\pi D_{eq} L_e} \qquad (1)$$

where D_{eq} is the fiber equivalent diameter. At least six specimens were tested per condition. Samples that experienced fiber breakup or internal debonding between contiguous bundles were discharged in the following analyses.

Results and discussion

During melt processing, hemp fiber bundles are exposed to both temperature and mechanical stresses. These conditions can soften the intercellular material within the bundles, promoting their separation and causing significant fiber shortening, particularly during twin-screw extrusion. Optical microscopy of the composite containing 20 wt% hemp fibers shows that the fibers are mainly present as short, discontinuous bundles embedded in the PLA matrix. These bundles are the same structural elements that remain in the composite after compounding and are therefore the actual load-bearing units in the material. They are more complex than the single elementary fibers typically considered in conventional microdroplet or pull-out tests. For this reason, focusing on the interaction between hemp fiber bundles and the PLA matrix provides a more realistic basis for evaluating the interfacial shear strength in these systems.

The production of thermoplastic biocomposites reinforced with discontinuous natural fibers involves several consecutive steps. First, the raw materials, namely PLA pellets and hemp fibers, are selected and prepared. They are then compounded in an extruder to obtain composite pellets, which are subsequently molded into the final specimens. Among the processing parameters, temperature, pressure, and residence time play a central role in determining the quality and final properties of the composite.

Although pressure is a key parameter in real thermoplastic processing, it is often neglected in conventional micromechanical tests used to estimate interfacial shear strength, such as microdroplet and pull-out tests. This omission may be particularly important for natural fibers, where pressure can improve fiber–matrix wetting, promote bundle consolidation, and increase the effective contact area between the polymer and the fiber surface. The experimental approach used in this work was therefore designed to explicitly account for the role of pressure during specimen preparation.
The apparent interfacial shear strength obtained from pull-out tests clearly depends on the pressure applied during molding, as reported in Table 1.

Table 1: apparent interfacial shear strength (τ_y) of pull-out test specimens as a function of the molding pressure

Pull-out ID	Pressure [MPa]	τ_y [MPa]
PT00	0.05	5.5 ± 1.1
PT20	2.0	11.6 ±1.2
PT43	4.3	15.7 ±1.6

The trend shown in Table 1 can be explained by the improved contact between fiber and matrix at higher pressure. Under pressure, the PLA matrix can better conform to the rough hemp fiber surface and penetrate surface crevices, thereby increasing the effective contact area available for stress transfer. As a consequence, the force required to pull the fiber bundles out of the matrix increases, leading to higher apparent interfacial shear strength values. It is also worth noting that the τ_y value measured for specimens prepared at approximately 0.5 bar, which corresponds to the minimum pressure required to keep the material confined in the mold, is close to the value reported by Sawpan *et al.* [7] for PLA–hemp composites prepared without applying pressure. This agreement further supports the idea that molding pressure has a strong influence on the measured interfacial properties.
Overall, these results suggest that conventional pull-out tests may underestimate the actual interfacial strength of natural fiber–polymer systems when pressure is not properly considered. As a direct consequence, the critical fiber length calculated from these tests may be overestimated. In practical terms, this means that fibers considered too short to effectively reinforce the matrix may, under real processing conditions, still contribute significantly to load transfer.

Conclusions

The results of this study show that processing pressure plays a crucial role in the interfacial behavior and mechanical performance of thermoplastic biocomposites reinforced with natural fibers. Increasing the pressure during specimen preparation promotes matrix penetration into the surface irregularities of hemp fiber bundles, increases the effective fiber–matrix contact area, and improves stress transfer. This effect is not fully captured by conventional micromechanical tests when pressure is neglected. As a result, the interfacial shear strength may be underestimated and the critical fiber length may be overestimated. These findings indicate that processing pressure should be explicitly considered when evaluating interfacial properties and predicting the mechanical behavior of industrially processed natural fiber composites.

Finally, the importance of pressure may be less pronounced for synthetic fibers, which generally have smoother and less porous surfaces than natural fibers. Ongoing analyses are therefore focused on clarifying the role of fiber roughness in determining τ_y and, more broadly, the structural performance of bio-based and conventional composites, both of which strongly depend on fiber–matrix adhesion.

References

[1] M. Akter, M. H. Uddin, I. S. Tania, *Journal of Reinforced Plastics and Composites*, 41(17-18), 705-742 (2022).
[2] M. Nagalakshmaiah, S. Afrin, R. Malladi *et al. Green composites for automotive applications*, 197-215. (2019)
[3] A. P. More, *Advanced composites and hybrid materials*, 5(1), 1-20 (2022)
[4] H. M. Brodowsky, A. Hennig, *Materials Circular Economy*, 4(1), 5 (2022)
[5] A. Kelly, A. W. Tyson, Journal of the *Mechanics and Physics of Solids*, 13(6), 329-350 (1965)
6. J. Müssig, N. Graupner, *Progress in adhesion and adhesives*, 6, 69-130 (2021)
7. M. A. Sawpan, K. L. Pickering, A. Fernyhough, Composites Part A: Applied Science and Manufacturing, 42(9), 1189-1196 (2011)

Acknowledgments

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STRUCTURAL CONTROL AND AMYLOID REINFORCEMENT OF WASTE-DERIVED PROTEIN FILMS

M. Colombo[1], E. Testa[1], E. Fasoli[1], D. Gentile[1], V. Barbera[1] , M. Galimberti[1]

[1] Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Via E. Bassini 6, 20131 Milano, Italy

Introduction

The transition towards a circular bioeconomy requires the development of advanced materials from underutilized organic waste streams [1]. Proteins derived from industrial by-products and waste, such as black soldier fly (*Hermetia illucens*, BSF) larvae and sericin, represent promising feedstocks for biodegradable plastics [1, 2]. Amyloid fibrils are highly ordered protein aggregates characterized by a cross-sheet quaternary structure. They have emerged as exceptional building blocks due to their remarkable mechanical stability and functional versatility [1, 3]. This work investigates the fabrication of protein-based films where structural properties are tuned through the employment of pure fibrillated protein systems and blends with biodegradable polymers (*Figure 1*).

Results and discussion

Initial proteomic analysis was conducted to identify the soluble fraction and the molecular weight distribution of the protein extracts [1] . For BSF proteins, a myofibrillar-rich composition was observed, requiring alkaline conditions (pH 11.5) for optimal solubilization and subsequent fibrillization [1]. Thioflavin T (ThT) fluorescence assays, ATR-FTIR spectroscopy and TEM analysis (*Figure 2*) confirmed the transition from native conformations to an intermolecular -sheet-rich architecture [3].

The amyloid fibrils were utilized as structural crystallites to enhance the properties of different polymeric systems through two specific integration methods. In the first approach, fibrillated protein solutions (e.g., BSF fibrils) were blended directly with polyvinyl alcohol (PVOH) and glycerol [1]. This process results in an interpenetrating network where the fibrils organize into a continuous, nanostructured reinforcement within the PVOH matrix [1]. In the second approach, amyloid fibrils were produced, isolated, and lyophilized to be used as reinforcing nanofillers. These lyophilized fibrils were subsequently integrated into protein-based film-forming solutions, acting as rigid crystalline domains that distribute mechanical stress and improve the homogeneity of the protein matrix.In both configurations, the presence of amyloid crystallites significantly improved the material performance. For films based on BSF fibrils and PVOH, the integration of fibrils promoted mechanical reinforcement while maintaining thermal weldability [1]. Furthermore, the dense arrangement of these amyloid structures provides superior gas barrier properties. The resulting films exhibited remarkably low O and CO permeability coefficients, comparable to high-barrier synthetic polymers, demonstrating their high potential for sustainable packaging applications [1].

Conclusions

This study demonstrates that waste-derived proteins can be successfully converted into high-performance bioplastic films through controlled amyloid fibrillization [1]. By utilizing fibrils either directly in solution for blends with PVOH or as lyophilized reinforcements for other protein matrices, their role was successfully leveraged as structural crystallites to enhance mechanical strength and gas barrier properties [1]. This versatile strategy allows for the precise tailoring of material functionalities, offering a sustainable alternative to petroleum-based plastics in a circular economy context [1].

References

[1] E. Testa *et al.*, 'Amyloid-Like Self-Assembling of Black Soldier Fly Proteins and Development of Bioplastics', *ACS Sustain. Chem. Eng.*, vol. 13, no. 43, pp. 18713–18726, Nov. 2025, doi: 10.1021/acssuschemeng.5c07418.

[2] S. Roy Goswami, S. Mykolenko, X. Kong, and R. Mezzenga, 'Toughening Starch-Based Bioplastics with Soy Amyloid Fibrils Produced from Tofu Wastewater', *ACS Sustain. Chem. Eng.*, vol. 13, no. 21, pp. 8068–8077, Jun. 2025, doi: 10.1021/acssuschemeng.5c02165.

[3] T. Li *et al.*, 'Plant Protein Amyloid Fibrils for Multifunctional Sustainable Materials', *Adv. Sustain. Syst.*, vol. 7, no. 4, Apr. 2023, doi: 10.1002/adsu.202200414.

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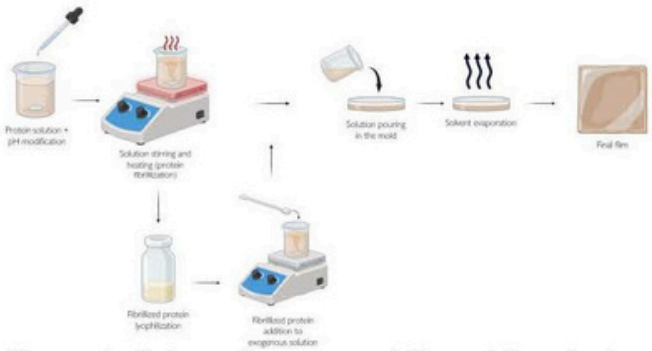


Figure 1. Schematic representation of the dual fibrillization pathways.

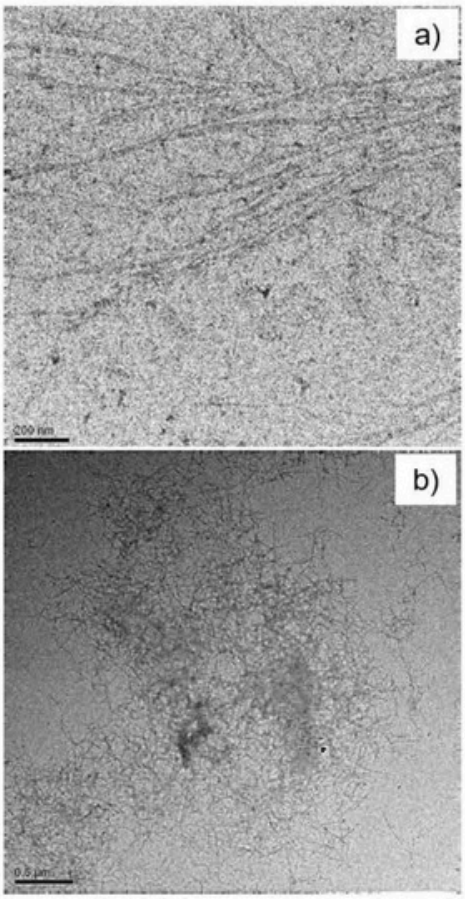


Figure 2. TEM images of proteins fibrils of BSF (upper) and sericin (lower).

PROSPECTIVE LIFE CYCLE ASSESSMENT OF TYRE MANUFACTURING: EVALUATING INDUSTRIAL DECARBONISATION PATHWAYS

V. La Matta[1], V. Ambrogi[1], M. Salzano de Luna[1], G. Filippone[1]

[1] Department of Chemical, Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125, Napoli, Italy
e-mail: valentina.lamatta@unina.it

(INSERIRE UN TESTO DI NON PIU' DI 2 PAGINE)

Introduction

The tyre sector is currently undergoing a transition towards more sustainable production systems, driven by the adoption of circular economy principles and decarbonisation strategies throughout the entire value chain [1-4]. Recent sustainability roadmaps published by leading tyre manufacturers show a strong convergence towards common technological approaches, including the increasing use of renewable and recycled raw materials, sustainable feedstocks, and the decarbonisation of manufacturing processes. Rather than relying on a single solution, these roadmaps propose a portfolio of complementary technological pathways, including sustainable feedstocks for synthetic rubbers, recovered carbon black, sustainable natural rubber, recycled steel and textile reinforcements, sustainable silica, bio-based additives, as well as renewable electricity and improved process efficiency. However, despite their increasing industrial relevance, the relative environmental effectiveness of these alternative pathways has not yet been quantitatively assessed within a consistent life cycle framework [5].

Life Cycle Assessment (LCA) is widely recognised as a robust methodology for evaluating the environmental performance of products and industrial systems. Nevertheless, prospective LCA studies based on plant-specific industrial inventory data remain scarce for tyre manufacturing [5]. In this work, a cradle-to-gate LCA model of a widely used passenger car tyre, developed from primary industrial production data, is used as the reference system to investigate alternative sustainability scenarios derived from the common decarbonisation pathways currently emerging across the tyre industry.

Results and discussion

A cradle-to-gate LCA model of a representative passenger car tyre was developed using primary industrial production data, including raw material production and tyre manufacturing. Starting from this baseline, prospective scenarios were defined to reflect the sustainability transition currently pursued by the tyre sector. The scenarios were developed by introducing alternative material and manufacturing strategies derived from the common sustainability priorities identified across the industry and designed to represent plausible future configurations of tyre manufacturing. Comparative LCA was then adopted to evaluate the environmental implications of the alternative scenarios while maintaining the same tyre design and manufacturing configuration, enabling a consistent comparison of different decarbonisation strategies.

The comparative LCA highlighted different environmental responses depending on the sustainability strategy considered, confirming that the effectiveness of each pathway is strongly influenced by the specific intervention adopted and the impact category evaluated. Overall, the scenario analysis provided a consistent framework for comparing alternative decarbonisation options under the same system boundaries, allowing the identification of the most promising strategies for reducing the cradle-to-gate environmental impacts of tyre manufacturing and supporting future sustainability-oriented decision-making.

Conclusions

This work proposed a prospective LCA framework to assess prospective decarbonisation scenarios for tyre manufacturing, starting from a plant-specific cradle-to-gate model based on primary industrial data. The scenario-based approach enabled the environmental implications of different industrial decarbonisation strategies to be consistently compared under the same modelling assumptions. The results highlighted the importance of quantitatively evaluating sustainability pathways before their implementation, demonstrating how LCA can support the prioritisation of material and manufacturing strategies capable of effectively

reducing the environmental footprint of tyre production.

References

[1] Pirelli. *Sustainability Strategy & Targets Update*. Milan, Italy; 2024.
[2] Goodyear Tire & Rubber Company. *2024 Sustainability Report*. Akron, OH, USA; 2025.
[3] Bridgestone Corporation. *Sustainability Report*. Tokyo, Japan; 2024.
[4] Continental AG. *Sustainability Report*. Hanover, Germany; 2024.
[5] Dong Y, Zhao Y, Hossain MU, He Y, Liu P. *Life cycle assessment of vehicle tires: A systematic review*. Cleaner Environmental Systems. 2021;2:100033.

FROM THIOL-ENE CHEMISTRY TO BIO-BASED POLYMERIC NETWORKS: MULTIFUNCTIONAL LIMONENE-DERIVED MATERIALS

N. Ferrentino[1,2], G. Viscusi[2], D. Pappalardo[1], G. Gorrasi[2].

[1] Department of Sciences and Technologies, University of Sannio, via de Sanctis snc, 82100, Benevento, Italy.
[2] Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132, Fisciano, 84084, Italy.
e-mail: naferrentino@unisannio.it

Introduction

The development of sustainable polymeric materials requires the design of versatile synthetic platforms able to produce high-performance materials from renewable feedstocks while simultaneously promoting polymer waste valorization. Among naturally occurring terpenes, limonene has emerged as an attractive bio-based platform due to the presence of reactive carbon-carbon double bonds suitable for thiol-ene reactions.[1] Its epoxidized derivative, limonene epoxide (LO), further expands its synthetic versatility by combining an epoxy functionality with an exocyclic double bond, enabling the preparation of multifunctional epoxy monomers and thermosetting materials.[2]

Thiols are extremely versatile building blocks in polymer chemistry, owing to their ability to undergo quantitative thiol-ene reactions under mild conditions. Furthermore, the thiol structure significantly influences the resulting material, enabling the synthesis of both linear polymers and crosslinked networks.[3]

Besides the use of renewable monomers, the reuse of recycled polymers represents an effective strategy for reducing plastic waste. Managing the end-of-life of polyvinyl butyral (PVB), a polymer widely used as an interlayer in laminated safety glass, is challenging, consequently, incorporating recycled PVB into new polymer matrices represents an effective strategy for the valorization of polymer waste.[4]

Another important challenge concerns the replacement of conventional petroleum-derived epoxy curing agents with renewable alternatives. In this regard, bio-based di- and tricarboxylic acids have emerged as environmentally friendly curing agents capable of promoting epoxy ring-opening reactions.[5]

Results and discussion

To demonstrate the versatility of thiol chemistry as a sustainable synthetic platform, linear and branched thiols were exploited through two complementary approaches based on limonene and LO.

In the first approach, linear (2,2'-(ethylenedioxy)diethanethiol) (DiO-SH) and branched thiols, such as pentaerythritol tetrakis(3-mercaptopropionate (Tetra-SH) and trimethylpropane tris(3-mercaptopropionate) (Tris-SH), were directly reacted with limonene *via* UV-induced thiol-ene reaction to produce poly(thioether-*co*-limonene) copolymers and crosslinked networks, respectively (Figure 1). The incorporation of increasing amounts of recycled PVB in the crosslinked materials led to the formation of semi-interpenetrating polymer networks (semi-IPNs), whose mechanical properties were influenced by both thiol functionality and PVB content. Specifically, Tetra-SH produced more densely crosslinked structures compared to Tris-SH, resulting in a higher elastic modulus and greater mechanical strength. PVB further increased the stiffness of the crosslinked material without significantly reducing the strain at break. Moreover, the polymeric materials exhibited excellent UV-shielding capability, with Ultra Protection Factor (UPF) values increasing progressively with PVB content.[6]

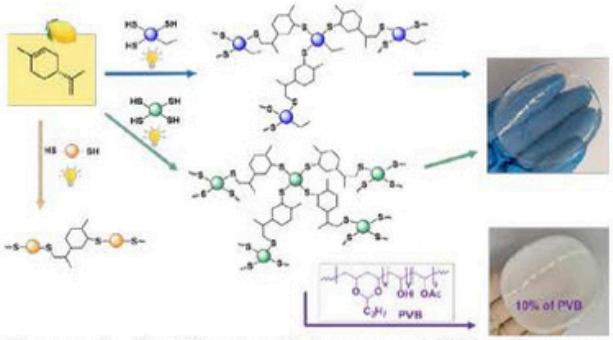
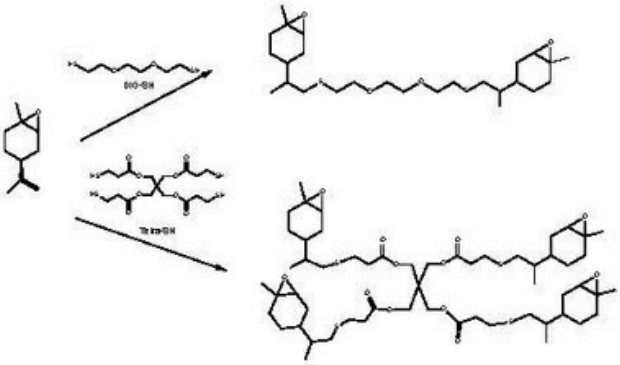


Figure 1. Synthesis of linear poly(thioether-co-limonene) copolymers and a crosslinked polymeric material via the reaction of limonene with linear and branched thiols, respectively, under 365 nm UV light irradiation.

In the second approach, linear (DiO-SH) and branched (Tetra-SH) thiols were reacted with the exocyclic double bond of LO to synthesize multifunctional epoxide precursors, limonene bis-epoxide (Bis-LO) and limonene tetra-epoxide

(Tetra-LO) (Scheme 1). The resulting multifunctional epoxides were subsequently reacted with dicarboxylic acids of varying chain length as well as a tricarboxylic acid. The reactions were carried out under different temperatures and epoxide-to-carboxylic group molar ratios in order to investigate the effect of these parameters on the final material properties. Bis-LO generated soluble oligomeric epoxy resins with high reaction yields, whereas Tetra-LO produced crosslinked networks.



Scheme 1. Synthesis of limonene bis-epoxide (Bis-LO) and limonene tetra-epoxide (Tetra-LO).

Conclusions

This study demonstrates the versatility of thiol chemistry as a sustainable platform for the preparation of advanced limonene-based polymeric materials. Starting from the same linear and branched thiols, two complementary bio-based materials were successfully developed. Direct thiol-ene polymerization with limonene enabled the preparation of poly(thioether-*co*-limonene) crosslinked materials incorporating recycled PVB, combining good mechanical performance and UV-shielding capability. In parallel, thiol-ene reaction with limonene epoxide generated multifunctional epoxy precursors that were converted into epoxy resins through curing with bio-based di- and tricarboxylic acids.

These results highlight the potential of this synthetic platform for the design of high-performance materials within a circular economy framework.

References

[1] Negro, V.; Mancini, G.; Ruggeri, B.; Fino, D. *Bioresour. Technol.* 214, 806–815 (2016).

[2] E. Louisy, V. Khodyrieva, S. Olivero, V. Michelet, A. Mija, *ChemPlusChem*, 87, e202200190 (2022).

[3] M. Claudino, M. Jonsson, M. Johansson. *RSC Adv.* 3 (27) 11021–11034 (2013).

[4] Kumar, P.; Khan, N.; Kumar, D. *Green Chem. Technol. Lett.* 2 (4), 185–194 (2016).

[5] Barros, A.; Nepomuceno, N.; Nicácio, P.; Souza, M.; Silva, I.; Luna, C.; Fook, M.; Araújo, E.; Wellen, R. *J. Polym. Environ.* 32 (5), 2431–2447 (2024).

[6] Ferrentino, N.; Viscusi, G.; Russo, S.; Abbatiello, L.; Morante, N.; Gorrasi, G.; Pappalardo, D. *Materials Today Chemistry* 48 102957 (2025).

Acknowledgments

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EMERGING CONCEPTS FOR SUSTAINABLE BIOCOMPOSITES

C. Di Bernardo[1], C. Noè[1], M. Messori[1]

[1] Dept. of Material Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10128, Torino (TO), Italy

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e-mail: carlo.dibernardo@polito.it

Introduction

The growing demand for sustainable materials and the transition toward a circular bioeconomy is driving a profound transformation in polymer composite design. Beyond the static reinforcement, the design of next generation biocomposites is increasingly driven by the need to reconcile high-performance material requirements with sustainability and circular economy principles. This contribution provides a consolidated perspective on recent advances in biocomposite engineering, integrating insights from traditional composite systems, including recent developments in sustainable tire composites, alongside emerging strategies appliable in dynamic polymer networks and hydrogel-based architectures.[1–3]

A central paradigm shift in biocomposite design lies in the transition from static systems to adaptive bio-integrated materials. In this context, the integration of bio-based fillers, renewable matrices, and functional interfaces enables the development of multifunctional materials where mechanical performance, transport properties, and environmental compatibility are simultaneously optimized.[4–6]

Beyond conventional composites, dynamic covalent polymers and covalent adaptable networks (CANs) have been introduced as a new class of reprocessable and reconfigurable matrices that bridge thermosets and thermoplastics.[7] Here, we will discuss on double network architectures in Priamine-based CAN systems and their potentiality as soft elastomer composites.

In parallel, photocurable hydrogel-based biocomposites are discussed as tuneable templates for biomedical applications, with good sorption properties and antibacterial activity.[8] Overall, these three applications present a perspective on current advancements in the field, holding promises for the future developments of biocomposites, where the convergence between bio-resourced feedstock, dynamic chemistries and multifunctionality became the central topics in the field. [9]

Results and discussion

The current research increasingly focused on designing materials that can have a reduced carbon footprint and added functionality at the same time.

For example, integrating bio-resourced fillers as biochar in tire composites, proved to be a valuable way for reducing environmental footprint in automotive industry. Biochar offers an alternative to the more traditional carbon black (CB, fossil origin) without losing in mechanical properties. In particular, we studied the replacement of CB in a commercial formulation with 4 different biochar grades from different natural sources. The mechanical properties evaluations, together with rheology data, highlighted that up to 50% of CB could be replaced with oil-seed rape biochar (OSR700), keeping similar performances to the standard one.[10]

At the same time, designing new polymer matrices including bio-based monomers has attracted interest for structuring reprocessable networks. Especially Priamine 1071 proved to be a cheap, non-toxic and reactive diamine to synthetize covalent adaptable networks. The resulting beta-amino ester presented in this contribute proved to be a flexible and fast-relaxing polymer, suitable for strain sensoring. Carbonaceous fillers, like conductive CB, are known to forward conductivity to organic matrixes. In particular, herein we are reporting the possible use of CB-filled CANs as strain sensor for flexible and soft electronics.

Lastly, collagen-based hydrogels are presented as a photocurable platform for bio-resourced absorbents with tailorable porosity and their relative composites with Zn-loaded mesopourous silica as antibacterial principle. Particularly, antibacterial properties were tested against S. aureus and E. coli, showing bacteria-growth inhibition in all cases.

Conclusions

In summary, we have presented 3 different approaches to obtain sustainable biocomposites. We foresee that these approaches can have a powerful role in the next generation of sustainable materials.

References

(1) Rajeshkumar, L.; Ramesh, M.; Bhuvaneswari, V.; Balaji, D.; Deepa, C. *J. Mater. Chem. B*, *11* (15), 3307–3337 (2023).

(2) Sun, J. Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. *Nature, 489:7414* 2012, *489* (7414), 133–136 (2012).

(3) Sun, M.; Felsenthal, L. M.; Kim, S.; Choi, E. Y.; Reed, L. J.; Elling, B. R.; Dichtel, W. R. *Chem. Rev.*,*126* (3), 1829–1948 (2026).

(4) Tian, L.; Gao, F. L.; Li, Y. X.; Yang, Z. Y.; Xu, X.; Yu, Z. Z.; Shang, J.; Li, R. W.; Li, X. *Adv. Funct. Mater.*, *35* (17), 2418988 (2025).

(5) Liu, D.; Shi, L.; Dai, Q.; Lin, X.; Mehmood, R.; Gu, Z.; Dai, L. *Trends Chem., 6* (4), 186–210 (2024).

(6) Xue, J.; Liu, D.; Li, D.; Hong, T.; Li, C.; Zhu, Z.; Sun, Y.; Gao, X.; Guo, L.; Shen, X.; Ma, P.; Zheng, Q. *Advanced Materials*, *37* (2), 2312596 (2025).

(7) Zhang, V.; Kang, B.; Accardo, J. V.; Kalow, J. A. *J. Am. Chem. Soc.*, *144* (49), 22358–22377 (2022).

(8) Brinkman, W. T.; Nagapudi, K.; Thomas, B. S.; Chaikof, E. L. *Biomacromolecules*, *4* (4), 890–895 (2003).

(9) Wang, P.; Hu, M.; Wang, H.; Chen, Z.; Feng, Y.; Wang, J.; Ling, W.; Huang, Y. *Advanced Science*, *7* (20), 2001116 (2020).

(10) Di Bernardo, C.; Messori, M.; Noè, C. *ACS Sustain. Chem. Eng.*, *13* (37), 15421–15434 (2025).

TUNING PLLA CRYSTALLIZATION KINETICS VIA REACTIVE EXTRUSION BRANCHING STRATEGIES

A. Longo[1], M. L. Di Lorenzo[1], A. Staiano[1], V. Marturano[1], G. Dal Poggetto[1], S. Mallardo[1], M. Dobrzyńska-Mizera[2], Monika Knitter[2], Karol Bula[2], Agnieszka Kuc[2]

[1] Istituto per i Polimeri, Compositi e Biomateriali (IPCB); Consiglio Nazionale delle Ricerche (CNR), Via Campi Flegrei 34, 80078, Pozzuoli, Italia
[2] Institute of Materials Technology, Division of Plastic Processing, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland.

e-mail: alessandra-longo@cnr.it

Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable and renewable thermoplastic polyester widely studied to replace oil-based polymers [1]. Despite its advantages, its commercial potential is still limited by its slow crystallization kinetics, which prevents it from reaching the crystallinity levels required for adequate mechanical and thermal resistance in many applications [2].

Then, improving the crystallization kinetics can represent a viable strategy to expand the industrial applicability of PLLA.

Some strategies have been proposed to address this challenge, such as adding nucleating agents [3] and plasticizers [4], as well as designing long-chain branched (LCB) architectures. Among all, branched PLLAs obtained via chain extension have shown an accelerated crystallization [5] together with enhanced melt strength, rheological behavior, and thermal stability [6].

Among the various chemical pathways exploited to promote branching, peroxides [21–26] are frequently utilized in conjunction with multifunctional allylic or acrylic coagents [27–28]. Peroxide decomposition generates free radicals that react with the double bonds of these coagents, forming macroradicals that recombine with polymer chains to yield highly crystalline branched structures [35].

In this contribute, we investigate the influence of multifunctional coagents on the crystallization kinetics of PLLA. The study evaluates the effect of branching agents on PLLA chain structure and crystallization kinetics. Understanding these structure-property relationships is essential to optimize PLLA's performance, expanding its viability for sustainable industrial applications.

Results and discussion

Side branches of varying molecular weight and stereoregularity has been introduced on linear chain of a commercial PLLA via reactive extrusion in a Brabender melt mixer. By varying the reaction agents, branched PLLAs with distinct architectures and crystallization kinetics were synthesized.

The resulting chemical structures were characterized. Thermal properties were evaluated by differential scanning calorimetry (DSC), analyzing the overall crystallization rate of the branched PLLAs both in isothermal and non-isothermal conditions; while crystal nucleation and growth were studied with Polarized Optical Microscopy (POM) to study the influence of chain topology on crystallization kinetics. The introduction of side branches altered the crystallization behavior of PLLA. In particular, the branched PLLAs exhibited a concentration-dependent effect, where an optimal coagent content substantially enhanced both nucleation density and rate, thereby accelerates the overall crystallization kinetics. Conversely, exceeding this threshold led to a reduction in nucleation efficiency, highlighting a strong correlation between branching architecture and crystallization development.

Conclusions

In this contribution, branched PLLAs were successfully synthesized via reactive extrusion, to tailor the polymer architecture. Characterization of the crystallization behavior revealed a concentration-dependent correlation between branching and kinetics. From an application perspective, this contribution provides a robust framework to overcome the performance drawbacks of commercial PLLA, opening new routes for its sustainable exploitation in high-performance industrial packaging and engineering technical parts.

References

[1] M.L. Di Lorenzo, R. Androsch, *Adv. Polym. Sci.* 279 (2018)
[2 M.L. Di Lorenzo, R. Androsch, *Adv. Polym. Sci.* 282 (2018)
[3] Y. Zhu et al., *Journal of Polymer Research*, 31(9), 253 (2024)
[4] E. E. Mastalygina, K. V. Aleksanyan, *Polymers*, 16(1), 87. (2023)
[5] M.G. McKee, S. Unal, G.L. Wilkes, T.E. Long, *Prog. Polym. Sci.*, 30 (2005)
[6] V. Bourg, et al, *Polymers*, 13 (2021),

Acknowledgments
HORIZON-EIC-2024-Pathfinder Challenges-01:"Nature inspired alternatives for food packaging and films for agriculture", GA 101223095 "BiObased theRmal resistaNt food packaging" (BORN).
Funded by the European Union. Views and opinions expressed are however those of the authors only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

DESIGNING VANILLIN-BASED DYNAMIC NETWORKS FOR THE DEVELOPMENT OF SUSTAINABLE THERMOSETS FOR FUTURE GENERATION COMPOSITES

M. Mollo[1], C. Noè [1], and M. Messori[1,2]

[1] Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24,10129, Turin (TO), Italy
[2] National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence (FI), Italy
e-mail: marta.mollo@polito.it

Introduction

In the field of polymer science, thermosets have been employed in a wide range of applications, from aerospace and automotive sectors to coatings, 3D printing and composite materials industries. [1] Their chemically cross-linked networks translate into high mechanical and thermal properties. Despite these qualities, the intrinsic persistence of thermosets is also contributing to the growing awareness regarding plastic pollution and its environmental impact.

This work addresses the sustainability of thermosetting systems through a dual-strategy approach. First, the incorporation of Dynamic Covalent Bonds (DCBs) into the polymer structure was crucial. DCBs can undergo reversible exchange reactions under external stimuli enabling the material to flow and be reshaped without losing its cross-linked integrity.[2] Second, vanillin alone or vanillin and priamine were used as green building blocks. These bio-based formulations can be later integrated with carbon fibers to generate composites tailored for aerospace applications.

Results and discussion

Two distinct formulations were prepared and fully characterized with results that demonstrate the versatility of two type of systems: the first work demonstrates that is possible to achieve both a high-performance recyclable resin formulation, exhibiting no chemical degradation and better flame resistance (fig. 1) when compared to fossil-based alternatives, while the second work presents the development of a healable resin-system with shape-memory behavior (fig. 2).The dynamic properties of the networks were assessed by performing stress relaxation tests followed by a recycling procedure(fig. 3). The latter is conducted by taking the broken cross-linked samples subjected to a previous mechanical failure via tensile testing, and reprocessing them in a hot press to restore the original form. Notably, no significant change in the mechanical properties was observed, demonstrating the feasibility of recycling the cross-linked epoxy networks.

Conclusions

The study demonstrates that vanillin is a promising candidate to replace petroleum derivatives, representing a new frontier that aligns with the principles of circular economy and offers a path worth exploring.

References

[1] M. A. Rashid, „A Critical Review of Sustainable Vanillin-modified Vitrimers: Synthesis, Challenge and Prospects“, Reactions, Vol. 4 (2023)

[2] H. Zhang, „Recycling strategies for vitrimers“, International Journal of Smart and Nano Materials, Vol. 13 (2022).

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Figure 1: UL 94 Flame Retardancy Test

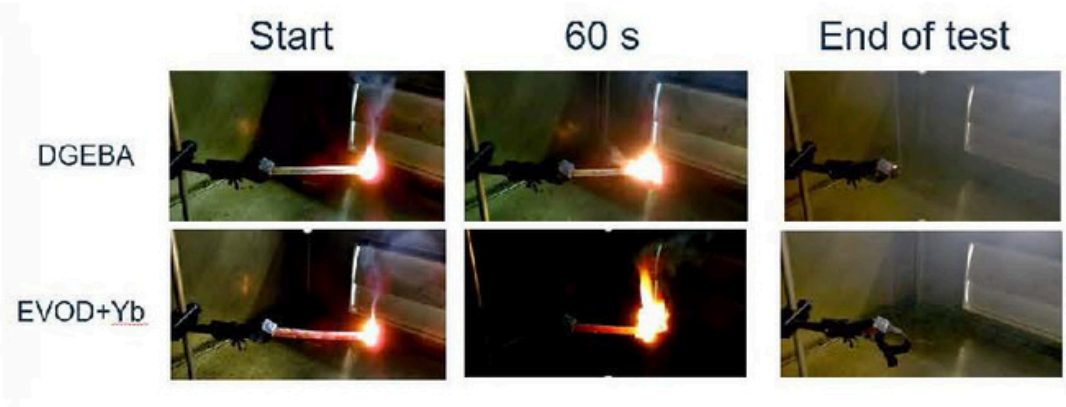


Figure 2: Shape memory test

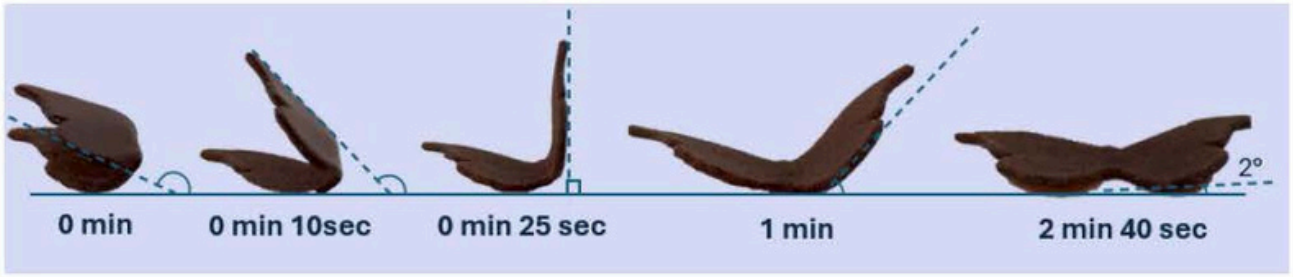
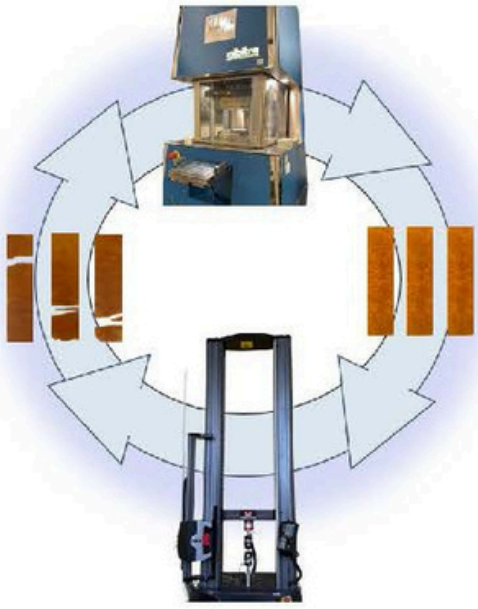


Figure 3: Reprocessing Cycle



MELT-PROCESSING OF DIALCOHOL CELLULOSE FIBRES/STARCH BLENDS: PROCESSING STRATEGIES, STRUCTURE AND PROPERTIES

Enrica Pellegrino[1,2], Giada Lo Re[2], Alberto Fina[1]

[1]Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, viale Teresa Michel 5, 15121 Alessandria, Italy
[2]Chalmers University of Technology, Department of Industrial and Materials Science, Rännvägen 2A, 412 58 Göteborg, Sweden

Introduction

Starch and cellulose are complex carbohydrate polymers that cannot be melt-processed in their native form, as strong hydrogen bonding intermolecular interactions raise the glass transition temperature above the degradation temperature. Chemical modification of cellulose pulp into dialcohol cellulose (DALC) fibres overcomes this limitation by breaking the C_2-C_3 bond in the glucopyranose ring, improving chain mobility and lowering the glass transition temperature. As previously demonstrated [1,2,3], DALC fibres can be effectively melt-processed using only water as a processing aid.
Starch can similarly be melt-processed in the presence of a suitable plasticizer, where shear stresses during compounding promote crystal destructuration. In this work, DALC fibres plasticized with 60 phr of water (60 parts per 100 parts of dry DALC) were blended with starch plasticized by isosorbide (starch:isosorbide = 65:35) [4,5]. Isosorbide was chosen for its ability to inhibit starch retrogradation over time [4,5].

Results and discussion

Two production methods were tested to prepare DALC/starch blends: [1] a one-step process where wet DALC fibres were added directly into the microcompounder together with starch and isosorbide (SI), enabling co-extrusion and co-plasticization; and [2] a two-step process where pre-plasticized thermoplastic starch (TPS) pellets were prepared first and then compounded with wet DALC fibres. Figure 1 shows the processing design to obtain the blends, and Table 1 reports the different blend compositions investigated.

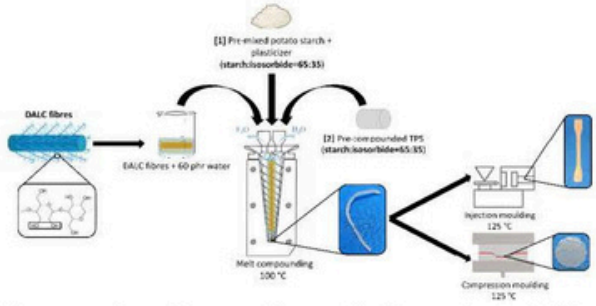


Figure 1. Processing design to obtain DALC/starch blends by one-step [1] and two-step [2] processing routes.

Table 1. Composition of the DALC/starch blends prepared by one-step [1] and two-step [2] processing routes.

Sample	DALC (wt.%)	SI/TPS (wt.%)
DALC	100	0
85DALC-15SI	85	15
85DALC-15TPS	85	15
70DALC-30SI	70	30
70DALC-30TPS	70	30
60DALC-40SI	60	40
60DALC-40TPS	60	40
50DALC-50SI	50	50
50DALC-50TPS	50	50
30DALC-70TPS	30	70
15DALC-85TPS	15	85
TPS	0	100

The addition of increasing amounts of starch/isosorbide (SI) (one-step) or TPS pellets (two-step) led to a decrease in melt-viscosity during processing, connected to improved processability. The two-step route yielded lower viscosity values since starch destructuration was achieved in the first step. X-ray diffraction (XRD) scans showed that in the one-step process, peaks

associated with plasticized starch only appear at high SI content (from 40 wt.%), indicating the presence of unplasticized starch granules at lower contents, which acts as a reinforcing phase and is reflected in the increase in Young's modulus observed from tensile test. For the two-step route, scanning electron microscopies on cryo-fractured surfaces reveal a two-phase morphology (DALC and TPS) with excellent interfacial adhesion, as no debonding at the DALC fibre surface was observed. Dynamic mechanical thermal analysis (DMTA) confirmed the two-phase structure through two distinct α-transition temperatures. Adding TPS reduced Young's modulus but the modulus curve follows a bell-like shape with a maximum at 40 wt.% TPS, which is likely related to the formation of a co-continuous phase. Elongation at break improves significantly at high TPS contents (above 70 wt.%). Successful mechanical recycling was demonstrated for the blend containg 30 wt.% of wet DALC fibres and 70 wt.% of TPS. Bio-disintegration tests in industrial composting conditions showed that all materials are compostable, with faster disintegration observed at higher TPS content.

Conclusions

Melt-processable DALC/starch blends were successfully prepared using either the one-step co-extrusion method or the two-step processing route. The processing strategy and blend composition have a significant impact on melt-viscosity during processing, as well as on the resulting morphology, mechanical properties and end-of-life behaviour. The two-step approach enables better starch plasticization. A two-phase morphology with good interfacial adhesion is observed, and a continous phase is assumed when 40 wt.% of TPS is added. The result is fully bio-based, compostable materials with the potential for mechanical recycling, offering a promising pathway towards sustainable, melt-processable thermoplastics from renewable resources.

References

[1] Lo Re, G., Engel, E. R., Björn, L., Sicairos, M. G., Liebi, M., Wahlberg, J., ... & Larsson, P. A. (2023). Melt processable cellulose fibres engineered for replacing oil-based thermoplastics. *Chemical Engineering Journal*, 458, 141372.

[2] Engel, E. R., Lo Re, G., & Larsson, P. A. (2025). Melt processing of chemically modified cellulosic fibres with only water as plasticiser: Effects of moisture content and processing temperature. *Carbohydrate Polymers*, 348, 122891.

[3] Pellegrino, E., Al-Rudainy, B., Larsson, P. A., Fina, A., & Lo Re, G. (2025). Impact of water plasticization on dialcohol cellulose fibres melt processing-structure-properties relationship. *Carbohydrate Polymer Technologies and Applications*, 9, 100642.

[4] Area, M. R., Rico, M., Montero, B., Barral, L., Bouza, R., López, J., & Ramírez, C. (2019). Corn starch plasticized with isosorbide and filled with microcrystalline cellulose: Processing and characterization. *Carbohydrate Polymers*, 206, 726-733.

[5] Area, M. R., Montero, B., Rico, M., Barral, L., Bouza, R., & López, J. (2020). Properties and behavior under environmental factors of isosorbide-plasticized starch reinforced with microcrystalline cellulose biocomposites. *International Journal of Biological Macromolecules*, 164, 2028-2037.

Beyond Biodegradability: Comparative LC-MS Profiling of Plastic Additive Release from Fossil-Based and Biodegradable Agricultural Mulch Films into Soil

V. Giglio[1], F. Convertino[2], E. Schettini[2], S.C. Carroccio[1]

1) *Institute for Polymers, Composites, and Biomaterials CNR-IPCB, Via Paolo Gaifami 18, Catania 95126, Italy*

Department of Soil, Plant and Food Sciences (DISSPA), University of Bari, Via Amendola 165/A, Bari 70126, Italy

Introduction

Plastic mulch films are widely used in modern agriculture to control weeds, retain soil moisture, and enhance crop yields. In recent years, biodegradable mulch films (BMF) based on aliphatic-aromatic copolymers such as polybutylene adipate-co-terephthalate (PBAT) have been promoted as sustainable alternatives to conventional fossil-based polyethylene (PE) films, due to their ability to fragment and mineralize in soil, thus avoiding the need for mechanical removal and reducing plastic residue accumulation.[1] However, beyond the polymer matrix itself, both PE and PBAT films contain a variety of plastic additives (PAs), including antioxidants (e.g., Irganox 1010, Irganox 1076, Irgafos 168), UV stabilizers (e.g., UV1164, Octabenzone), plasticizers (e.g., phthalates), and slip agents (e.g., TBAC),that may be released into the surrounding soil during ageing and degradation.

In our previous study [2], we demonstrated preferential release of certain PAs from PBAT-based films into soil, while other potentially hazardous compounds tended to persist in the microplastic fragments generated during biodegradation. The observed behaviour was governed by the physico-chemical properties of the additives: polar compounds showed higher mobility in soil, while hydrophobic ones remained associated with the polymer matrix and its microplastic debris, suggesting possible long-term persistence.

The present work extends this investigation in two directions: (i) the field burial experiment has been prolonged to evaluate additive fate over longer timescales; and (ii) a comparative LC-MS assessment of PAs has been carried out on both a conventional PE film and a PBAT-based biodegradable film, together with the soils in contact with each material sampled at multiple burial time points (T0, 32 days, 276 days) under real agricultural field conditions.

Results and discussion

Films and soil samples were collected at defined time intervals. Plastic additives were extracted from both films and soil matrices and quantified by UHPLC-MS/MS. The analytical method allowed simultaneous identification and quantification of antioxidants, UV stabilizers and plasticizers at trace levels. The two film materials were compared both in terms of initial additive composition and temporal evolution of PA distribution between the film matrix and the soil.

Preliminary results obtained on the film matrices showed that PE films remained physically intact throughout the burial period, with PA content remaining essentially stable at all time points. In contrast, PBAT films exhibited visible physical degradation over time, with progressive release of micro- and nanoplastic particles into soil (figure 1). Correspondingly, the PA profile of PBAT films varied significantly with increasing burial time: the relative concentrations of several additives (Irgafos 168, Irganox 1010, TBAC, UV1164) changed markedly between T0, 32 days, and 276 days, indicating that the progressive degradation of the polymer matrix acts as the key driving force for additive leaching. The soil data, currently under processing, will complete the picture by quantifying the actual transfer of PAs to the agricultural soil for both fossil-based and biodegradable film systems.

Conclusions

This comparative study highlights that the biodegradability of the polymer matrix fundamentally alters the dynamics of plastic additive release into the environment. While the physical degradation of PBAT accelerates the mobilization of PAs, the fate of hydrophobic compounds associated with microplastic residues remains a concern even for materials marketed as biodegradable. These results underscore the need to systematically include additive fate in the environmental sustainability assessment of

agricultural plastic films, going beyond the sole consideration of polymer biodegradability.

References

[1] F. Convertino, S.C.Carroccio, M.C.Cocca, S. Dattilo, A.C Dell'Acqua, L. Gargiulo, L. Nizzetto, P.M. Riccobene, E. Schettini, G. Vox, D. Zannini, P. Cerruti, , *STOTEN*, vol. 948, 174697 (2024)

[2] V. Giglio, D. Dvorakova, F. Convertino, A.S. Tsagkaris, A. Messina, G. Proietto Salanitri, A.C Dell'Acqua, E. Schettini, S.C. Carroccio. *Journal of Hazardous Materials*, vol. 499 140039 (2025).

Acknowledgments

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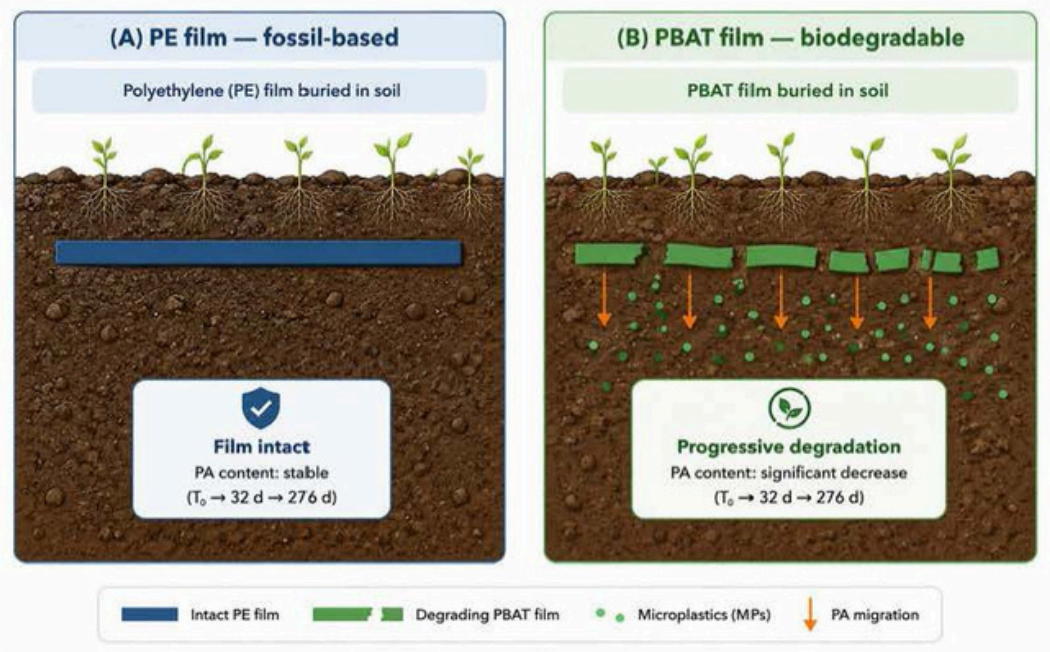


Figure 1. Experimental concept illustrating the contrasting behavior of PE and PBAT mulch films during soil burial. PE remains intact, whereas PBAT progressively degrades, facilitating additive migration and microplastic formation.

MULTISCALE POLYMER ANALYSIS: CORRELATING CHEMICAL STRUCTURE, THERMAL BEHAVIOR, AND RHEOLOGICAL RESPONSE THROUGH COMPLEMENTARY ANALYTICAL TECHNIQUES

Alberto Rubin Pedrazzo[1], Carmine Invigorito[1], Sandra Lanteri[1], Paolo Saccagno[1], Simone Marchesi[1]

[1] Anton Paar Italia Srl, Via Albenga, 78, 10098 Rivoli (TO), Italia
e-mail: alberto.rubinpedrazzo@anton-paar.com

Introduction

The properties and processing behavior of polymeric materials are strongly influenced by molecular organization, crystalline phase composition, thermal history, and structural evolution under external stimuli. Since these characteristics span different spatial and temporal scales, a single analytical technique cannot provide a complete description of the material.
A multiscale strategy based on complementary analytical techniques can connect chemical and crystalline structure with thermal behavior, nanoscale organization, and macroscopic rheological response. The present work illustrates how X-ray diffraction, differential scanning calorimetry, gas pycnometry, Raman spectroscopy, and small-angle X-ray scattering can be integrated to obtain a more comprehensive understanding of polymer structure and processing behavior.

Results and discussion

The complementary analysis of polypropylene demonstrates that XRD can resolve amorphous, α-crystalline, and β-crystalline fractions, while DSC reveals variations in melting behavior and transition enthalpy associated with material history and repeated processing. Skeletal-density measurements provide an additional parameter for evaluating structural differences among polymer samples. Real-time Raman monitoring of polyethylene during cooling follows the evolution of characteristic spectral features associated with crystallization. The presentation also highlights the observation of an additional amorphous solid state occurring between the amorphous liquid and crystalline solid states during polyethylene crystallization.
SAXS provides access to characteristic dimensions, structural organization, and nanoscale morphology. When combined with rheology, RheoSAXS directly correlates changes in scattering patterns with material response under shear. In non-ionic surfactant systems, increasing shear promotes structural ordering and can induce a transition from planar lamellae to onion-like multilamellar structures, depending on temperature and shear conditions.

Conclusions

The integration of diffraction, thermal analysis, spectroscopy, density measurement, and rheology-coupled scattering provides a robust multiscale framework for polymer characterization.
XRD, DSC, and gas pycnometry deliver complementary information on crystalline phases, thermal behavior, and density, while Raman and RheoSAXS enable real-time or in-situ observation of structural transformations during processing. This combined analytical approach strengthens structure–process–property correlations and supports polymer development, process optimization, and quality control.

WHEN MOLECULAR IMPERFECTION WORKS: SUSTAINABLE POLYESTER COPOLYMERS WITH INDUSTRIAL POTENTIAL

Licia Gaeta[1], David H. Lamparelli[1], Luciano Di Maio,[2] Claudio Pellecchia[1]

[1] Dipartimento di Chimica e Biologia "A. Zambelli", Università degli Studi di Salerno, via Giovanni Paolo II
[2] Dipartimento di Ingegneria Industriale, Università degli Studi di Salerno, via Giovanni Paolo II 132, Fisciano (SA) 84084, Italy

e-mail: dlamparelli@unisa.it

Introduction

Thermoplastic elastomers (TPEs) combine the elasticity of conventional rubbers with the melt processability and recyclability of thermoplastics through phase-separated architectures in which rigid domains act as reversible physical crosslinks.

The development of sustainable TPEs requires mechanical performance with industrially viable synthesis and circular end-of-life options. ABA polyester triblock copolymers represent an attractive alternative to conventional SBS elastomers because they can be produced from renewable monomers while remaining recyclable and biodegradable.

Recent advances have demonstrated that well-defined polyester thermoplastic elastomers can be efficiently synthesized by ring-opening polymerization using sustainable catalytic systems and can also be chemically recycled back to the corresponding monomers [1–4].

In this work, scalable synthetic strategies based exclusively on commercially available ε-caprolactone (CL) and L-lactide (LA) are investigated to develop sustainable polyester elastomers and efficient toughening agents for commercial poly(lactic acid) (PLA).

Results and discussion

A series of ABA segmented copolyesters composed of semicrystalline PLLA hard blocks and random poly(CL-stat-LA) soft midblocks was synthesized through sequential ring-opening polymerization strategies, ranging from controlled solution polymerization with purified monomers to scalable one-pot bulk process employing technical-grade monomers and $Sn(Oct)_2$ catalyst (Figure 1).

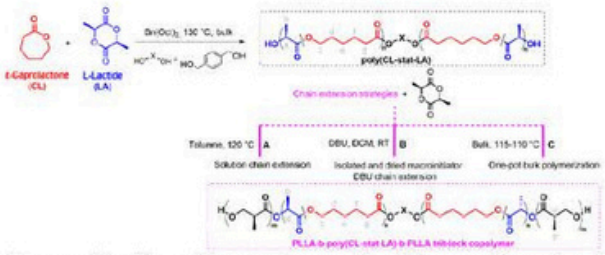


Figure 1. Reaction scheme for the synthesis of ABA triblock copolymers.

The solution-polymerized copolymers exhibited excellent thermoplastic elastomer behavior, with Young's moduli between approximately 20 and 90 MPa, tensile strengths above 8–11 MPa and elongations at break exceeding 600–800%, demonstrating that phase-separated PLLA domains efficiently act as reversible physical crosslinks. Cyclic tensile tests revealed pronounced energy dissipation during the first deformation cycle followed by elastic recovery above 90–95%, confirming their elastomeric nature.

To improve industrial applicability, a simplified solvent-free one-pot process was subsequently developed using technical-grade monomers under melt-processing conditions. Although these conditions generated broader molecular-weight distributions, partial transesterification phenomena and less defined molecular architectures because of incomplete chain extension, the resulting materials still displayed typical thermoplastic elastomer behavior, combining tensile moduli around 50 MPa, elongations above 300% and elastic recovery higher than 95%.

Complementary GPC, quantitative ^{13}C NMR, and differential scanning calorimetry (DSC) analyses consistently demonstrated that the bulk process generates longer caprolactone-rich sequences together with a broader distribution of molecular architectures and a distinct crystalline microstructure compared with the more

homogeneous solution-polymerized triblock copolymers.
These results demonstrate that perfectly defined ABA architectures are not essential for obtaining technologically relevant elastomeric performance.

The synthesized copolymers were subsequently evaluated as toughening modifiers for commercial PLA. Surprisingly, the structurally heterogeneous bulk-produced copolymer largely outperformed the more perfectly defined triblock copolymers, increasing the strain-at-break of PLA from approximately 4% to above 90% at 25 wt% loading while preserving a Young's modulus close to 1 GPa. By contrast, the well-defined triblocks produced only limited improvements in ductility despite their superior intrinsic elastomeric properties.

DSC revealed that all investigated PLA/copolymer blends exhibit a single glass transition reasonably described by the Fox equation, indicating substantial miscibility of the amorphous phases and excluding macroscopic phase separation as the origin of the different mechanical responses. The principal differences instead arise from the crystalline morphology developed during solvent-casting-induced film formation: the bulk-produced copolymer preserves a significant crystalline fraction while promoting the formation of smaller and less perfect crystallites, whereas the structurally regular triblock copolymers largely suppress crystallization. These observations indicate that crystalline morphology, rather than molecular perfection or blend miscibility alone, governs the outstanding toughening efficiency of the industrially produced modifier.

Furthermore, preliminary bulk depolymerization experiments demonstrated the efficient chemical recycling of the prepared elastomers, affording recoveries higher than 99% for LA and 93% for CL, further supporting the circularity potential of these fully bio-based materials.

Conclusions

This work shows that scalable one-pot polymerization provides a practical route toward sustainable polyester thermoplastic elastomers based exclusively on industrially available monomers. More importantly, it shows that structural perfection is not a prerequisite for high-performance materials: the heterogeneous architecture generated under industrially relevant conditions retains excellent elastomeric properties and acts as highly efficient PLA toughening agents.

The results further demonstrate that the superior toughening efficiency originates primarily from the crystalline morphology developed during processing rather than from differences in blend miscibility. Overall, this contribution demonstrates that molecular imperfection generated under industrially relevant polymerization conditions can become a functional advantage, providing a scalable strategy for producing high-performance, recyclable and fully bio-based PLA materials.

References

[1] G. Gravina, G. Pierri, C. Pellecchia, *Mol. Catal.* 555, 113891 (2024).
[2] G. Gravina, E. Romano, A. Liporace, M. C. D'Alterio, G. Talarico, C. Pellecchia, ACS Sustainable *Chem. Eng.* 13, 19613–19624 (2025).
[3] G. Gravina, J. N. A. Tagoe, R. Di Girolamo, M. Gentile, L. Di Maio, C. Pellecchia, *ACS Polym. Au* 6, 468–479 (2026).
[4] M. A. Hillmyer, W. B. Tolman, Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable, *Acc. Chem. Res.* 47, 2390–2396 (2014).

Acknowledgments

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BIO-BASED AND ANTIFUNGAL BY DESIGN: UV-CURED ESO/ESSENTIAL OIL COMPOSITES FOR NEXT-GENERATION ACTIVE PACKAGING

M. Valentini[1], I. Khomenko[2], E. Betta[2], M. Tonezzer[3], J. Zhang[1,2,3], F. Biasioli[2], A. Cosola[1], C. Noè[1]*, M. Messori[1]

[1]Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy;
[2]Sensory Quality Unit, Research and Innovation Centre, Fondazione Edmund Mach, Trento, Italy
[3]Department of Chemical and Geological Sciences, University of Cagliari, Monserrato, Italy
e-mail: camilla.noe@polito.it

Introduction

Global hunger remains a critical challenge, with food loss and waste a major contributing factor despite the heavy reliance of the food supply chain on plastic packaging. Active packaging (AP), which releases or absorbs substances to extend shelf-life, offers a promising solution, particularly through essential oil (EO)-based systems, which are GRAS-classified, exhibit antimicrobial and antioxidant activity, and often show synergistic effects when combined [1]. However, commercial adoption remains limited due to consumer concerns over active materials and sensory impacts, driving interest in bio-based, food-contact-compliant matrices such as vegetable oil-derived resins [2]. Epoxidized soybean oil (ESO), obtained from renewable, low-cost soybean feedstock, is well-suited for UV-driven cationic photopolymerization. This study develops an ESO-based active device incorporating an antifungal EO mixture, designed for insertion into food packaging to release volatile antifungal and antioxidant compounds, thus reducing post-harvest food losses.

Results and discussion

Photo-rheology and ATR-FTIR analyses showed that increasing EO content delayed the onset of crosslinking while accelerating gelation once initiated, likely due to a UV-shielding effect of some aromatic group present in the EO mixture combined with a plasticizing action of EOs that enhances chain mobility. This resulted in a progressive decrease in final epoxy conversion, from 81% for neat ESO to 70% at the highest EO loading. These results are in good agreement with the Gel% decrease.

DMTA confirmed this plasticizing effect, showing a slight reduction in glass transition temperature and storage modulus with increasing EO content, consistent with a less densely crosslinked, more flexible network.

PTR-ToF-MS and GC–MS analyses demonstrated sustained release of EO components over time (Figure 1,A), confirming suitability for headspace-active applications, and additionally identified secondary VOCs generated by oxidation of both EOs and the ESO matrix, relevant for food-contact safety evaluation.

Finally, antifungal tests against *Penicillium spp.* confirmed effective inhibitory activity, in line with the sustained release of antifungal EO compounds (Figure 1,B and C) Overall, these results reveal a clear structure–property–function relationship, where EO-induced plasticization and reduced crosslinking facilitate active compound release, without compromising network robustness, supporting the potential of ESO-based UV-cured systems for sustainable active packaging.

Conclusions

Overall, this work demonstrates that ESO-based UV-cured systems represent a sustainable, bio-derived, and food-contact-compliant platform for active packaging, capable of combining renewable material design with effective antimicrobial performance, paving the way for further optimization toward industrial-scale application.

References

[1] T. Modjinoua, D.Versacea, S. Abbad-Andaloussib, V. Langloisa,E. Renard, Materials Today Communications 12 (2017) 19–28

[2] M. Ramos, A. Beltrán, M Peltzer, A. J.M. Valente, M del Carmen Garrigós,LWT - Food Science and Technology 58 (2014) 470e477

Acknowledgments

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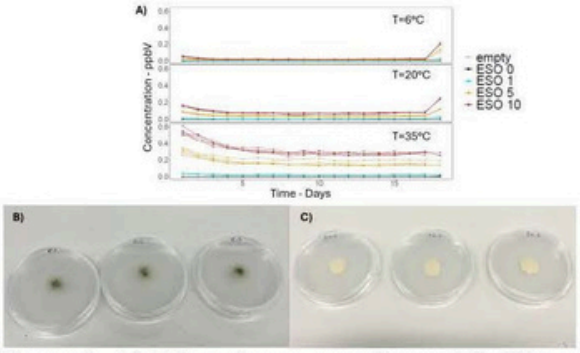


Figure 1. A) EOs release over time at 3 different temperatures and antifungal tests with Penicillium spp. of B) Control, C) in the presence of the active material.

NATURAL ANTIOXIDANT EFFECT OF HAZELNUT SHELL POWDER IN PBS BIOCOMPOSITES UNDER ACCELERATED UV AGING

L. Vitiello[1], S.C. Carroccio [1], L. Aliotta [2], V. Gigante [2], B. Dal Pont [3], J. Passaro [3], P. Russo [3]

[1] Institute for Polymers, Composites and Biomaterials, National Research Council, Via P. Gaifami 18, 95126, Catania, Italy
[2] Department of Civil and Industrial Engineering, University of Pisa, Via Lucio Lazzarini , 56122, Pisa, Italy
[3] Institute for Polymers, Composites and Biomaterials, National Research Council, Via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy
e-mail: pietro.russo@cnr.it

Introduction

The increasing demand for sustainable polymeric materials has promoted the development of biodegradable composites reinforced with agricultural by-products [1]. Among biodegradable polyesters, poly(butylene succinate) (PBS) is considered a promising alternative to conventional plastics because of its good mechanical properties and biodegradability [2]. However, its long-term durability under outdoor exposure remains a key issue for many applications. Lignocellulosic fillers derived from agricultural waste not only reduce the environmental impact and cost of composite materials but may also provide additional functional properties owing to the presence of naturally occurring antioxidant compounds [3,4].
In this work, biocomposites based on PBS filled with hazelnut shell powder were developed and their mechanical properties and resistance to accelerated photo-oxidative aging were investigated. The molecular modifications occurring during aging were evaluated by combining Size Exclusion Chromatography (SEC) and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS). The mechanical properties of the composites were also evaluated through tensile and impact tests.

Results and discussion

PBS-based biocomposites containing 10, 20 and 30 wt.% hazelnut shell powder were produced by melt extrusion, followed by injection molding to obtain standardized specimens. Table 1 reports the sample ID and their corresponding composition.

Table 1: Sample ID and composition of the investigated samples.

Sample ID	Composition
PBS	Neat PBS
10NC	PBS + 10wt.% Hazelnut shells
20NC	PBS + 20wt.% Hazelnut shells
30NC	PBS + 30wt.% Hazelnut shells

Mechanical characterization was performed on the manufactured samples.
Uniaxial tensile tests were carried out on ISO 527-1A dog-bone specimens at 10 mm/min to evaluate changes in the elastic modulus, tensile stress and elongation at break. The impact properties were evaluated using V-notched ISO 179 parallelepiped specimens. Due to the short length of the filler used and the filler irregularity, the addition of hazelnut shells reduces the tensile stress and the ductlity of PBS increasing, on the other hand an increment of the elstic modulus with the NC content was registered (from 0.71GPa for pure PBS to 1.31 GPa for 30NC) (Figure 1). The addition of NC decreased the impact properties respect to pure PBS (from 8.5 kJ/m^2 to 4.35 kJ/m^2 for 30NC).

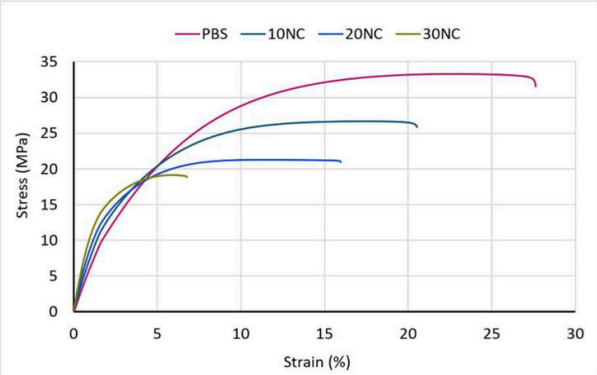


Figure 1. Representative stress-strain curves of the PBS-based composites

Accelerated weathering tests were carried out in a QUV chamber equipped with UVA-340 lamps,

which provide one of the best laboratory simulations of the short-wavelength ultraviolet portion of natural sunlight. Aging was performed at 60 °C, and specimens were collected after 30, 60 and 90 days, corresponding approximately to 6, 12 and 18 months of outdoor solar exposure, respectively. Both unaged and aged specimens were characterized by SEC and MALDI-TOF MS to investigate changes in molecular architecture induced by photo-oxidative degradation.

SEC analyses revealed that after 90 days of accelerated aging, the decrease in number-average molecular weight (M_n) became progressively smaller with increasing hazelnut shell content, indicating that the filler effectively limited polymer chain degradation (Figure 2a). The polydispersity index (PD) was approximately 1.8 for all materials before aging. After 90 days of exposure, a more pronounced increase in PD was observed for neat PBS, whereas the composites exhibited lower variations, suggesting a more controlled degradation process in the presence of the filler (Figure 2b).

MALDI-TOF MS provided further insight into the structural evolution of the polymer chains before and after aging. The spectra highlighted differences in the oligomeric species generated during photo-oxidation, confirming that the incorporation of hazelnut shell powder mitigated the molecular degradation of the PBS matrix.

The improved stability of the biocomposites is tentatively attributed to the preferential oxidation of naturally occurring polyphenolic compounds present in the hazelnut shell filler. These compounds may act as sacrificial antioxidants, scavenging reactive oxygen species generated during UV exposure and consequently delaying the oxidative degradation of the polymer matrix.

Conclusions

The results demonstrate that hazelnut shell powder can be successfully incorporated into PBS to produce fully bio-based composites with enhanced stiffness and improved resistance to photo-oxidative degradation. Although increasing filler content led to a reduction in tensile strength, ductility, and impact performance, a significant increase in elastic modulus was achieved, highlighting the reinforcing effect of the lignocellulosic filler.

Moreover, increasing filler content reduced the molecular weight loss and limited the increase in molecular weight distribution during accelerated UV exposure. MALDI-TOF analyses further confirmed the lower molecular degradation of the PBS matrix in the presence of the natural filler.

These findings suggest that hazelnut shell powder can act as a multifunctional bio-based additive, combining reinforcement with antioxidant activity, thereby enhancing the durability of PBS-based biocomposites intended for outdoor applications. Further investigations aimed at correlating the molecular changes with mechanical performance and identifying the degradation products in greater detail will contribute to a deeper understanding of the protective mechanisms provided by this agricultural by-product.

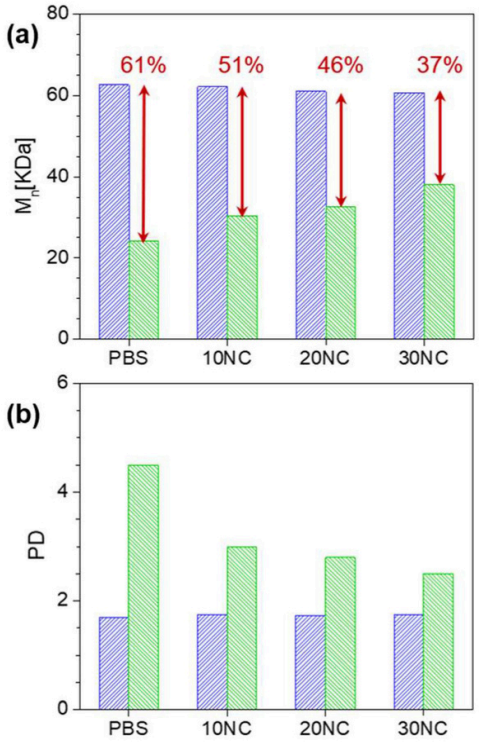


Figure 2. Number-average molecular weight (a) and polydispersity index (b) of the PBS-based composites before and after 90 days of accelerated aging

References

[1] B. Haruna, I. Abdullahi, U. Abdullahi *Journal of Engineering and Applied Science*, vol. 73, 19 (2026)

[2] S. Ayu Rafigah, A. Khalina, A. Saffian Harrnaen et al *Polymers*, vol. 13, 1436 (2021)

[3] B. Cevik, Y. Avsar *Materials Testing,* vol. 67, 1675-1686 (2025)

[4] A. Blasi, A. Verardi, C. G. Lopresto, S. Siciliano, P. Sangiorgio *Recycling (MDPI)*, vol. 8, 61 (2023)

Mechanical Recycling of Multi Coupled Material Body Seals Based on Thermoplastic Elastomers in the Automotive Industry

F. Cano[1], G. Brocani[2], S. Ponti[2], G. Ciaccio[2], V. Brunella[1]

[1] University of Turin, Department of Chemistry, Via P. Giuria 7, Turin, 10125, Italy
[4] Stellantis, C.so Agnelli 220, Turin, 10135, Italy
e-mail: flavia.cano@unito.it

Introduction

The increasing need for sustainable materials in the automotive sector has encouraged the development of recycling strategies for polymer-based components. Thermoplastic elastomers (TPEs) are promising candidates because they combine rubber-like elasticity with the processability and recyclability of thermoplastics. Their ability to be remelted and reprocessed makes them attractive for reducing material waste, vehicle weight, and the environmental impact of automotive components.[1-3]

Automotive sealing systems are relevant examples of complex TPE-based parts. They are designed to satisfy different functional requirements and are therefore composed of several materials, including thermoplastic vulcanizates (TPVs), styrenic thermoplastic elastomers (TPS), polypropylene (PP), and polyester flock. However, this multi-material structure makes recycling difficult, mainly because the different materials cannot be easily separated at end of life.

In this work, the mechanical recycling of post-industrial automotive body sealing profiles was investigated without prior material separation. The aim was to evaluate whether these complex TPE-based components could be reprocessed into a fully recycled material and potentially reintegrated into automotive applications, supporting circular economy strategies in the automotive industry.

Results and discussion

The post-industrial sealing profiles were mechanically recycled through milling and grinding, in order to reduce the material size and obtain granules suitable for further processing. No additives were introduced during the process. The ground material was then reprocessed into plates made of 100% post-industrial recycled material.

Thermo-chemical characterization was performed to evaluate the composition and stability of the recycled compound. Thermogravimetric analysis showed a multistep degradation behavior (Fig.1), related to the presence of different polymeric phases in the original component. The main degradation step was associated with the decomposition of the polymeric matrix, while the high residual mass indicated a significant amount of inorganic fillers. DSC and ATR-FTIR analyses further supported the presence of a complex but stable composition after recycling.

Mechanical testing was carried out to assess the performance of the recycled material. Hardness, tensile properties, tear resistance, compression set, and ageing resistance were evaluated before and after thermal ageing in air at 125°C for 168 h. The results showed that the recycled material maintained stable mechanical properties after ageing, indicating good resistance to thermal exposure (Tab. 1). This behavior is particularly relevant for automotive applications, where materials must retain their properties during service life.

The mechanical properties were also compared with those of commercial TPEs, especially TPVs used for exterior automotive applications. The comparison showed that the recycled material reached comparable performance, suggesting that it could be reused in selected automotive components. Finally, exterior weathering resistance was evaluated by measuring the color variation, expressed as ΔE, after UV exposure (Fig. 2). The values remained below the acceptance limit of 1.5 defined by the internal automotive standard, both before and after washing. This result indicates that the recycled material did not undergo significant aesthetic degradation.

Conclusions

This study demonstrates that complex automotive sealing systems based on thermoplastic elastomers can be mechanically recycled without prior separation of their different material fractions. The recycled material showed good thermo-chemical stability, satisfactory mechanical performance, and limited degradation after both thermal ageing and UV exposure.

The comparison with commercial TPVs suggests that the recycled compound could be considered for reintegration into automotive applications, contributing to material circularity and reducing the environmental impact of polymeric components. Overall, mechanical recycling

appears to be a feasible and promising end-of-life strategy for post-industrial TPE-based sealing systems.

References

[1] Ma K, An H-Y, Nam J, et al. *Nat Commun.* 2024;15(1):7904.
[2] Sha Y, Sun W, Ding S, et al. *ACS Polym Au.* 2025;5(5):432–444.
[3] R. Abdul Vahith. *IJMST.* 2026;2(1):1–10.

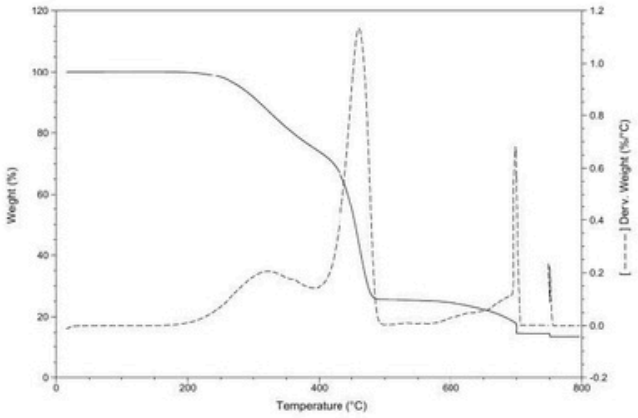


Figure 1. TG and DTG curves showing multistep degradation of the new material and a high residual mass due to inorganic fillers.

Table 1: Mechanical results

CHARACTERISTICS (moulded slabs)	UNIT	100% PIR	100% PIR post ageing
Hardness	ShA	90,5	90,2
	m-IRHD	91,8	91,1
Tensile strength	MPa	9,7	9,8
Elongation at break	%	434	435
Tear strength type C	N/mm	58,6	56,8
Tear strength type T	N/mm	11,4	11,9
Compression set 72h @ 90°C	%	77,2	

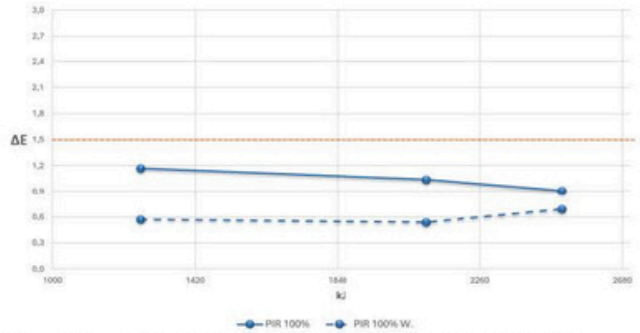


Figure 2. ΔE results before and after washing the surface of the samples after weathrering test.

EUGENOL-DERIVED POLYMERIC NETWORKS AS ECO-FRIENDLY AND CIRCULAR WET-STRENGTH AGENTS FOR HIGH-PERFORMANCE PAPER PRODUCTS

R. Sergi[1], C. Negrell[2], S. Caillol[2], A. Piozzi[1], A. Martinelli[1], F. Rea[3], P. Di Cosimo[3], D. Caschera[4], L. Galantini[1], I. Francolini[1]

[1] Department of Chemistry, Sapienza University of Rome, Piaz.le Aldo Moro 5, 00185, Rome, Italy.
[2] Institut Charles Gerhardt UMR 5253–CNRS, UM, ENSCM, 8 rue de l'Ecole Normale, F-34296 Montpellier Cedex 5, France
[3] Gima Water & Air s.R.l (GWA), Via Fratta Rotonda Vado Largo, 03012 Anagni, Italy
[4] *Institute for the Study of Nanostructured Materials, ISMN-CNR, 00016 Monterotondo Stazione, Roma, Italy*
e-mail: riccardo.sergi@uniroma1.it

Introduction

The paper and cellulosic materials industry is constantly seeking additives capable of imparting mechanical strength under wet conditions ("wet strength agents"), a crucial property for applications ranging from food packaging to hygiene products. Traditionally, this market has been dominated by synthetic, petroleum-derived resins, such as polyamide-epichlorohydrin (PAE) or urea-formaldehyde resins. However, the presence of toxic chlorinated by-products (such as 1,3-dichloro-2-propanol) and the progressive depletion of fossil resources are driving macromolecular research towards sustainable, biocompatible, and bio-based alternatives.

In this scenario, natural phenols derived from biomass represent an extremely promising chemical platform for the synthesis of new functional additives and polymers [1]. Among these, eugenol, the main component of clove essential oil, stands out for its versatile molecular structure. The coexistence of an aromatic ring, a hydroxyl group, and a terminal allyl function allows eugenol to be exploited as a precursor in various polymer synthesis routes, including epoxy resin curing, radical polymerization, or thiol-ene click chemistry. In addition to the high thermal and mechanical stability intrinsic to the aromatic architecture, eugenol imparts distinct, broad-spectrum antioxidant and antimicrobial properties to the resulting materials [2].

In this work, by exploiting synergies between the chemistry of natural phenolic derivatives and the demand for eco-compatible industrial additives, we present the synthesis and characterization of novel polymeric wet-strength agents based on eugenol derivatives. The macromolecular systems were designed to cover the cellulose fibers and form noncovalent interactions with them, thus offering a viable green alternative to commercial formulations.

Results and discussion

The synthesis of eugenol-based macromolecular architectures proved to be a highly effective strategy for engineering next-generation, bio-based wet-strength agents. Different synthetic pathways were successfully explored to overcome the current performance limitations of conventional petroleum-derived resins: a facile polymerization of eugenol yielding a homopolymer (polyEU) without the use of organic solvents, and a radical step-growth thiol-ene click polymerization of chemically derived eugenol. For the thiol-ene click system, tailoring the monomer-to-dithiol molar ratio provided an optimal balance to avoid the high viscosity or insufficient crosslinking efficiencies observed at non-stoichiometric values. The resulting copolymer matrix was subsequently mixed with either a commercial trifunctional crosslinker or a fully bio-based diallyl eugenol counterpart. Then, photo-cured occurred under UV light, demonstrating exceptional network formation and high gel fractions. Structural incorporation and network development over time were validated through spectroscopy, while thermogravimetric analysis highlighted a significantly enhanced thermal stability for the polymerized architectures compared to pure eugenol, which undergoes rapid volatilization. When applied to cellulose substrates, these eugenol-derived architectures completely altered the surface behavior of the paper. While untreated paper exhibits immediate water absorption due to its hydrophilic nature, impregnation with the eugenol-based systems successfully introduced robust and stable hydrophobic properties. Unlike conventional synthetic resin treatments, where water drops are

typically absorbed within a short timeframe, the eugenol-coated substrates maintained their high contact angles stably over time. Morphological investigation via Field-Emission Scanning Electron Microscopy explained this behavior, illustrating a transition from the highly porous, bare fiber network of untreated paper to an encapsulated microstructural arrangement where the polymer effectively covers the cellulose fibers and forms continuous bridges across fiber junctions. This microstructural arrangement closely mimics the natural protection and structural function of lignin within plant cell walls, acting as a physical barrier that shields the fiber-fiber contact zones from moisture attack. Mechanical evaluation through tensile testing highlighted the efficiency of these networks under demanding environmental conditions. Impregnation with the eugenol homopolymer polyEU enhanced the wet tensile strength and overall stability under wet conditions, while photo-crosslinked thiol-ene click eugenol-based copolymers achieved outstanding performance reinforcements under fully wet conditions. Crucially, the network cured using the fully bio-based eugenol crosslinker performed comparably to, or even exceeded, the commercial counterpart. This high crosslinking density traps the macromolecular network around the cellulose fibres, providing strong mechanical interlocking and water resistance. This is achieved without the need for the toxic formaldehyde or chlorinated compounds that are typical of conventional industrial additives. Consequently, these eco-friendly networks effectively maintain the structural integrity of the paper matrix, matching industrial wet-strength requirements and offering a sustainable alternative to traditional synthetic resin systems.

Conclusions

In conclusion, this work demonstrates that eugenoli s a promising bio-based platform for the development of high-performance wet-strength agents. Both the solvent-free homopolymerization route and the thiol-ene photo-curing strategy produced polymeric networks able to modify cellulose surface properties from hydrophilic to hydrophobic, while effectively coating the fibers and forming inter-fiber bridges.

Morphological analyses confirmed that these bio-based polymers effectively cover cellulose fibers and form durable inter-fiber structural bridges, perfectly replicating the moisture-shielding protection mechanism found in natural lignin.

The modified paper substrates showed improved tensile strength, stiffness, and wet stability, reaching performance levels comparable to industrial benchmarks. These results highlight the potential of eugenol-based polymers as sustainable alternatives to conventional fossil-based wet-strength resins.

References

[1] Francolini, I., Galantini, L., Rea, F., Di Cosimo, C., & Di Cosimo, P. International journal of molecular sciences, 24.11, 9268, 2023.

[2] Delliere, P., Bakkali-Hassani, C., & Caillol, S. *Current opinion in green and sustainable chemistry*, *51*, 100988, (2025).

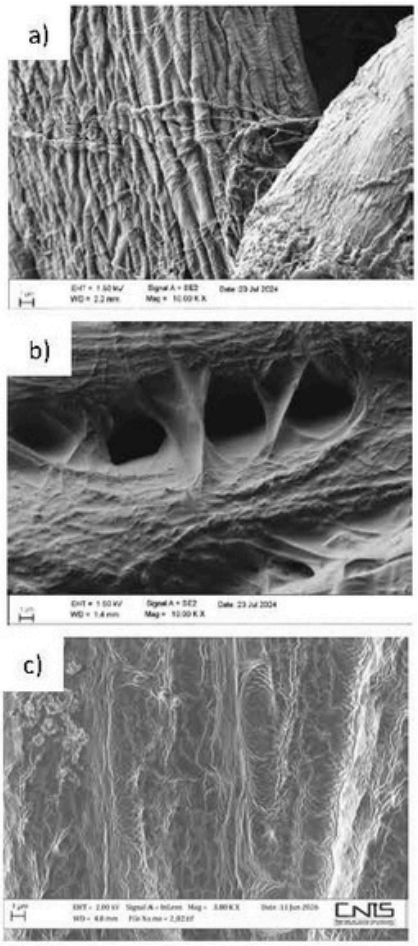


Figure 1. FE-SEM micrographs of cellulose fibers: a) untreated, b) coated with polyEU, and c) coated with polymers obtained by thiol-ene polymerization

Table 1: results from sessile drop test

Sample	CA (°)
Untreated paper	0
Paper + poly EU 5%	103±6
Paper + r(AEUG-HDT)_D10_5%	124 ± 5

ENGINEERING CIRCULAR POLYESTERS THROUGH MOLECULAR ARCHITECTURE: FROM THERMOPLASTIC ELASTOMERS TO DYNAMIC COVALENT NETWORKS

Licia Gaeta[1], Camilla Noè[2], Maria Gentile[1], David H. Lamparelli[1], Michele Gammino[3], Roberto Scaffaro[3], Luciano Di Maio,[4] Claudio Pellecchia[1]

[1] Dipartimento di Chimica e Biologia "A. Zambelli", Università degli Studi di Salerno, via Giovanni Paolo II 132, Fisciano (SA) 84084, Italy
[2] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[3] Dipartimento di Ingegneria, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, PA, Italy
[4] Dipartimento di Ingegneria Industriale, Università degli Studi di Salerno, via Giovanni Paolo II 132, Fisciano (SA) 84084, Italy

e-mail: cpellecchia@unisa.it

Introduction

The development of sustainable polymeric materials requires overcoming a longstanding trade-off between performance, processability, and end-of-life management. In this context, molecular architecture represents a powerful design parameter for tailoring material properties while preserving the inherent recyclability of polyester-based systems. This research explores how catalyst design and macromolecular architecture can be combined to create a new generation of circular polyester materials ranging from thermoplastic elastomers to dynamic covalent networks.

Results and discussion

The first part of this work focuses on the synthesis of architecturally controlled ABA triblock copolyesters through iron-catalyzed ring-opening polymerization of renewable cyclic esters [1]. Highly active Fe(II) complexes enable the controlled formation of block copolymers [2] composed of semi-crystalline poly(lactide) hard segments and flexible amorphous polyester midblocks (Figure 1). By varying block composition, molecular weight, and phase morphology, the mechanical behavior can be tuned over an exceptionally broad range, from soft elastomeric materials to high-strength rubbers and toughened bioplastics (Figure 2) [3].

Figure 1. Reaction scheme for the synthesis of ABA triblock copolymers.

The versatility of this platform demonstrates how precise control over polymer architecture can generate materials with performances comparable to conventional thermoplastic elastomers while maintaining the sustainability advantages of polyester chemistry.

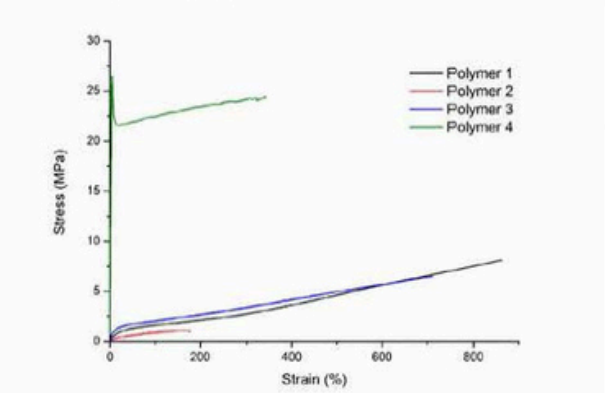


Figure 2. Uniaxial tensile tests for representative ABA triblock polymers.

Recent developments further highlight the scalability of these synthetic methodologies and their compatibility with industrially relevant processing conditions. Remarkably, copolymers synthesized from unpurified technical-grade ε-caprolactone and L-lactide using industrial Sn(II) octanoate under solvent-free melt polymerization conditions retain excellent elastomeric behavior despite their more heterogeneous architectures and prove highly effective as PLA toughening agents, increasing the strain-at-break of commercial PLA from ~4% to over 90% at only ~25 wt% loading. Overall, the results highlight how controlled but also deliberately imperfect molecular architectures in PLA-based triblock copolymers can be leveraged to achieve

sustainable thermoplastic elastomers with excellent and tunable mechanical performance, as well as highly effective toughening agents for brittle bioplastics.

A complementary architectural strategy has been investigated through the preparation of bio-based vitrimer networks derived from star-shaped poly(lactide) oligomers and DGEIs, a renewable isosorbide-based epoxy crosslinker (Figure 3). In these systems, the topology of the precursor macromolecules directly influences network structure, crosslink density, segmental mobility, and dynamic bond exchange kinetics.

Figure 3. Synthesis, reprocessing, and chemical recycling of PLA-based dynamic polymer networks.

As a result, thermomechanical properties, shape-memory performance, surface characteristics, and hydrolytic stability can be modulated through the rational selection of molecular architecture. The incorporation of transesterification-mediated bond exchange introduces vitrimer behavior, allowing stress relaxation and network rearrangement while preserving structural integrity [4].

Beyond property optimization, molecular architecture also plays a central role in determining material circularity. The thermoplastic copolyesters can be efficiently depolymerized to recover valuable monomeric building blocks, whereas the vitrimer networks undergo controlled chemical recycling under mild conditions, yielding reusable low-molecular-weight products. The same approach has been successfully extended to fiber-reinforced vitrimer composites, enabling simultaneous recovery of both the polymer matrix constituents and structurally intact carbon fibers.

Conclusions

This work demonstrates how molecular architecture can serve as a unifying design principle for the development of next-generation sustainable polyester materials. By combining earth-abundant metal catalysis with precise control over polymer topology and network structure, it is possible to access a broad spectrum of materials ranging from high-performance thermoplastic elastomers to dynamic vitrimer networks and recyclable composites. The results highlight how variations in chain architecture, phase organization, and dynamic covalent connectivity directly govern mechanical performance, thermal behavior, durability, reprocessability, and end-of-life options. Importantly, these materials do not require a compromise between functionality and sustainability, as high mechanical performance can be achieved alongside efficient chemical recycling and recovery of valuable resources. The ability to tailor properties through molecular design while preserving circularity provides a versatile platform for the development of renewable and recyclable polymer systems. Overall, this approach contributes to the advancement of sustainable materials technologies and supports the transition toward a circular polymer economy based on high-value, closed-loop polyester materials.

References

[1] G. Gravina, G. Pierri, C. Pellecchia, *Mol. Catal.* vol. 555, 113891 (2024).
[2] G. Gravina, E. Romano, A. Liporace, M. C. D'Alterio, G. Talarico, C. Pellecchia, *ACS Sustainable Chem. Eng.* 2025, vol. 13, 19613−19624 (2025).
[3] G. Gravina, J. N. A. Tagoe, R. Di Girolamo, M. Gentile, L. Di Maio, C. Pellecchia, *ACS Polym. Au* vol. 6, 468−479 (2026).
[4] L. Gaeta, M. Gammino, C. Noè, M. Gentile, R. Scaffaro, C. Pellecchia, *ACS Sustainable Chem. Eng.*, doi.org/10.1021/acssuschemeng.6c05601, in press.

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Altri

CONTRIBUTI ORALI

Materiali polimerici ibridi e (nano)compositi sintesi, caratterizzazione e applicazioni

Transparent self-extinguishing silica-epoxy nanocomposites based on Novolac resin

A. Bifulco[1], S. Lehner[2], A. Arpaia[1], J. Passaro[3], P. Russo[3], A. Aronne[1], S. Gaan[2]
[1] Department of Chemical, Materials and Production Engineering (DICMaPI), University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy
e-mail: aurelio.bifulco@unina.it
[2] Laboratory for Advanced Fibers, Empa Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland
[3] Institute of Polymers, Composites and Biomaterials (IPCB), National Research Council (CNR), Via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy

Introduction

The increasing industrial demand, along with rising pollution and phosphorus (P) depletion, is driving the scientific community to develop flame retardant (FR) epoxy nanocomposites (ENCs) that use lower phosphorus content and more sustainable additives [1].

Results and discussion

The reaction between DGEBA (bisphenol A diglycidyl ether) or Novolac-based resins and APTES (3-aminopropyltriethoxysilane) enables the formation of organic-inorganic silanized epoxy structures. These hybrid moieties can further condense with tetraethyl orthosilicate (TEOS), a silica precursor, generating an in situ silica phase via sol-gel processes [2, 3]. High-resolution transmission electron microscopy revealed that, in DGEBA-based systems, the silica phase consists of well-organized multilamellar nanoparticles (NPs) [2]. Conversely, in Novolac-based systems, fully amorphous silica NPs are dispersed within a hybrid co-continuous polymer network [3].

Figure 1: Main outcomes related to silica-epoxy nanocomposites based on Novolac resin

The incorporation of DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-based flame retardants into silica-epoxy systems derived from DGEBA or Novolac resins yields nanocomposites characterized by high transparency, no-dripping behavior, and a UL-94 V-0 rating in vertical burning tests, along with a significant reduction (up to 80%) in the peak heat release rate during cone calorimetry, even at phosphorus loadings as low as 3 wt.% [2, 3].
In the case of Novolac systems, transparency is retained even at silica nanoparticle contents exceeding 4 wt.% due to their amorphous nature (see Figure 1) and the liquide nature of the employed DOPO derivative [3].

Conclusions

The in situ sol-gel generation of inorganic phases has been studied in combination with a DOPO-based flame retardant to synthesize ENCs exhibiting no-dripping behavior and self-extinguishing properties (V-0 rating in UL-94 flammability tests), while maintaining very low phosphorus contents (1-3 wt.%).

Acknowledgments

I would like to greatly thank all the colleagues and friends who have collaborated with me over the years in studying such functional hybrid polymer-based systems, sol-gel architectures, and more sustainable strategies.

References

[1] A. Bifulco, J. Chen, A. Sekar, R. W.W. Klingler, A. Gooneie, S. Gaan, *Journal of Materials Science & Technology*, 199, 156-183 (2024).
[2] A. Bifulco, D. Parida, K.A. Salmeia, R. Nazir, S. Lehner, R. Stämpfli, H. Markus, G. Malucelli, F. Branda, S. Gaan, *Materials and Design*, 193, 108862 (2020).
[3] S. Lehner, A. Arpaia, J. Passaro, M. Góra, R. Pauer, P. Rupper, P. Russo, A. Aronne, A. Bifulco, S. Gaan, *Polymer Degradation and Stability*, 244, 111839 (2026).

SOLVENT-FREE PROCESSING OF HIGH β-PHASE POLY(VINYLIDENE FLUORIDE) FILMS FOR ENERGY CONVERSION APPLICATIONS

L. Broggio [1,2], G. Moretti [1], S. Dirè [1], A. Dorigato [1,2]

[1] Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123, Trento, Italy
[2] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Florence, Italy
e-mail: lorenzo.broggio-1@unitn.it

Introduction

Poly(vinylidene fluoride) (PVDF) is a semicrystalline fluoropolymer that has attracted considerable attention as a flexible electroactive material because of its ferroelectric nature, good chemical resistance, and capability to exhibit significant piezoelectric response when processed into polar crystalline phases. The electromechanical activity of PVDF originates from the polar β crystalline phase, where the aligned C–F dipoles in the *all-trans* arrangement produce a net polarization under mechanical or electrical stimuli. Despite its attractive electroactive properties, PVDF crystallizes predominantly into the non-polar α phase under conventional processing conditions, limiting its piezoelectric performance [1]. Considerable research efforts have therefore been devoted to promoting the formation of polar crystalline phases through mechanical stretching, electrical poling, and the development of fluorinated copolymers and terpolymers. However, these approaches often involve additional processing steps, more complex and costly materials, as well as the use of solvents, electrical or chemical treatments, and hazardous gases, which may hinder large-scale industrial implementation. Recent studies have demonstrated that compressive deformation can also promote the formation of the electroactive β phase without conventional stretching treatments [2]. In this work, a commercial low-cost PVDF grade is used to create β-poly (vinylidene fluoride) with ferroelectric behavior through a straightforward solvent-free cold pressing and annealing process.

Ambofluor® 24 commercial low cost PVDF (M_w = 360-400 kDa, T_m = 165-178 °C), produced by Ambofluor GmbH & Co. KG (Hamburg-Nord, Germany), was hot pressed at 190 °C for 5 minutes under a load of 10 tons, to obtain a film of 120 μm nominal thickness. Stacks composed of 1, 4, 6, 8 or 10 layers of the hot pressed PVDF film were then cold pressed at room temperature. The cold pressed films were then annealed and kept for 5 minutes at the annealing temperature, followed by water quenching and pressure release. Different pressures were investigated to a maximum of 1000 MPa, while different annealing temperatures were explored from room temperature to the melting temperature of PVDF. In addition to the physical, thermal, and mechanical characterization, capacitance measurements were carried out to assess the permittivity and dielectric loss of the material, while P-E curves were obtained to identify the suitable polarization temperature and electric field ranges for the poling cycle. A contact poling cycle was designed to improve the macroscopic piezoelectric properties of the materials, finally assessed through the measurement of the piezoelectric strain coefficient (d_{33}).

Results and discussion

The cold-pressed and annealed PVDF exhibits a higher β-phase content and a reduced α-phase fraction, as evidenced by the FTIR spectra reported in Figure 1, reporting the FTIR spectrum of hot pressed PVDF and of a 10 layers stack of cold pressed and annealed at 160 °C PVDF.

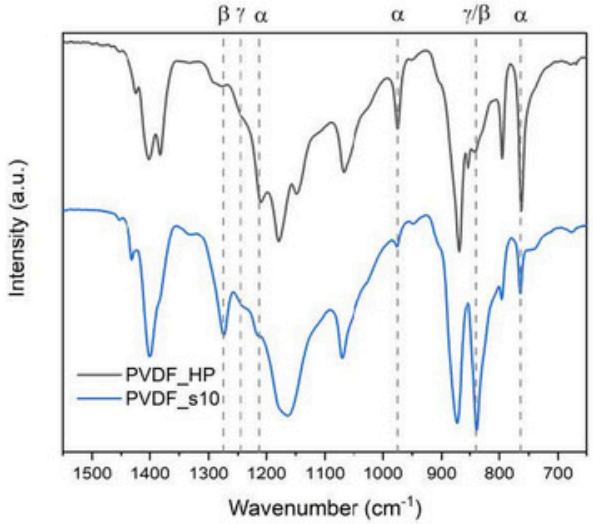


Figure 1. FTIR (ATR mode) spectrum of hot pressed PVDF and of a 10 layers stack of cold pressed (1000 MPa) and annealed (160 °C) PVDF, in the range between 600 cm^{-1} to 1600 cm^{-1}.

With increasing compressive stress, the β phase is more prone to form. Moreover, the increasing number of stacked layers, with respect to the single layer, favors the transformation process due to the higher strain to which samples are subjected under the same pressure [2]. The higher β-phase fraction was also confirmed by the differential scanning calorimetry (DSC) and has a positive effect on the piezoelectric strain coefficient (d_{33}) that increased from 5.0 pC/N for the hot pressed sample to 16 pC/N in the cold pressed and annealed ones.

Conclusions

In conclusion, high β phase PVDF films with ferroelectric properties were successfully developed and characterized using a simple, easily implementable, and scalable process. This work indicates the possibility of obtaining flexible electroactive components with a cost-effective approach that significantly enhances the piezoelectric response of PVDF.

References

[1] T. Furukawa, *Phase Transitions*, vol. 18, 143-211 (1989).
[2] N. Meng *et al.*, *Nature Communications*, vol. 10, 4535 (2019).

Acknowledgments

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HYBRID MICROGELS BASED ON PNIPAM AND NATURAL PROTEINS: FROM MOLECULAR INTERACTIONS TO BIOMATERIAL APPLICATIONS

E. Buratti[1], D. Errico[1], F. Longo[1,2], M. Sguizzato[3], S. Buoso[4], T. Posati[5], G. Sotgiu[4,5], E. Mazzoni[6], M. Bertoldo[3]

[1] Department of Environmental and Prevention Sciences, University of Ferrara, via Luigi Borsari, 46, Ferrara, 44121, Italy
[2] Department of Inorganic, Organic Chemistry and Biochemistry, Faculty of Chemical Sciences and Technology, University of Castilla-La Mancha, 13071 Ciudad Real, Spain
[3] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, via Luigi Borsari, 46, Ferrara, 44121, Italy
[4] Kerline Srl, Via P. Gobetti 101, 40129 Bologna, Italy
[5] Institute for Organic Synthesis and Photoreactivity, National Research Council (CNR-ISOF), via P. Gobetti, 101, 40129 Bologna, Italy
[6] Department of Translational Medicine, University of Ferrara, Via Fossato di Mortara 64/B, 44121 Ferrara, Italy
e-mail: elena.buratti@unife.it

Introduction

In recent years, hybrid microgel systems combining synthetic and natural polymers have emerged as highly promising platforms in the biomedical field, offering a unique synergy between structural control and bioactivity [1]. Among synthetic matrices, poly(N-isopropylacrylamide) (PNIPAM) microgels are widely investigated due to their thermo-responsive behavior, characterized by a Lower Critical Solution Temperature (LCST) around 32 °C, which is ideally suited for physiological applications. To impart bioactivity and tailored functionality to these synthetic networks, the integration of natural proteins has emerged as a powerful strategy. A particularly sustainable and circular approach involves the utilization of proteins extracted from textile industry by-products, such as from wool and silk production. Within this framework, we exploited three different proteins, keratin, extracted from wool waste through sulfitolysis [2] and sericin and fibroin, extracted from silk waste through degumming [3], to prepare hybrid systems with PNIPAM microgels. While keratin can introduce intrinsic bioactive features for tissue regeneration, fibroin and sericin can offer exceptional mechanical robustness and outstanding antioxidant properties, respectively.

In this study, hybrid microgel systems were prepared following two distinct approaches [4]: a synthetic pathway, via the polymerization of PNIPAM microgels directly in the presence of the proteins, and a physical method, by mixing preformed PNIPAM microgels with the biopolymers. We investigated the formation of these colloidal systems, tracking variations in particle size and thoroughly evaluating the molecular interactions established between the microgels and the proteins as a function of the preparation method, particle charge, and size. Finally, to assess the biomedical potential of these materials, a drug loading e releasing test was performed, and thin films were fabricated from the hybrid dispersions to investigate their cytocompatibility for use in tissue engineering.

Results and discussion

The investigated preparation strategies, the synthetic pathway and the physical mixing (Figure 1), were applied to all three proteins, leading to different results in terms of hybrid structure and stability.

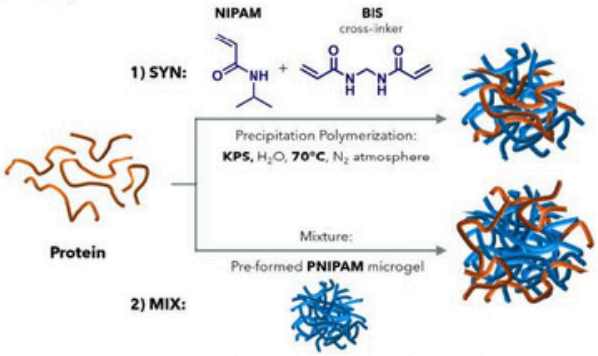


Figure 1. Schematic representation of the two different methods to prepare hybrid microgels: 1) synthesis of PNIPAM microgels in presence of protein; 2) mixing protein with pre-formed PNIPAM microgel.

Regarding the systems with keratin and sericin, stable colloidal particles were successfully obtained through both the synthetic and physical

pathways, as confirmed by the TEM images in Figure 2, showing the hybrid prepared via the synthetic route with (a) keratin and (b) sericin. DLS analysis of these systems at different compositions (from 10 to 40% of protein) revealed that the presence of keratin led to a decrease in hybrid particle size compared to pure PNIPAM microgels, whereas the integration of sericin resulted in an increase in the overall dimensions. Spectroscopic techniques (FTIR and NMR) along with elemental analysis identified the grafted architecture of hybrid microgels with keratin and a physical absorption of sericin.

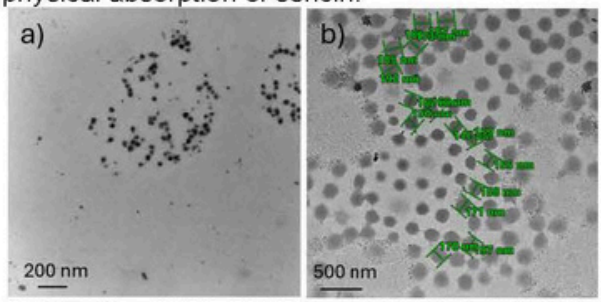


Figure 2. TEM images of hybrid microgels prepared by the synthetic route with (a) 20% of keratin and (b) 20% of sericin.

To explore the potential as delivery systems, caffeic acid was loaded in the hybrid microgels with keratin. The drug entrapment efficiency was evaluated via UV-Vis spectroscopy, showing a higher efficiency (up to 90%) compared to the pure PNIPAM microgel.

Regarding the fibroin, due to its high aggregation tendency, the synthetic route did not allow to obtain colloidal particles, so the mixing strategy was used to prepare hybrids at different compositions.

The hybrid microgels, prepared with different biopolymers, compositions and methods, were used to obtain substrates for cell culture. Firstly, thin films were prepared by solvent casting and thermal treatment at 160°C to promote the proteins' crosslinking; then, a stability test in water was carried out to evaluate the resistance to dissolution. Both systems with keratin and fibroin showed good stability, while with sericin a disaggregation of the supports was observed, due to a partial crosslinking of the protein.

Swelling tests were performed at 25 and 40 °C on the water-stable hydrogels. Different swelling ratios were observed, with higher values correlating with both a higher PNIPAM content in the system and lower temperature, due to the hydrophilic state of the particles at 25°C. The porosity of these hydrogels was confirmed by SEM analysis (Figure 3a), encouraging the utilization of these matrices as supports for cell growth. Cell culture tests were conducted at 37 °C, showing a good vitality for the hybrid scaffolds. Upon cooling at room temperature, the PNIPAM network reverted to a hydrophilic state, successfully promoting non-enzymatic cell detachment. Subsequently, the gene expression profiles of αSMA, collagen I and CK18 were evaluated (Figure 3b). The results demonstrated that the quantitative expression of these target genes was strongly dependent on both the composition and the method preparation of the hybrid hydrogels.

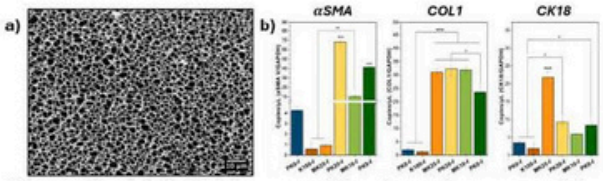


Figure 3. (a) SEM image of hydrogel prepared by hybrid microgel with 20% of keratin; (b) gene expression of αSMA, collagen I and CK18.

Conclusions

This work successfully investigated the integration of PNIPAM microgels with different structural proteins (keratin, sericin, and fibroin) derived from textile industry by-products. These proteins interact differently with the synthetic microgel due to their distinct hydrophilicity, stability, and chemical reactivity. While keratin and sericin yielded stable colloidal particles through both the synthetic and physical pathways, fibroin's high aggregation tendency restricted its processing exclusively to the physical method. Preliminary tests for pharmaceutical and biomedical applications demonstrated that the combination of both components leads to remarkable synergistic effects. The incorporation of keratin within the microgels enhanced the encapsulation efficiency of caffeic acid compared to pure PNIPAM microgel. Furthermore, when processed into thin films, the hybrid materials showcased a dual functionality: the presence of the proteins successfully promoted cell viability and growth, while the thermo-responsive nature of PNIPAM enabled non-enzymatic cell detachment upon cooling. These findings yield highly promising results for the rational design of advanced bio-instructive substrates.

References

[1] G. L. do Lago, M. I. Felisberti, *European Polymer Journal*, 125, 109538 (2020)

[2] A. Aluigi, M. Zoccola, C. Vineis, C. Tonin, F. Ferrero, M. Canetti, *Int. J. Biol. Macromol.*, 41(3), 266-273 (2007)

[3] L. Ottaviano, S. Buoso, R. Zamboni, G. Sotgiu, T. Posati, *J. Funct. Biomater.*, 16(1), 20 (2025).

[4] E. Buratti, M. Sguizzato, G. Sotgiu, R. Zamboni, M. Bertoldo, *Gels*, 10(6), 411 (2024)

TOWARDS SUSTAINABLE ELECTRICAL CABLE INSULATION: DESIGN OF A NOVEL POLYETHYLENE-BASED COMPOSITE SYSTEM

Maria Teresa Letizia[1,2], Gianluca Viscusi[2], Giuliana Gorrasi[2], Roberto Pantani[2]

[1]University School for Advanced Studies IUSS, Pavia, Italy
[2]Department of Industrial Engineering, University of Salerno, Fisciano, Italy
e-mail: maria.letizia@iusspavia.it

Introduction

Polyethylene (PE) is one of the most popular polymers in industry owing to its ease of processing and favorable combination of chemical and physical properties. However, PE does not meet the requirements for electrical insulation applications due to its low mechanical strength and thermal resistance. One way to overcome this limitation is to introduce intermolecular chemical bonding through a cross-linking process, thereby enhancing mechanical and thermal properties. This process yields cross-linked polyethylene (XLPE), which is the most widely used insulating material for power cables due to its excellent mechanical and insulating performance [1].

Although cross-linking enhances PE performance, it also raises significant sustainability concerns. Once cross-linked, XLPE behaves as a thermoset, making recycling particularly difficult because of its permanent three-dimensional network [1].
The sustainability of PE-based materials for electrical cable insulation can be enhanced through several approaches.
One strategy involves blending different polyolefins (e.g., LLDPE/HDPE) or incorporating fillers into a polyolefin matrix (e.g., ZnO into polypropylene) to develop eco-friendly thermoplastic systems. By tailoring the composition, these approaches improve the mechanical and electrical properties while preserving the recyclability of the material [2, 3].
Click chemistry-based curing offers an alternative route to PE cross-linking, enabling the formation of reversible three-dimensional networks through thermally activated, catalyst-free reactions. Unlike conventional XLPE, the resulting dynamically cross-linked material combines the thermomechanical performance required for electrical cable applications with the ability to be recycled by remelting [4].

The present work aims at developing sustainable solutions for the production of electrical cable insulation materials by designing a composite system containing functionalized phases capable of reacting via thermally-activated reactions.

Results and discussion

A reactive PE-based composite system was prepared by incorporating functionalized ZnO into an LLDPE matrix containing a maleic anhydride-grafted phase via melt compounding in a twin-screw extruder.
Filler functionalization with 3-glycidyloxypropyltrimethoxysilane (GPTMS) enabled a thermally activated reaction between the epoxy group and maleic anhydride, leading to the formation of a structure with enhanced physical properties compared with neat LLDPE.

Thermal, rheological, mechanical, and barrier properties were investigated at each stage of the production process, including filler functionalization, composite preparation, and the cross-linking reaction.
FT-IR spectroscopy and thermogravimetric analysis (TGA) were used to confirm successful filler functionalization. In parallel, dynamic scanning calorimetry (DSC), rheological tests, and dynamical mechanical analysis (DMA) were performed on blends containing different amounts of the maleic anhydride-grafted phase to identify the optimal polymer matrix composition.
Subsequently, the final product was obtained by activating the reaction withing the composite system. The progress of the reaction was monitored over time via rheological measurements, with an increase in both complex viscosity and storage modulus confirming its occurrence. The resulting systems exhibited improved performance compared to unmodified LLDPE, including higher Young's modulus and enhanced water vapor barrier properties.

Conclusions

To address the sustainability challenges associated with both the production and end-of-life management of XLPE, the electrical power sector is actively seeking low environmental impact alternatives.
In this work, a composite system based on LLDPE was designed to undergo thermally activated reactions between functionalized ZnO (ZnO-GPTMS) and a maleic anhydride-grafted phase. The results confirmed the formation of a material with improved physical properties compared with

neat LLDPE, including higher elastic modulus and enhanced water vapor barrier properties.
The outcomes are promising and open avenues for future work, including the enhancement of the reaction yield through optimization of system composition and reaction conditions.

References

[1] Shapiro et al., *ACS Applied Polymer Materials*, vol. 6, 11859−11876 (2024).
[2] Li et al., *Materials*, vol. 11 (2018).
[3] Zhou et al., *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 24, 1380-1389 (2016).
[4] Ouyang Y., *ACS Applied Polymer Materials*, vol. 2, 2389-2396 (2020).

CYCLODEXTRIN-GRAFTED CHITOSAN SCAFFOLDS FOR ENHANCED CURCUMIN DELIVERY

Elisabetta Lacolla[1], Clarissa Ciarlantini[1], Iolanda Francolini[1], Andrea Martinelli[1], Eleftheria Dossi[2], Marta Fernández-García[3], Carolina Muñoz-Núñez[3], Alexandra Muñoz-Bonilla[3], Antonella Piozzi[1]

[1]Chemistry Department, University La Sapienza, Piazzale Aldo Moro 5, 00185 Rome, Italy
[2]Centre for Defence Engineering and Physical Science, Cranfield University, Defence Academy of UK, Shrivenham, SN6 8LA, UK
[3]Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), C/ Juan de la Cierva 3, 28006 Madrid, Spain

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides widely studied in biomedicine for their capacity to encapsulate hydrophobic compounds via host–guest inclusion complex formation [1]. Their hydrophobic internal cavity and hydrophilic external surface make them particularly suitable for improving the solubility, stability, and bioavailability of poorly water-soluble drugs [2]. However, the biomedical application of pristine CDs is often limited by weak intermolecular interactions and poor structural stability. To overcome these limitations, CDs can be chemically incorporated into polymeric matrices, obtaining multifunctional supramolecular systems with enhanced loading capacity and controlled release behavior [3].

Among natural polymers, chitosan (CS) represents one of the most promising candidates due to its biodegradability, biocompatibility, mucoadhesiveness, and intrinsic antibacterial activity. Furthermore, the presence of reactive amino groups along the CS polymeric backbone enables easy chemical functionalization and the development of tailored delivery systems [4].

In the present work, β- and γ-CDs were first functionalized with maleic or succinic anhydride to introduce pendant carboxylic groups on the macrocycles. Subsequently, the modified CDs were covalently attached to CS via EDC/NHS activation, enabling coupling between the activated carboxyl groups of the cyclodextrins and the primary amine groups of chitosan, with the formation of amide linkages. The resulting conjugates were processed through freeze-drying to generate porous three-dimensional scaffolds, which were subsequently ionically crosslinked with sodium tripolyphosphate (TPP) to improve their dimensional stability in aqueous environments. Curcumin (CUR), selected as a model hydrophobic bioactive compound due to its antioxidant, antiinflammatory, and antimicrobial properties, was encapsulated within the scaffolds through a solvent evaporation method [5]. This study focused on evaluating how the cyclodextrin type and the specific functionalization strategy influence drug encapsulation efficiency, amorphization, thermal stability, morphology, and release behavior. Finally, the antioxidant and antibacterial properties of the curcumin-loaded systems were investigated to assess their potential as multifunctional platforms for controlled drug delivery applications.

Results and Discussion

The covalent conjugation of functionalized CDs onto the CS backbone was unequivocally confirmed through FT-IR and ^{1}H-NMR spectroscopy. FT-IR spectroscopy revealed a characteristic band around 1730 cm^{-1}, assigned to the C=O stretching vibration of ester bond formed in the modified CDs, as well as a peak near 1640 cm^{-1} indicative of newly formed amide bonds between CD carboxyl groups and CS amino functionalities. ^{1}H NMR spectroscopy enabled accurate quantification of the degree of substitution (DS), showing higher values for β-CD derivatives (~25%) compared to γ-CD derivatives (~12%). This difference indicates that the steric effects associated with the macrocyclic structure play a key role in limiting the accessibility of polymer chains during the functionalization process. The morphology of the systems, analyzed via FE-SEM and reported in Figure 1, demonstrated that the integration of CDs significantly alters the pore architecture. While pure CS exhibits open channels of approximately 270 µm, the addition of β-CD and γ-CDs induced a more pronounced contraction of the structure. This is due to the increased viscosity of the solution, which interferes with ice crystal formation during the freeze-drying process. Subsequent ionic cross-linking with TPP dimensionally stabilized the matrices, further reducing the pore diameter (70-100 µm) due to strong electrostatic interactions that compact the network. Considering the incorporation of CUR into the CD-functionalized systems, it was observed that the presence of CDs promoted a homogeneous distribution of the active compound, preventing aggregation and preserving the porous architecture of the scaffold. Consequently, the CD-containing matrices maintained pore interconnectivity after cross-linking with TPP, resulting in a more open and

less compact network compared to the CUR-loaded pristine CS control system.

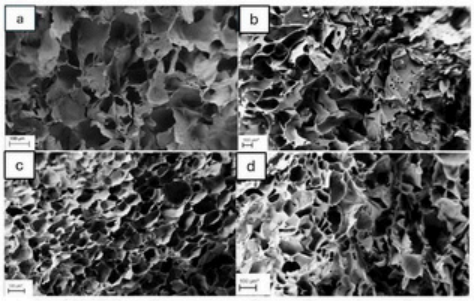


Figure 1. SEM micrographs showing the surface features and pore structure of (a) unmodified CS, (b) CS_βCDS, (c) CS_βCDS_TPP, and (d) CS_γCDS_CUR_TPP. All images were acquired at a scale bar of 100 µm.

Moreover, DSC results confirmed that CUR incorporation resulted in a fully amorphous dispersion of the drug within the functionalized matrices. The disappearance of the CUR crystalline melting peak at 170°C indicates effective molecular dispersion and the formation of inclusion complexes, unlike the pristine CS system, where some residual crystallinity persisted. This phenomenon is crucial for overcoming the intrinsic hydrophobicity of curcumin, thereby markedly improving its bioavailability. TGA analysis revealed that CD grafting significantly enhanced the thermal stability of CS scaffolds due to the formation of an extensive intermolecular hydrogen-bonding network. In contrast, TPP crosslinking slightly reduced the degradation temperature by inducing a more homogeneous and less crystalline polymer structure, whereas the CUR introduction did not significantly alter the thermal stability, as it was efficiently entrapped within the matrix. Swelling experiments demonstrated a clear pH-dependent response, with the matrices absorbing up to fivefold more water at acidic pH (5.0) compared to physiological conditions. This effect was ascribed to the protonation of remaining amino groups in CS, which leads to electrostatic repulsion among polymer chains and enhances solvent penetration into the structure. This mechanism governs the sustained release of CUR, which follows an anomalous diffusion kinetic models (Korsmeyer-Peppas). From a biological perspective, the DPPH assay showed higher EC50 values for CUR-loaded scaffolds than for free CUR. This is mainly due to the limited accessibility of the antioxidant caused by its entrapment within the CS matrix or CD complexes under non-swelling methanolic conditions. Finally, antimicrobial tests, reported in Figure 2, demonstrated strong, strain-dependent efficacy of the developed scaffolds. Against *S. aureus*, all CUR-loaded systems achieved complete bacterial eradication (a 6-log reduction), highlighting the synergistic effect between the intrinsic membrane-disrupting activity of CS and the substained CUR release. In contrast, *E. faecalis* proved more resistant; notably, only scaffolds functionalized with both CD and CUR achieved complete bacterial elimination, confirming the crucial role of CDs in improving CUR solubility and bioavailability. Finally, ongoing in vitro biological studies are being conducted to assess the potential of these platforms for applications in tissue engineering.

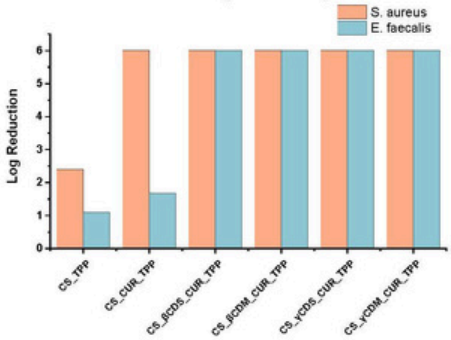


Figure 2. Logarithmic decreases in S. aureus and E. faecalis populations after 24 h exposure to unmodified CS, CUR-loaded CS, and CUR-containing CD-functionalized CS scaffolds.

Conclusions

In this work, multifunctional Chitosan-based 3D scaffolds covalently functionalized with β- and γ-Cyclodextrins were successfully developed to improve the stabilization and delivery of Curcumin. CD functionalization led to the full conversion of CUR into an amorphous state and its uniform distribution throughout the matrices, resulting in improved bioavailability and supporting a sustained, non-Fickian release profile in acidic environments. The systems also exhibited a pronounced pH-responsive swelling behavior, highlighting their suitability for controlled drug delivery applications. Most importantly, the synergistic interaction between chitosan and cyclodextrin-complexed curcumin led to complete bacterial eradication (a 6-log reduction) against both *S. aureus* and *E. faecalis*, demonstrating that cyclodextrin inclusion complexes play a crucial role in enhancing the therapeutic efficacy and antimicrobial performance of curcumin.

References

[1] V. Sehgal, S. P. Pandey, P. K. Singh, *Carbohydrate Polymers*, 323, 121348, (2024).
[2] B. Tian, S. Hua, J. Liu, *Carbohydr. Polym.*, 232, 115805, (2020).
[3] Y. Zhao, Z. Zheng, C. Yu, H. Wei, *Journal of Materials Chemistry B*, 12, 39–63, (2024).
[4] I. Aranaz, A.R. Alcántara, M.C. Civera, C. Arias, B. Elorza, A. Heras Caballero, N. Acosta, *Polymers*, 13, 3256, (2021).
[5] S. Pan-On,P. Dilokthornsakul, W. Tiyaboonchai, *Journal of Controlled Release,* 348, 335–345, (2022).

LONG VS. SHORT CHAIN COVALENT FUNCTIONALIZATION IN THE PREPARATION OF MECHANOCHROMIC POLYMERS

B. Bertoncini [1,2], S. Gabellini [3], C. Adamo [1], A. Pucci [2], S. Scurti [3], M. Carlotti [2]

[1] Chimie ParisTech, PSL Research University, Paris, France.
[2] Chemistry and Industrial Chemistry Department, University of Pisa, Pisa, Italy.
[3] Industrial Chemistry "Toso Montanari" Department, University of Bologna.

e-mail: stefano.scurti2@unibo.it and marco.carlotti@unipi.it

Introduction

Mechanochromic materials are an emerging class of smart systems capable of converting mechanical deformation into optical signals, enabling direct visualization of stress distribution and material failure processes.[1] Among them, perylene bisimide (PBI)-based systems are particularly attractive due to their outstanding photostability and their ability to form reversible emissive aggregates, whose disassembly under mechanical stress leads to measurable spectral changes.

A key but still underexplored parameter in the design of these systems is the nature of the spacer linking the mechanophore to the polymer matrix, which can strongly influence both force transduction efficiency and macroscopic mechanical properties. In this work, we systematically investigate this effect by comparing a long-chain macromechanophore (M-PBI, based on poly(ε-caprolactone) spacers) with a short-chain analogue (P-PBI) (*Figure 1a*), as well as a physically blended control system (S-PBI). These mechanophores are covalently incorporated into two technologically relevant polymers: a thermoplastic elastomer (SEBS-g-MAH) and a semicrystalline polyethylene (LLDPE-g-MAH).[2]

Results and discussion

The macromechanophore M-PBI was synthesized via ring-opening polymerization of ε-caprolactone from hydroxyl-functionalized PBI precursors, yielding a flexible, polymer-extended mechanophoric system suitable for covalent incorporation into reactive polymer matrices.

Thermal analysis shows that incorporation of mechanophores has minimal impact on SEBS-g-MAH, whereas LLDPE-based systems exhibit a moderate decrease in crystallinity with increasing crosslinker content, independent of spacer length. Mechanical testing reveals that SEBS maintains high extensibility upon functionalization, while LLDPE is more sensitive to crosslinking, with short-chain P-PBI causing premature failure at higher loadings. In contrast, M-PBI induces a more gradual reduction in ductility, likely due to the presence of flexible PCL segments that act as entropic springs and partially mitigate network stiffening.

Optically, covalently bound systems (M-PBI and P-PBI) exhibit strong aggregation-induced emission in the 640–660 nm range, whereas physically blended S-PBI shows predominantly monomeric emission and negligible mechanochromic response. Upon tensile deformation, both M-PBI and P-PBI systems display a decrease in aggregate-to-monomer emission ratio (I_E/I_M), consistent with strain-induced disaggregation of PBI aggregates. M-PBI provides the most pronounced optical response, as highlighted by the emission spectra shown in *Figure 1b* and *c*.

In addition, M-PBI exhibits partial reversibility under cyclic loading in SEBS matrix, demonstrating robust and repeatable strain sensing behavior.

Conclusions

This study demonstrates that spacer engineering is a key strategy for balancing optical sensitivity and mechanical performance in PBI-based mechanochromic polymers. The macromechanophore M-PBI enables efficient and, in elastomeric matrices, reversible mechanochromic response without significantly compromising the mechanical properties of the host polymers. In contrast, short-chain mechanophores (P-PBI) can lead to increased stiffness and, at higher loadings, premature failure, especially in semicrystalline LLDPE systems. The use of long, compliant spacers therefore provides an effective route to decouple mechanosensitivity from mechanical degradation. These findings establish a general design principle for the development of robust mechanochromic materials and can be extended to other aggregation-induced emissive systems and commodity polymer matrices, paving the way

toward practical strain-sensing plastics with minimal structural modification.

References

[1] B. Bertoncini, I. Pusceddu, M. Carlotti, M. Turelli, C. Adamo, A. Pucci, Chem. Asian J., 2026, 21 (1), e01000.
[2] B. Bertoncini, S. Gabellini, C. Adamo, A. Pucci, S. Scurti, M. Carlotti, Chem. Methods, 2026, 21 (1), e70106

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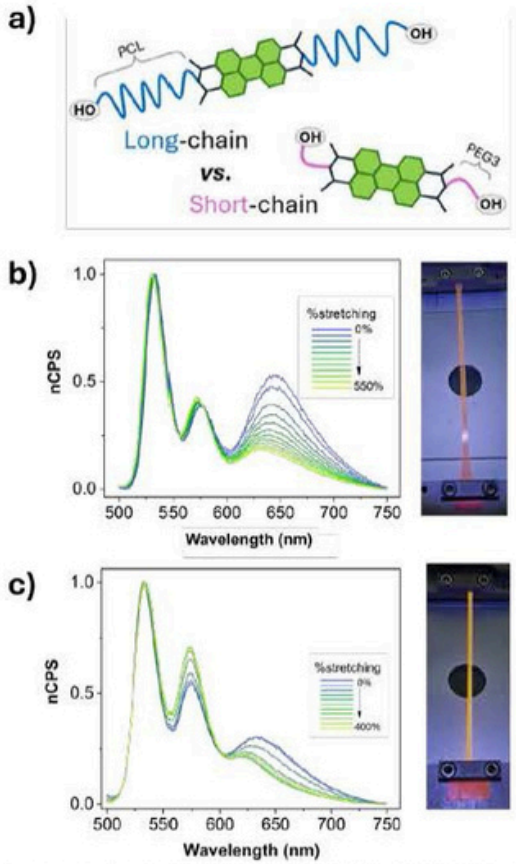


Figure 1. a) Schematic structure of M-PBI and P-PBI mechanophores. b) Normalized emission spectra (λ_{exc}=480 nm) of SEBS and LLDPE samples with 0.1 eq of M-PBI. Pictures on the right show the aspect of the stretched M-PBI films under a UV lamp (λ_{exc}= 365 nm).

EFFECT OF SILANE COUPLING AGENT CONTENT ON STRAIN-INDUCED CAVITATION IN SILICA-FILLED SBR

A. Bianucci[1], C. Marano[1]

[1] Department of Chemistry, Materials and Chemical engineering "Giulio Natta", Politecnico di Milano, P.za Leonardo da Vinci 32, 20133, Milano, Italia

e-mail: alice.bianucci@polimi.it

Introduction

Elastomers are often reinforced with filler particles like silica to achieve the mechanical properties required for industrial applications. However, terminal silanol groups on the silica surface cause particles to aggregate through hydrogen bonding, causing a poor dispersion within the rubber matrix. To overcome this issue, silane coupling agents (SCAs) are used to chemically modify the silica surface. SCAs molecules form covalent bonds with the rubber molecules, significantly improving the filler dispersion and maximising its reinforcing ability.

While beneficial for the mechanical properties, filler particles introduce microscopic structural complexities that promote strain-induced cavity formation (*1*, *2*). This occurs through two different mechanisms: *cavitation*, when a void forms in the bulk of the rubber matrix, and *debonding*, when failure of the rubber-filler interface occurs (*3*). Since SCAs strengthen rubber-filler interactions, higher concentrations are expected to reduce the occurrence of debonding.

The aim of this work is to study the evolution of cavity formation as a function of the compound composition.

The materials studied in this work are supplied by Pirelli Tyre S.p.A and consist of a styrene-butadiene rubber (SBR) filled with 75 phr of silica, pre-treated with a TESPT (bis-triethoxysilylpropyl-tetrasulphide) coupling agent. Three compounds are considered, differing in the content of TESPT coupling agent (3.75 phr, 6 phr and 8.25 phr).

Uniaxial tensile tests up to rupture were performed at room temperature at a strain rate of 1 min^{-1} on dumbbell specimens. Because strain-induced cavity formation causes a volume increase, the volume ratio was evaluated as

$$\frac{V}{V_0} = \lambda_1\lambda_2\lambda_3 \qquad (1)$$

where V and V_0 are the volume in the stretched and unstretched conditions, and λ_1, λ_2 λ_3 represent the stretch ratios in the loading, width and thickness direction, respectively. The stretch ratios were measured using Digital Image Correlation (DIC) analysis on both the front and lateral sides of the specimens. Cavity evolution at the microscale was also characterised through *in-situ* micro-computed tomography (micro-CT) scans performed at the SYRMEP beamline (Elettra Synchrotron, Trieste). The geometry of the specimens is shown in Figure 1. For each specimen, tomographic imaging was performed at strain intervals of 50%, up to a maximum strain of 400%.

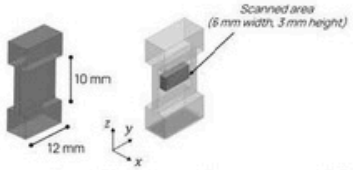


Figure 1. Geometry of the specimens used to perform micro-CT imaging.

Results and discussion

Figure 2 shows the stress-strain behaviour of the three compounds. Increasing yhe TESPT content leads to a progressively stiffer material. This stiffening effect can be attributed to the sulphur present in the TESPT coupling agent, which partially participates in the vulcanization reaction, therefore increasing the overall crosslink density of the compound.

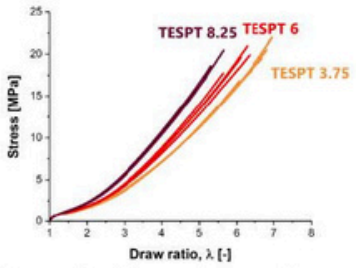


Figure 2. Stress-draw ratio curves obtained from uniaxial tensile tests.

The results from volume variation measurements are presented in Figure 3, where the volume ratio calculated using Equation 1 is plotted as a function of the draw ratio applied in the loading direction. It can be observed that a higher coupling agent content results in a greater volume increase. Additionally, despite some dispersion in the data, the TESPT content seems to affect also the value of draw ratio at which the strain-induced volume increases initiates.

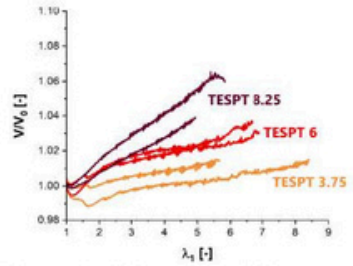


Figure 3. Volume variation as a function of the draw ratio applied in the loading direction.

Regarding the micro-CT experiments, each scan produced a set of 2048 grayscale images with a resolution of 1.6 µm/pixel. Due to the density contrast with the rubber matrix, cavities are identified as dark regions, while filler aggregates and other inclusions appear bright. Post-processing image analysis was performed with the aim of quantifying the volume and number of cavities present in the explored volumes.

The number of cavities was evaluated as a function of both their size (expressed as equivalent diameter) and of the applied strain. The smallest cavities that could be observed have an equivalent diameter of 5 µm, while the biggest cavities have an equivalent diameter of about 15 µm. As the applied strain increases, the relative fraction for small cavities decreases, while the fraction of large cavities increases. However, the absolute volumes of both small and large cavities increase with strain. This suggests that voids initially formed at low strains grow in size, but new small voids continue to form as the strain increases.

To compare the three analyzed compounds, both the total number of cavities and their total volume are plotted as a function of strain in Figure 4. The results show that both the cavity number and total cavity volume increase with higher TESPT content. These findings are consistent with the results obtained by measuring the strain-induced volume variation during uniaxial tensile tests.

Conclusions

The strain-induced cavity formation in silica-filled SBR compounds was investigated across varying contents of coupling agent (TESPT) content. Macroscopic volume variation measurements through DIC analysis and microscopic micro-CT analyses brought consistent results between each other. Both techniques demonstrated that an increase in TESPT content increases the material's propensity to form cavities under stretching, resulting in a larger total number of cavities and greater total volume of voids.

The increase in the propensity of the material to form cavities with increasing coupling agent content is not expected, since a higher TESPT content would be expected to strengthen the rubber-filler interface and therefore decrease debonding. The observed behaviour may be linked to the increase in crosslink degree caused by the the sulphur contained in the coupling agent. To confirm this, another set of compounds is being tested: in this case, not only the TESPT content is varied, but also the sulphur content, in order to compensate for the sulphur contained in the coupling agent and maintain a constant crosslink density.

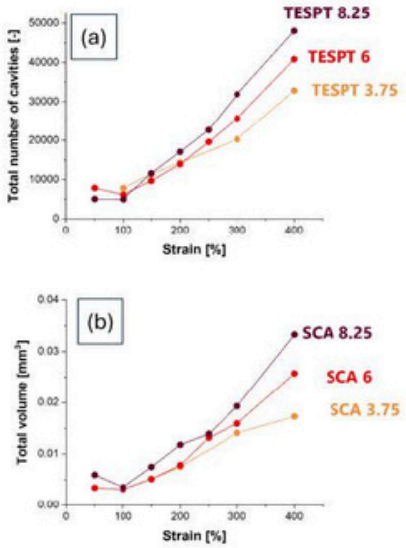


Figure 4. . (a) Total number of cavities as a function of the applied strain; (b) total volume of cavities as a function of the applied strain.

References

1. H. Zhang *et al.*, *Macromolecules.* **45**, 1529–1543 (2012).
2. J. De Crevoisier *et al.*, *Polym. Test.* **31**, 663–670 (2012).
3. A. N. Gent, B. Park, *J. Mater. Sci.* **19**, 1947–1956 (1984).

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SYNTHESIS AND NANOSTRUCTURATION OF DPP-BASED FLUORESCENT POLYESTERS FOR BIOIMAGING

Simone Gabellini, Stefano Scurti

Dept. of Industrial Chemistry "Toso Montanari", University of Bologna, Via P. Gobetti 85, 40129, Bologna, Italy
e-mail: simone.gabellini3@unibo.it

Introduction

Diketopyrrolopyrroles (DPP) emerged over the years as a highly efficient fluorophore for different applications such as sensing, semiconductors and optoelectronics, mainly as a monomer to obtain highly conjugated polymers.
These polymers, although showing high performances, exhibit poor processability and require expensive and complex to upscale polymerizations, such as aryl-aryl coupling polymerization mediated by specific catalysts.[1]
Alternative non-conjugated have received considerably less attention than conjugated DPP polymers, allowing for room of research. In this context, we synthesized polyesters with covalently integrated DPPs, optimizing the polymeric chain to avoid the fluorescence quenching typical of these fluorophores, known as aggregation caused quenching (ACQ), which is caused by π interactions between different fluorophores, inducing non radiative decay pathways.[2]
As proof of concept for the possible applications of these polymers, we nanostructured them to obtain nanoparticles tested as staining dyes for bioimaging.

Results and discussion

For this work we used a para bromine substituted DPP, chosen for its high quantum yields and reaction yields; the presence of an aryl halide also allows for possible orthogonal polymerizations for future projects.[3]
Since this work focuses on easily processable polyester, we functionalized the two amide groups performing an N-alkylation using 6-Br-1-exhanol. This introduced two hydroxyl moieties, making the DPP a co-monomer for polycondensation reactions.
As previously mentioned, DPPs require spacers to avoid ACQ effects, so we decided to integrate in as defects in the polymerization of poly(butilenadipate) PBA, testing different fluorophore amount (from 0,5 up to 5% mol/mol of DPP concentration) and molecular weights to observe their effects on the photo-physical properties of the polymer.
This showed that both parameters influenced the quantum yields, the best being those of the highest concentration of the fluorophore (5%) (Table 1) and highest molecular weight obtained (34,4 KDa) (Table 2).
Finally, nanoparticles were prepared through nanoprecipitation to improve the stability and fluorescence of the polymers using water as the dispersion medium, which also guarantees better biocompatibility of the system. Nanoparticles were made using PBA with 5% mol/mol of DPP and the lowest (4.8 KDa) and highest (34.4 KDa) molecular weights to investigate how these parameters can influence nanoparticles preparation and stability.
The nanoparticles have been characterized through Dynamic Light Scattering (DLS) at different pH to observe their behavior in different possible biological environments. Nanoparticles obtained from the low molecular weight polymer exhibited on average lower diameters and a higher stability over 20 days in pH ranging from 4 to 12 (Figure 1), compared to those obtained from the high molecular weight polymer.
Epifluorescence microscopy tests on rat's brain tissues (Figure 2) have been done using the nanoparticles to assess their possible application as staining dyes, showing a particular affinity of the NPs obtained from the low molecular weight polymer for myelin coatings in mid brain tissue sections.

Conclusions

A highly fluorescent polyester (φ=73%) has been obtained using poly(butilenadipate) PBA with covalently integrated DPP. Different concentrations of the fluorophore and molecular weights have been tested showing their effects on the fluorescence of the polymer.
In particular, the best result for quantum yields on the bulk polymer (73%) were obtained using the highest tested concentration of DPP (5%) and the highest molecular weight (34,4 KDa).
The nanoparticles exhibited the best quantum yields in the samples obtained from the low molecular weight polymer (φ=0,32).

Furthermore, epifluorescence microscopy tests showed affinity of the NPs for myelin coatings in a rat's mid brain tissue section, making these nanoparticles suitable as staining dyes for targeted observation.

References

(1) Tieke, B. et Al., Beilstein J. Org. Chem., 6 (2010)
(2) Bao, W. W. et Al., Front. Chem., 8 (2020)
(3) Grzybowski, M. et Al., Adv. Opt. Mater., 3 (2015)

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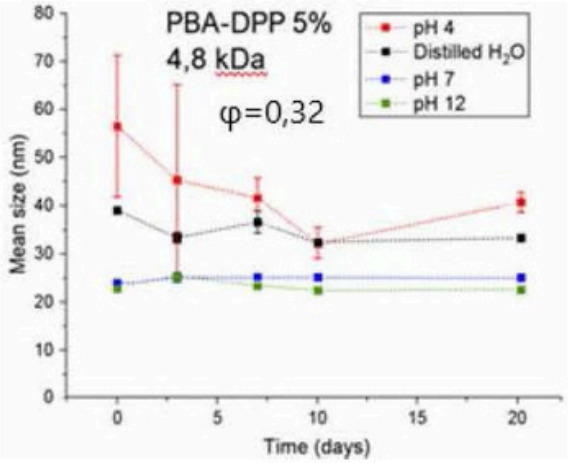


Figure 1: DLS characterization of NPs obtained from low molecular weight polymer

Table 1: Effect of DPP concentrations on polymer's quantum yields

Sample	$[DPP]_{th\ (\%)}$	Stokes shift (cm^{-1})	Quantum yield (%)
PBA-DPP_1	1	962	0.58
PBA-DPP_2	2	1032	0.68
PBA-DPP_5	5	1216	0.73

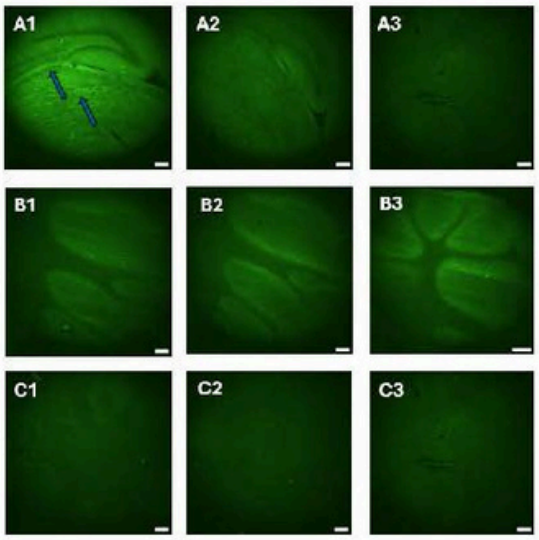


Figure 2: Epifluorescence microscopy on rat's brain tissues stained with the fluorescent nanoparticles

Table 2: Effect of DPP concentrations on polymer's quantum yields

Time (h)	(kDa) M_n	PI	Quantum yield (%)
0.5	4.8	1.8	0.67
1	4.9	1.8	0.67
3	6.1	1.8	0.62
7	11.9	1.8	0.56
12	34.4	1.9	0.73

SILICA-BASED NANOSTRUCTURED MIXED OXIDES VIA SOL-GEL FOR THE ENHANCEMENT OF FIRE RESISTANCE AND RECYCLABILITY OF EPOXY RESINS

C. Imparato [1], A. Bifulco [1], G. Malucelli [2], S. Gaan [3], A. Aronne [1]

[1] Dept. of Chemical, Materials and Production Engineering, Università degli Studi di Napoli Federico II, Piazzale Tecchio 80, 80125 Naples, Italy
[2] Dept. of Applied Science and Technology, Politecnico di Torino, Viale Teresa Michel 5, 15121 Alessandria, Italy
[3] Empa Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Advanced Fibers, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland
e-mail: claudio.imparato@unina.it

Introduction

Epoxy resins are a primary choice in several industrial applications, including the fabrication of secondary structures and protective coatings in interiors and transport means, owing to their chemical and thermal stability. On the other hand, the high flammability and difficult recycling are major drawbacks of epoxy resins that need to be addressed. Appropriately designed additives are required to reduce the flammability and improve the fire behaviour of epoxy-based materials avoiding the use of toxic flame retardants (e.g., halogenated compounds) or high loadings of phosphorus [1]. The design of covalent adaptable networks (CANs), such as vitrimers, containing exchangeable bonds and usually a catalyst, enables reshaping and reprocessing of the polymer at the end-of-life. Metal-based acid additives (e.g. Zn(II) complexes) can catalyze dynamic bond exchange by transesterification in epoxy-based CANs. Silica and metal oxides are generally cheap and safe additives that can positively affect the thermal and fire properties of epoxy resins, while providing them with additional functions, including reprocessability [1].

In this context, sol-gel methodology offers two approaches for the synthesis of nanostructured multicomponent oxide-based additives with tailored composition and morphology, namely: i) *ex-situ* preparation of micro- or nanoparticles to be incorporated into the polymer; ii) *in-situ* growth of nanoscale structures within the matrix [2].

Here, examples of both routes to synthesize mixed oxide nanofillers based on silicon, phosphorus and niobium are presented.

Results and discussion

The first study concerns the use of pre-synthesized binary and ternary oxide particles as functional fillers in epoxy-based vitrimers. Mixed oxides containing phosphorus and/or niobium have surface acidic properties that make them useful for acid-catalyzed biomass conversion reactions. Binary (Si-P, Si-Nb) and ternary (Si-Nb-P) oxides were synthesized by a simple and green sol-gel process, using tetraethoxysilane (TEOS), phosphoric acid, and ammonium niobium oxalate as precursors, and water as the only solvent. Homogeneous products with P/Nb units cross-condensed in the silicate network were obtained, showing different strength and distribution of Brønsted and Lewis acid sites [3].

These particles were added to an epoxy resin (bisphenol A diglycidyl ether, DGEBA) cured with citric acid, alone or mixed with a phosphine oxide derivative (DPPOIPA), to investigate the effect of the acidic oxide particles on fire performances and reprocessability (see Figure 1) [4]. The epoxy polyester composites containing DPPOIPA exhibited good thermomechanical reprocessing, confirmed by the characterization of recycled samples, thus proving the ability of the solid acid catalysts to promote dynamic bond exchange through transesterification. The reprocessing was less effective without the phosphine oxide and unsucessful in the absence of any catalyst [4].

Figure 1. Schematic preparation of epoxy polyester vitrimers containing gel-derived mixed oxide particles, showing thermomechanical reprocessability and flame retardancy.

At the same time, the mixed oxides supported flame retardancy and smoke suppression, allowing a self-extinguishing behaviour (V-0 rating at the UL 94 vertical burning test), along with remarkable reduction in peak of heat release rate and total smoke release (both up to about 60%), as revealed by cone calorimetry tests. These results, achieved with 10 wt% oxide particles and only 2 wt% P in the matrix, can be ascribed to a combination of gas phase and condensed phase effects, with a central role played by the porous silica-based particles [4].

The second study shows an in-situ sol-gel method to generate Si-P oxide nanostructures into an epoxy resin. A hydrolytic sol-gel procedure was developed on the basis of previous research on the growth of nanosized silica in the epoxy matrix [5], starting from reactive precursors (3-aminopropyl triethoxysilane, TEOS, and phosphoric acid), as illustrated in Figure 2 [6].

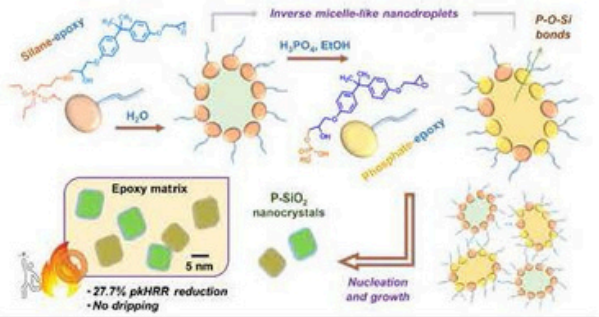


Figure 2. Representation of the formation mechanism of P-SiO_2 nanocrystals in an epoxy matrix by sol-gel.

The hybrid nanocomposites were characterized by solid state nuclear magnetic resonance spectroscopy and transmission electron microscopy, which revealed a peculiar morphology, with P-modified silica lamellar nanocrystals dispersed in the network, interconnected with the polymer chains through chemical bonds. The thermal and fire behaviour was studied through thermogravimetric and dynamic-mechanical analysis, cone calorimetry and pyrolysis combustion flow calorimetry. Besides an overall improvement in thermal stability, the results indicated promising flame retardant features, even with small amounts of Si (1-2 wt%) and P (1 wt%). The Si-O-P structures promoted the production of an abundant coherent char, allowed for a marked reduction in the peak of heat release rate (up to 28%) and prevented dripping during vertical burning tests. Moreover, the modification of the polymer matrix did not cause significant adverse effects on its thermomechanical properties [6].

Conclusions

Mixed oxides produced by sol-gel can act as multifunctional additives for thermosets such as epoxy resin. Particularly, Si-P, Si-Nb and Si-Nb-P oxides reveal the potential of acid solids in the development of fire-safe covalent adaptable networks, owing to their porous structure and tunable ratio and strength of acid sites. Also, the incorporation of P-modified silica-based nanostructures grown into an epoxy matrix allows a uniform dispersion of small nanocrystals, leading to a positive impact on thermal and fire properties with low additive loadings. The *in-situ* sol-gel approach appears promising for nanocomposites showing different functional properties, combined with safety and sustainability.

References

[1] W.W. Klingler, A. Bifulco, C. Polisi, Z. Huang, S. Gaan, *Composites Part B: Engineering*, 258, 110667 (2023)

[2] A. Bifulco, C. Imparato, A. Aronne, G. Malucelli, *Journal of Sol-Gel Science and Technology*, 115(1), 226-250 (2025)

[3] G. Garbarino, G. Pampararo, E. Finocchio, G. Busca, A. Gervasini, S. Campisi, B. Silvestri, C. Imparato, A. Aronne, *Microporous and Mesoporous Materials*, *343*, 112190 (2022)

[4] V. Palumbo, W.W Klingler, N. Drigo, T. Markaj, A. Bifulco, C. Imparato, A. Imboden, S. Lehner, A. Arpaia, E. Finocchio, A. Aronne, S. Gaan, *Sustainable Materials and Technologies*, 45, e01477 (2025)

[5] F. Branda, A. Bifulco, D. Jehnichen, D. Parida, R. Pauer, J. Passaro, S. Gaan, D. Pospiech, M. Durante, *Langmuir*, 37(29), 8886-8893 (2021)

[6] A. Bifulco, R. Avolio, S. Lehner, M.E. Errico, N.J. Clayden, R. Pauer, S. Gaan, G. Malucelli, A. Aronne, C. Imparato, *ACS Applied Nano Materials*, 6(9), 7422-7435 (2023)

ELECTROSPUN MALTODEXTRIN-DERIVED CARBON FIBERS: A SUSTAINABLE PLATFORM FOR GOLD-BASED CATALYSTS

Luca Gianoglio[1,2], Claudio Cecone[1,2], Andrea Jouve[3], Sara Morandi[1], Maela Manzoli[4], Francesco Trotta[1], Marco Zanetti[1,2], Pierangiola Bracco[1,2]

[1] Department of Chemistry, University of Torino, Via Pietro Giuria, 7, 10125, Torino (TO), Italy
[2] SUSPLAS@UniTo, Sustainable Plastic Scientific Hub, University of Turin, Via Pietro Giuria 7, 10125 Turin, Italy
[3] GAME Lab – Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino (TO), Italy
[4] Department of Drug and Science and Technology, University of Torino, Via Pietro Giuria, 9, 10125, Torino (TO), Italy
e-mail: luca.gianoglio@unito.it

Introduction

The polymer industry is still heavily dependent on fossil resources, motivating the development of sustainable materials for electrospinning applications. Bio-based maltodextrins, obtained from starch hydrolysis (DE < 20), are attractive precursors due to their low cost, renewability, and excellent fiber-forming ability in aqueous systems. In parallel, gold nanoparticles are widely recognized as efficient heterogeneous catalysts for biomass valorization, particularly in oxidation reactions of lignin- and cellulose-derived platform molecules. Carbon-based electrospun fibers provide ideal catalytic supports owing to their high surface area, porosity, and tunable structure. In this context, this work proposes a one-step electrospinning approach to fabricate carbon fibrous supports decorated with gold nanoparticles, integrating material synthesis and catalyst formation in a sustainable process without fossil-derived solvents or precursors.

Results and discussion

Electrospinning of aqueous maltodextrin/citric acid solutions containing $HAuCl_4 \cdot 3H_2O$ produced homogeneous nonwoven mats across the entire Au loading range (0.05–5 wt.%), demonstrating that the presence of the gold precursor does not affect fiber formation under the selected conditions. Subsequent pyrolysis at 700 °C under N_2 led to submicrometric carbon fibers decorated with metallic Au nanoparticles formed in situ through reduction of Au(III). Elemental analysis (EDS) confirmed that the final Au content matched nominal values, while XRD evidenced metallic Au reflections embedded in an amorphous carbon matrix. At low Au loadings, TEM revealed partial coverage of nanoparticles by a thin carbon layer, which may limit active site accessibility. A mild air activation treatment (350 °C, 15 min) effectively improved exposure of Au nanoparticles and generated local porosity around them without altering the overall fibrous morphology.

Nitrogen physisorption measurements indicated comparable textural properties among samples, with an average specific surface area of 411 ± 86 m^2/g. Catalytic evaluation in glycerol oxidation (50 °C, 3 atm O_2) showed a strong dependence of performance on Au loading and nanoparticle size. Higher loadings (5 and 1 wt%) resulted in larger nanoparticles (28.0 ± 23.5 nm and 25.2 ± 15.9 nm) and lower activities (34 and 60 h^{-1}), whereas lower loadings produced smaller nanoparticles (8.2 ± 4.8 nm and 7.4 ± 6.0 nm) with significantly enhanced activity (939 and 1700 h^{-1}). This trend is consistent with the known structure–activity relationship for Au-catalyzed oxidation reactions, where smaller nanoparticles provide higher catalytic efficiency. Product distribution was mainly oriented toward glycolic acid, with minor formation of glyceric and formic acids.

Conclusions

This work demonstrates a sustainable and versatile one-step electrospinning strategy for the fabrication of carbon-based fibrous catalysts derived from bio-based precursors. Homogeneous maltodextrin-derived mats were successfully obtained across a wide range of Au loadings, confirming excellent spinnability of the aqueous formulations. Pyrolysis enabled the direct conversion of the electrospun structures into carbon fibers decorated with in situ-formed gold nanoparticles. The resulting materials exhibit tunable catalytic performance in glycerol oxidation, highlighting the potential of electrospinning as an effective platform for

designing sustainable catalysts for biomass valorization.

References

[1] C. Cecone, G. Hoti, M. Zanetti, F. Trotta and P. Bracco, RSC Adv., 12, 762–771 (2021)
[2] M. Stucchi, S. Capelli, S. Cardaci, S. Cattaneo, A. Jouve, A. Beck, G. Sáfrán, C. Evangelisti, A. Villa and L. Prati, Catalysts, 10, 30332 (2020)
[3] F. Rodríguez-Reinoso, The role of carbon materials in heterogeneous catalysis, Plenary Lecture, Vol. 36 (1998)

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MULTIFUNCTIONAL AND SUSTAINABLE VITRIMER SYSTEMS

L. Gamberini[1], M. L. Focarete[1], L. Iannucci[2], C. Gotti[3], M. Bartoli[4], F. Rizzi[5,6], A. Zucchelli[3,7], M. L. Curri[5,6,8], S. Grassini[2], G. Malucelli[9], A. Liguori[1]

[1] Department of Chemistry "Giacomo Ciamician" and INSTM UdR of Bologna, University of Bologna, via P. Gobetti 85, Bologna, 40129, Italy.
[2] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, Turin, 10129, Italy.
[3] Advanced Mechanics and Materials, Interdepartmental Center for Industrial Research (CIRI-MAM), University of Bologna, Viale Risorgimento 2, Bologna, 40136 Italy
[4] Istituto Italiano di tecnologia - Center for Sustainable Future Technologies, Via Livorno 60, 10144 Torino, Italy
[5] Institute for Chemical and Physical Processes, CNR-IPCF SS Bari, Via Orabona 4, 70126 Bari, Italy
[6] National Interuniversity Consortium of Materials Science and Technology (INSTM), Bari Research Unit, Via Orabona 4, 70126 Bari, Italy.
[7] Department of Industrial Engineering, University of Bologna, Viale del Risorgimento, Bologna, 40136, Italy.
[8] Department of Chemistry, University of Bari, Via Orabona 4, 70126 Bari, Italy.
[9] Department of Applied Science and Technology, Politecnico di Torino, Viale Teresa Michel 5, Alessandria, 15121, Italy.

e-mail: anna.liguori@unibo.it

Introduction

Organic thermoset coatings are widely used as protective layers due to their excellent chemical and mechanical resistance. However, they remain vulnerable to damage such as scratches, cracks, and delamination, which reduce their service life and increase maintenance costs. To overcome these limitations, increasing attention has been devoted to intrinsic self-healing materials based on dynamic covalent bonds, which enable damage repair upon external stimuli, particularly heat. Over the past two decades, several dynamic chemistries, including Diels-Alder adducts, olefin metathesis, imine, and disulfide bonds, have been successfully applied to develop self-healing and anticorrosion coatings [1,2]. In this contribution [3], a solvent-free, bio-based photocurable resin containing dynamic imine bonds was developed to produce intrinsically self-healing vitrimeric coatings. To further improve performance, the resin was reinforced with functionalized silica nanoparticles (SiNPs), which promote homogeneous dispersion and covalent integration into the polymer network. The incorporation of 2 wt% SiNPs accelerated scratch closure, enabling healing at lower temperatures than the unfilled system. Although increasing the SiNP content slightly reduced the anticorrosion performance due to enhanced water uptake, the nanoparticles significantly improved scratch resistance through mechanical reinforcement. Finally, the vitrimeric coatings were shown to be chemically removable via dynamic imine exchange with a diamine, allowing recovery of oligomeric fragments and highlighting the potential of these materials for more sustainable protective coating technologies.

Results and discussion

The bio-based vitrimeric resin was successfully synthesized from methacrylated vanillin, a flexible diamine, and methacrylated eugenol, while silica nanoparticles were functionalized through sequential aminosilanization and Schiff-base reactions to promote covalent integration within the polymer network. TEM, FTIR, ζ-potential, and TGA analyses confirmed the successful surface modification of the nanoparticles, whereas visual inspection demonstrated a markedly improved dispersion of the functionalized SiNPs in the resin compared with pristine silica.

Free-standing networks obtained by UV curing exhibited the characteristic ester and imine signals of the vitrimeric structure. The incorporation of 2 wt% functionalized SiNPs did not significantly affect the chemical structure or thermal properties of the network, whereas increasing the filler content to 5 wt% led to incomplete curing, as demonstrated by reduced thermal stability, lower glass transition temperature, and decreased gel content. Stress relaxation experiments performed above Tg showed rapid stress dissipation for all formulations, confirming the activation of dynamic imine exchange reactions responsible for the vitrimeric behavior, with the 2 wt% composite

exhibiting the fastest relaxation. The coatings displayed homogeneous morphologies, although nanoparticle aggregation became more evident as the filler content increased.

Self-healing experiments performed on both glass and steel substrates demonstrated efficient thermally activated scratch closure for all formulations, with healing kinetics strongly dependent on temperature. The incorporation of 2 wt% functionalized SiNPs significantly accelerated scratch closure, allowing complete healing within less than 5 min at temperatures as low as 80 °C without applying external pressure. Furthermore, repeated damage–healing cycles confirmed that the self-healing capability was retained after multiple repair events, highlighting the reversible nature of the imine exchange reactions.

Besides promoting self-healing, functionalized silica nanoparticles remarkably enhanced scratch resistance. While the pristine vitrimeric coating was readily damaged during pencil hardness tests, both nanocomposite formulations effectively resisted scratching, demonstrating the reinforcing effect of the covalently integrated silica phase. Pull-off adhesion tests also revealed excellent adhesion of all coatings to steel substrates, with failure occurring within the adhesive layer rather than at the coating–substrate interface, indicating strong interfacial bonding.

Electrochemical impedance spectroscopy confirmed the excellent corrosion protection provided by the vitrimeric coatings in 3.5 wt% NaCl solution. The pristine formulation maintained impedance modulus values above 10^7 Ω cm² throughout 336 h of immersion, whereas increasing nanoparticle loading progressively reduced the barrier performance because of enhanced water uptake associated with the silica phase. Nevertheless, all coatings retained satisfactory protective properties over the entire testing period.

Finally, the dynamic nature of the imine network enabled complete chemical removal of the coatings by treatment with ethylenediamine. The vitrimeric films detached from the substrates through transimination reactions, allowing recovery of oligomeric fragments and clean substrate regeneration. This reversible debonding strategy, combined with the self-healing, scratch-resistant, and anticorrosion properties of the developed coatings, demonstrates the potential of these multifunctional bio-based vitrimers as sustainable protective materials.

Conclusions

A solvent-free, bio-based photocurable vitrimeric platform based on dynamic imine chemistry was successfully developed as a multifunctional protective coating. The resulting networks exhibited efficient thermally activated self-healing, rapid stress relaxation, and complete chemical removability through transimination, enabling substrate regeneration and material recovery. Functionalized silica nanoparticles were successfully integrated into the vitrimer network, improving nanoparticle dispersion and enhancing the overall coating performance. In particular, the incorporation of 2 wt% SiNPs accelerated scratch closure at lower temperatures and significantly improved scratch resistance without compromising adhesion to steel substrates. Although pristine coatings provided the highest long-term corrosion protection, all formulations exhibited satisfactory barrier properties in saline environments. Overall, this work demonstrates that bio-based imine vitrimers represent a promising strategy for the development of sustainable protective coatings combining self-healing, mechanical durability, corrosion resistance, and end-of-life recyclability.

References

[1] A. Liguori, S. Subramaniyan, J.G. Yao, M. Hakkarainen, Eur. Polym. J. 178 (2022) 111489.
[2] A. Liguori, K.I. Garfias Gonzalez, M. Hakkarainen, Polymer 283 (2023) 126252.
[3] A. Liguori, L. Gamberini, L. Iannucci, C. Gotti, M. Bartoli, F. Rizzi, A. Zucchelli, M. L. Curri, S. Grassini, G. Malucelli, M. L. Focarete,
Journal of Industrial and Engineering Chemistry, 2026.

FUNCTIONAL POLYMERS FOR THE OPTICAL DETECTION OF AMINES: FROM BIO-INSPIRED TO NATURAL SENSING UNITS

Angelo Nicosia[1], Lidia Mezzina[1], Laura Barone[1], Guido De Guidi[1], Placido Mineo[1]

[1] Department of Chemical Sciences and INSTM UdR of Catania, University of Catania, V.le A. Doria 6, 95125, Catania, Italy
e-mail: angelo.nicosia@unict.it

Introduction

The selective and real-time monitoring of volatile organic compounds (VOCs), particularly ammonia and aliphatic amines, represents a crucial target in environmental safety, industrial monitoring, and smart food packaging. Among various sensing technologies, optical and colorimetric chemosensors have attracted significant attention owing to their simplicity, low cost, and the possibility of easily visualizing the presence of pollutants, potentially even by the naked eye.

The development of such devices strongly relies on the immobilization of responsive chromophores into stable, processable solid matrices. Owing to their versatility, polymeric systems can be applied to diverse surfaces to produce flexible and durable optical sensors.

Traditionally, high-performance optical sensors have been developed by designing synthetic and semi-synthetic bio-inspired molecules, such as metalloporphyrins. Synthetic and semi-synthetic porphyrins excellently mimic biological pigments and possess outstanding spectroscopic properties, including high molar absorption coefficients and large spectral shifts upon interaction with polar species. However, from an industrial and environmental perspective, synthetic macrocycles present inherent drawbacks. Their fabrication requires demanding, non-green, multistep synthetic pathways, complex purification procedures, and the extensive use of toxic organic solvents. Furthermore, if used for intelligent food packaging, synthetic dyes raise severe safety concerns regarding their potential toxicity.

To overcome these safety and environmental drawbacks, the research paradigm is rapidly shifting toward the direct exploitation of natural edible pigments derived from renewable biomass. Curcumin has emerged as an ideal candidate because of its biocompatibility, low cost, and excellent sensitivity to chemical environmental variations (as an example, pH), which induces a detectable color change. However, incorporating natural dyes into polymer matrices for food packaging applications introduces a critical challenge: dye migration and leaching. In food science, the uncontrolled release of the active molecules into the food matrix is highly undesirable, despite its edibility, as it alters the organoleptic properties of the food and leads to a rapid loss of the colorimetric efficiency of the sensor. Traditional physical blending strategies fail to prevent this phenomenon. To avoid unwanted release, natural dyes must be covalently anchored to the polymer backbone in the chain or side chain.

This contribution explores our experience in the field of optical polymeric sensors, by shifting sensing moieties from bio-inspired molecules to the covalent integration of bio-sourced sensing units for the detection of volatile amines.

Results and discussion

The use of synthetic dyes allows the tailoring of the functional groups to be used for covalent linking to the selected polymeric backbone.

As a first approach, bio-inspired 5,15-(4-hydroxyphenyl)-5,20-(diphenyl)-21H,23H-porphine (P) was utilized as a sensing repetitive unit into ad-hoc synthesized copolyetherformals (PEF-P). These were prepared via an interfacial TBAB-assisted poly-condensation reaction [1]. The synthetic route resulted in a high average molecular weight copolymer (Mw = 21.1 kDa, PDI = 5.20) possessing excellent film-forming abilities. MALDI-TOF mass analysis identified the presence of linear and cyclic species containing porphyrinic units. The spectroscopic features of P were preserved even when it was incorporated into the copolymer main chain, exhibiting a few nanometers red-shifts in the absorption and emission spectra. Because of the introduction of metal cations within the P core (forming PEF-PZn and PEF-PCo derivatives), the polymeric sensor systems became sensitive to electron-donor species, such as amines. The sensing responses of both PEF-PZn and PEF-PCo in toluene solution depends on the chemical nature of the pollutant. Investigations with aromatic (pyridine) or non-aromatic (piperidine) pollutants demonstrated higher sensitivity to non-aromatic amines. Furthermore, due to cobalt electronic

configuration, PEF-PCo system showed enhanced sensitivity ($LOD_{pyridine}$ = 0.16 µM; $LOD_{piperidine}$ = 0.04 µM) to both pyridine and piperidine compared to PEF-PZn ($LOD_{pyridine}$ = 22 µM; $LOD_{piperidine}$= 0.5 µM). The optical sensing capabilities were further validated in the solid state against gaseous pollutants, showing spectral shifts and intensity enhancements of the Soret band after 1 min of exposure.

To transition toward a more sustainable and nature-driven strategy, an alternative pathway was established by directly utilizing natural dyes. Curcumin cannot be easily polymerized as a traditional monomer without altering its structure. To minimize this effect, a Cop-Curc-Zn copolymeric sensor was developed through a three-step procedure [2]: i) the copolymer backbone (Cop-Blank) was synthesized by bulk radical polymerization using AIBN as the initiator and vinyl acetate and acrylic acid as comonomers; ii) the Curcumin moiety was covalently attached side-chain to the acrylic acid repetitive units through a catalyzed esterification reaction (obtaining the system named Cop-Curc); iii) to make the copolymer responsive to amine-derivative molecules, the curcumin moiety in Cop-Curc was complexed with Zn(II).

The covalent binding of the Curcumin moiety as a side chain to Cop-Blank backbone was ascertained by GPC analysis (M_n = 12500 Da and M_w = 33700), using a dual detector (RI/UV–Vis) configuration: the overlapping of the signals from the UV-Vis detector (set at 420 nm, corresponding to the maximum absorption of Curcumin) with the dRI detectors confirmed the integration of Curcumin in the copolymer chains.

NMR spectroscopy corroborated these findings, revealing a Curcumin loading of approximately 0.46 %mol (2.22 %wt). Thermal analyses (TGA and DSC) showed minor influences of the Curcumin presence within the polymeric backbone with respect to Cop-Blank thermal properties. From a spectroscopic point of view, in THF solution, the covalent bonding of Curcumin to the acrylic acid repetitive units induced a broadening and a blue-shift of the absorption band compared to free Curcumin, showing the absorption band centered at 410 nm. Additionally, the fluorescence emission of Cop-Curc showed a red-shifted band centered at 500 nm (λ_{exc} 420 nm). The Cop-Curc-Zn absorption spectrum shows a red-shifted band with the main absorption at 424 nm and a shoulder at 444 nm. The metalation of the Curcumin moiety also altered the fluorescence properties of the system: the solution exhibited a fluorescence emission centered at 495 nm (λ_{exc} 434 nm), with a non-negligible quenching effect due to non-radiative processes, such as photoinduced electron transfer from the Curcumin moiety to the Zn(II) cation. The spectroscopic properties of the thin films of the copolymeric systems, layered onto polyethylene terephthalate (PET) substrates, were determined via DRS-UV-Vis spectroscopy. To verify the sensing capability of the copolymers, different chemical species were evaluated by exposing thin films to non-polar (toluene) and polar and electron donor solvents (acetone, ethanol, NH_3, Pyridine, and ethylene diamine). The metal complex in Cop-Curc-Zn, interacting with various electron donor species, exhibited specific red-shifts whose magnitude increased in the order: ethanol < NH_3 < pyridine < ethylenediamine. This pattern can be interpreted by considering both the pKb and vapor pressures of the detected substances.

Conclusions

The experimental results demonstrate success in the design of polymer-based optical sensors for volatile amines, shifting from bio-inspired macrocycles to natural pigment sensors. Both strategies, the main-chain integration of synthetic metalloporphyrins (PEF-PZn and PEF-PCo) and the side-chain covalent functionalization with natural curcumin onto a pre-formed copolymer (Cop-Curc-Zn), proved to be highly effective.

Formulated as thin films on plastic substrates, both polymeric systems displayed distinct spectroscopic variations driven by the coordination chemistry between the electron-donor amine and metallated sensors. This macromolecular flexible approach, in which the sensing unit can be easily substituted, opens up promising and safe avenues for the development of sustainable environmental monitoring tools and the design of intelligent food packaging materials.

References

[1] L. Mezzina, A. Nicosia, P. Mineo, *Dyes and pigments*, vol. 240, 112867 (2025)

[2] A. Nicosia, L. Mezzina, P. Mineo, *Progress in Organic Coatings*, vol. 211, 109823 (2026)

Acknowledgments

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INTERCALATED SODIUM BENTONITE IN THERMOPLASTICIZED CORN STARCH: TUNING OXYGEN BARRIER AND MECHANICAL PERFORMANCE FOR FLEXIBLE FOOD PACKAGING APPLICATIONS

M. Righetti[1,3], V. Brunella[1,2,3], M. Zanetti [1,2,3]

[1] Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125 Turin, Italy
[2] Instm Reference Centre, University of Turin, Via G. Quarello 15A, 10135 Turin, Italy
[3] SUSPLAS@UniTo, Sustainable Plastic Scientific Hub, University of Turin, Via Pietro Giuria 7, 10125 Turin, Italy
e-mail: matteo.righetti@unito.it

Introduction

During the last two decades, interest in polymers derived from renewable feedstocks has steadily grown, driven largely by environmental concerns and the awareness that petroleum reserves are finite. The widespread use of plastics, particularly packaging materials, single-use cups and bags, has contributed substantially to environmental pollution in recent years. Replacing non-biodegradable polymers with biodegradable alternatives represents one practical strategy for addressing the pollution generated by plastic waste [1]. Since the late 1980s, starch has increasingly been regarded as a viable packaging material, although its suitability has also faced scrutiny. Its low cost, broad availability, high purity, non-toxicity and inherent biodegradability/environmental compatibility have drawn considerable interest from the packaging sector, which nevertheless remains largely dependent on conventional, non-biodegradable synthetic plastics [2]. Thermoplastic starch (TPS) is obtained by disrupting the granular structure of native starch through plasticizing agents such as water, glycerol and sorbitol. Native starch is abundant in nature and benefits from inexpensive raw material sources, including agro-industrial by-products. However, TPS exhibits poor mechanical strength and barrier performance, which limits its direct use as a packaging material without modification. It is therefore necessary to blend TPS with other polymers or incorporate additives into the matrix in order to enhance the performance of the resulting packaging material [3].

The aim of this research project is to obtain new biobased and sustainable packaging solutions through a bio-nanocomposites material approach, by developing and characterizing thermoplasticized corn starch (TPCS) based bio-nanocomposite films incorporating Sodium Bentonite (BNa) as a lamellar inorganic filler at loadings ranging from 0.5 to 5 wt% for the enhancement of mechanical and barrier performances.

Results and discussion

Morphological characterization by XRD and field emission scanning electron microscopy (FESEM) coupled with energy-dispersive X-ray spectroscopy (EDX) revealed a predominantly intercalated clay morphology, with basal spacing (d_{001}) increasing from 1.248 nm in pristine BNa to values up to 1.712 nm in the composite films. At higher filler loadings (> 3 wt%), progressive aggregation and tactoids formation were observed, but oxygen barrier performance (*Figure 1*) was markedly enhanced upon Sodium Bentonite incorporation, with the lowest oxygen permeability recorded for TPCS05BNa (6.97×10^{-12} $cm^3 \cdot cm \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$), representing a reduction of approximately 35-fold relative to neat TPCS (2.43×10^{-10} $cm^3 \cdot cm \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$). These values are competitive with high-performance barrier materials such as EVOH under dry conditions, demonstrating exceptional oxygen protection potential for food packaging applications.

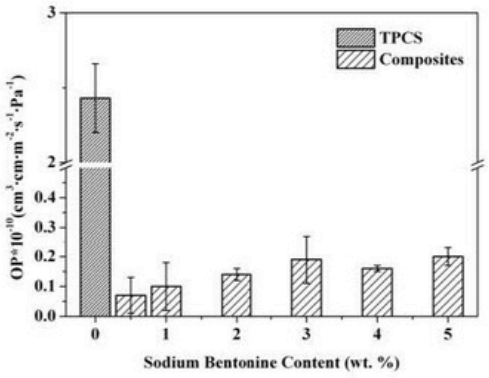


Figure 1. Oxygen Permeability (OP) of TPCS and composites polymeric films for different Sodium Bentonite contents.

The tortuous pathway introduced by the lamellar filler was identified as the primary mechanism governing this improvement, although the non-monotonic trend at higher loadings reflects the detrimental effect of filler aggregation on diffusion pathway efficiency.

Mechanical characterization revealed a pronounced reinforcement effect upon Sodium Bentonite addition. Young's Modulus and Ultimate Tensile Strength increased from 9.33 ± 2.04 MPa and 3.32 ± 0.35 MPa in neat TPCS to maximum values of 125.18 ± 38.3 MPa and 7.80 ± 1.13 MPa, respectively, at 4 wt% filler content (TPCS4BNa). This enhancement was accompanied by a systematic reduction in Elongation at Break, from 174.32 ± 15.38% to 85.22 ± 12.94%, reflecting the characteristic stiffness–ductility trade-off of filled polymer systems. Above 4 wt%, filler aggregation induced a slight deterioration of mechanical properties. Water vapor permeability remained high across all formulations, attributed to the intrinsic hydrophilicity of the starch–glycerol matrix.

Conclusions and Future Perspectives

This study demonstrates that starch-based bio nanocomposites incorporating lamellar clay fillers represent a promising and sustainable alternative to conventional petroleum-based polymers for oxygen barrier applications. However, the intrinsic hydrophilicity of the matrix remains a key limitation for moisture barrier performance. Future work should therefore focus on improving filler dispersion and exploring strategies to reduce water solubility and water vapor transmission rate such as matrix modification, incorporation of hydrophobic components or lamination of these with the TPCS based nacomposites in order to further enhance the applicability of these materials in real packaging systems.

References

[1] F.A. Aouada, L.H.C. Mattoso, E. Longo, *Industrial Crops and Products*, **34** (2011) 1502-1508

[2] B. Ayana, S. Supratim, B.B. Khatua, *Carbohydrate Polymers*, **110** (2014) 430-439

[3] K. Velasco, C.A. Utreras-Silva, A. Diaz-Barrios, A.E. Sommer-Marquez, J.P. Taruf, R.M. Michell, *Polymers* **13** (2021)

STUDY OF THE HIGH-PRESSURE H_2 EXPOSURE EFFECT ON THE MECHANICAL BEHAVIOUR OF NBR BASED COMPOUNDS

F. Passoni [1], C. Marano[1]

[1] Dipartimento Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy
e-mail: federico.passoni@polimi.it

Introduction

Hydrogen is increasingly regarded as a key energy carrier for decarbonisation, making the durability of polymeric components in high-pressure hydrogen environments a critical issue [1]. Elastomers used as seals and gaskets are particularly relevant, since H_2 can rapidly diffuse into rubber compounds, leading to sorption, swelling and plasticisation, with possible effects on mechanical response and strain recovery capability [2]. While some of these changes may be reversible after decompression, persistent modifications can also arise from irreversible microstructural changes, including chain scission, crosslink loss and altered polymer-filler interactions [3], [4].

This study investigates three formulations based on an acrylonitrile-butadiene rubber (NBR, 28% AN) filled with carbon black (CB) N330 and silica ULTRASIL VN3. The compounds differ in fillers content as well as in the content of polyvinylchloride (PVC) in the matrix (*Table 1*). The materials were supplied by Eni Versalis S.p.A.

Table 1 material compositions (quantities expressed in phr, i.e. parts by weight per hundred parts of the polymer blend (rubber + PVC))

		A	B	C
Matrix	***NBR***	100	100	80
	PVC	0	0	20
Filler	***CB***	30	40	30
	Silica	15	20	15

Using a custom-made high-pressure chamber developed at Politecnico di Milano, specimens for mechanical testing were exposed for 7 days to pure gaseous H_2 at (i) 100 bar and ambient temperature or (ii) 230 bar and 70°C. A 7-day exposure to N_2 at 300 bar and 70 °C was also performed to highlight the temperature effect, taking advantage of the lower diffusivity of N_2 through rubber compared with H_2 due to its bigger kinetic diameter (0.289 nm versus 0.364). After exposure, the specimens were stored in air at atmospheric pressure and ambient temperature for a monitored period of 48 h – 72 h before testing. Tensile tests in uniaxial loading conditions and fracture tests in pure shear deformation conditions were carried out at room temperature and at a nominal strain rate of 1 min^{-1} for tensile tests and 2.5 min^{-1} for fracture tests.

Results and discussion

Figure 1 reports the results of the tensile tests in terms of stress at break and strain at break. H_2 exposure at 100 bar and room temperature for 7 days shows a limited effect on the investigated NBR compounds. Based on the limited experimental campaign, no definitive conclusions can yet be drawn regarding the effect of high-pressure gas exposure on stress and strain at break. However, it seems that (i) for all the studied materials, exposure to high pressure at 70°C reduces both the stress and strain at break, regardless of the type of gas, and (ii) lower-pressure exposure at room temperature appears to affect the materials' behaviour differently.

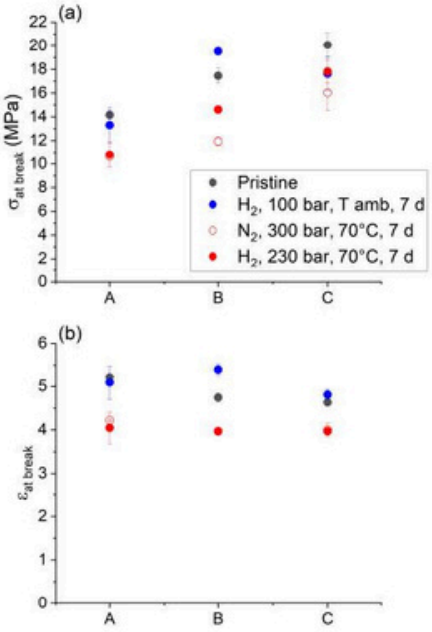


Figure 1 (a) Stress and (b) strain at break of the NBR based formulations in pristine conditions and after being exposed to high-pressure gases.

Fracture tests were carried out adopting a fracture mechanic's approach. Notched pure-shear specimens were used, and the fracture toughness was evaluated as the value of the energy-based parameter *J-Integral* at fracture onset, according to [5]:

$$J_c = \eta \frac{U_c}{B(W-a)}$$

where U_c is the input energy at crack onset, B is the specimen thickness, W-a is the ligament length, and η is a geometry-dependent factor equal to 1 for this geometry. In *Figure 2* the fractures toughness values are reported for the studied compounds, for the different exposure conditions.

After H_2 exposure at 100 bar and room temperature, for materials B and C the fracture toughness shows limited variations, compared with the pristine materials, while for material A the fracture toughness seems to significantly decrease.

On the other hand, when the H_2 exposure was at 230 bar and 70 °C, a more significant reduction in fracture toughness was obtained for all the three materials. A comparable decrease is observed when the exposure was performed in N_2, at 300 bar and 70 °C. This result is consistent with tensile tests results: severe pressure–temperature exposure conditions reduce materials' resistance, irrespective of the gas nature.

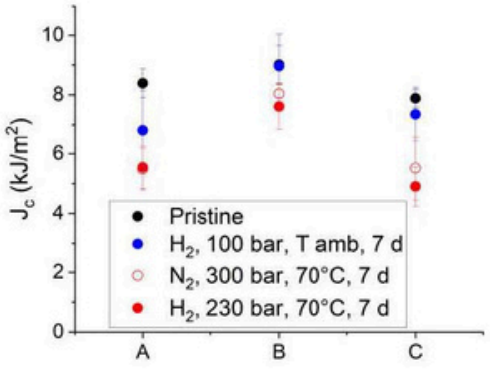


Figure 2 J_C at fracture onset for the three NBR-based compounds in pristine conditions and after exposure to pressurised gas, at different pressure and temperature conditions.

Conclusions

H_2 exposure at 100 bar and room temperature for 7 days produced not consistent changes in the tensile and fracture behaviour of the investigated NBR formulations. Conversely, the exposures performed at higher pressure and temperature caused premature tensile failure and a reduction in fracture toughness. With respect to tensile behaviour, the strain at break decreased by approximately 20% for compound A, 16% for compound B, and 14% for compound C compared with the pristine condition. Concerning fracture toughness, a relative decreases of approximately 34% for compound A, 15% for compound B, and 34% for compound C was observed.

The similar trends observed after H_2 and N_2 exposure under severe conditions suggest that pressure-temperature history plays a major role in the physical ageing of these compounds, rather than a purely gas-specific effect.

Acknowledgements

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References

[1] W. Balasooriya, C. Clute, B. Schrittesser, and G. Pinter, "A Review on Applicability, Limitations, and Improvements of Polymeric Materials in High-Pressure H_2 Gas Atmospheres," 2022, Taylor and Francis Ltd. doi: 10.1080/15583724.2021.1897997.

[2] C. Zhou, X. Liu, Y. Zheng, and Z. Hua, "A comprehensive review of H_2-induced swelling in rubber composites," Apr. 15, 2024, Elsevier Ltd. doi: 10.1016/j.compositesb.2024.111342.

[3] G. Theiler, N. Cano Murillo, K. Halder, W. Balasooriya, A. Hausberger, and A. Kaiser, "Effect of high-pressure H_2 environment on the physical and mechanical properties of elastomers," Int. J. H_2 Energy, vol. 58, pp. 389–399, Mar. 2024, doi: 10.1016/J.IJHYDENE.2024.01.148.

[4] M. Zaghdoudi, A. Kömmling, M. Böhning, and M. Jaunich, "Ageing of elastomers in air and in H_2 environment: A comparative study," Int. J. H_2 Energy, vol. 63, pp. 207–216, Apr. 2024, doi: 10.1016/j.ijhydene.2024.03.053.

[5] B. H. Kim and C. R. Job, "Single specimen test method for determining fracture energy (j,) of highly deformable materials," 1989.

DEVELOPMENT AND CHARACTERIZATION OF SANDWICH COMPOSITES WITH THERMAL MANAGEMENT AND MECHANICAL PROPERTIES

L. Simonini [1,2], S. Santagiuliana [1], A. Tomasini [1], G. Fredi [1,2], A. Pegoretti [1,2]

[1] Department of Industrial Engineering, University of Trento, Trento, Italy
[2] National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy

e-mail: laura.simonini@unitn.it

Introduction

The increasing demand for lightweight structures with integrated thermal management capabilities has driven the development of multifunctional composite materials. In advanced engineering sectors such as aerospace, automotive, and refrigerated transport, components must simultaneously ensure structural reliability, weight efficiency and temperature regulation. Phase change materials (PCMs) offer high latent heat storage capacity, enabling efficient absorption and release of thermal energy within specific temperature ranges. This work aims to develop and evaluate multifunctional sandwich composites combining thermal energy storage capability with high mechanical efficiency.

Results and discussion

Multifunctional sandwich panels were fabricated using an epoxy (EP) foam core embedded with 10 to 30 %wt of microencapsulated PCMs. The microencapsulation technique ensured uniform PCM dispersion within the foam matrix and prevented leakage during phase transitions. The thermally functionalized foam cores were combined with external skins made of epoxy/carbon fibre laminates to produce lightweight sandwich structures. Microstructural characterization was performed to assess PCM distribution and interfacial bonding between the core and the laminate skins. Mechanical performance was evaluated through flexural and compressive testing.

Microstructural analysis confirmed a homogeneous distribution of microencapsulated PCMs within the EP foam and good interfacial adhesion between the foam core and the carbon fibre-reinforced epoxy skins. Mechanical testing demonstrated that the developed sandwich composites exhibited good flexural and compressive properties. Thermal characterization revealed enhanced energy storage capacity, with the PCM-filled foams showing a distinct phase transition enthalpy and effective heat absorption and release within the targeted temperature range, as shown in Figure 1.

Conclusions

The results demonstrate a successful synergy between mechanical strength and thermal functionality in the developed composites. The integration of 20%wt of microencapsulated PCMs within EP foam cores enabled satisfactory latent heat storage without significantly sacrificing the structural performance. The strong core/skin interfacial bonding ensured mechanical reliability under loading conditions, while the carbon fibre skins provided high stiffness and favourable strength-to-weight ratios.

References

[1] L. Simonini, S. Santagiuliana, A. Tomasini, G. Fredi and A. Pegoretti, A. *Polymer Composites*, vol. 47, 460-473 (2026).

Acknowledgments

Air Force Office of Scientific Research (AFOSR) project "Multifunctional polymer composites for thermal energy storage: current trends and future perspectives", Grant Number: FA8655-23-1-7039

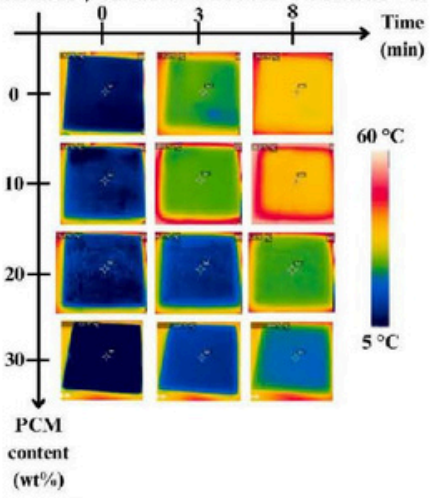


Figure 1. Thermography frames at different testing time (after 0, 3, 8 min) as a function of PCM concentration during heating.

ECO-FRIENDLY DYE–PORPHYRIN COPOLYMER FOR ORGANIC SOLAR CELLS: FROM TERNARY DONOR TO INTERFACIAL LAYER

M. MARINELLI,[1] R. MEDRI,[1] E. SALATELLI,[1] M. LANZI [1]

[1]*Dpt. Of Industrial Chemistry "Toso Montanari", University of Bologna, via Gobetti 85, 40129, Bologna, Italy.*

Email: massimiliano.lanzi@unibo.it

Introduction

Solar energy and the development of new photovoltaic technologies (PVs) are valid eco-friendly solutions to prevent today's energy shortage and environmental pollution results. In particular, organic solar cells (OSCs) are among the best promising devices for clean energy production. A typical OSC is commonly made by a bi-continuous and interpenetrating electron donor (ED, i.e., π-conjugated polymer) and electron acceptor (EA, i.e., fullerene derivative) composite blend, which acts as a photoactive layer and is placed between an anode (i.e., Indium Tin Oxide [ITO]) and a cathode (i.e., Al). Up to now, the photoconversion efficiency (PCE) of OSCs has exceeded 20%. Indeed, since efficiency is still the primary factor, much effort has been made to boost the photovoltaic performances of those bulk-heterojunction (BHJ) OSCs, acting both on the design of new high-performance active materials, morphology optimization, and device engineering [1].

The synthesis and use of a dye sensitizer (i.e., porphyrin and/or metal-porphyrin derivatives) is a well-known and valid strategy, since they are large planar π-aromatic systems, thermally and photochemically stable photoactive components, and typically have broad absorption regions owing to their Soret and Q bands. Moreover, such derivatives can be both blended with ED/EA materials or directly anchored to the π-conjugated polymeric backbone [2]. In order to enhance their light-harvesting properties in the visible and NIR regions, these derivatives could be paired with a solution-processable 3,4-dialkoxythiophene based polymers as second ED photoactive components. Therefore, the new concept of co-sensitization and development of ternary OSCs, obtained by using three photoactive materials with complementary absorption profiles, is of great interest [3]. The introduction of a third component typically broadens the light harvesting capability and enhances the charge transfer and/or transport properties, thus improving the final device performance.

Anode/cathode interfacial materials (AIM/CIMs) or holes/electron transport layers (HTL/ETLs) are usually conjugated polyelectrolytes with polar and/or ionic side chains, which are placed between the active layer and the metal electrode. In addition to solving the rising quest for green solvents to be soluble and processable from alcohols and/or water, this class of materials can reduce the work function of the electrode metal and produce a favorable energy level alignment for an effective and better charge extraction. Besides, oxidation phenomena are prevented and as a result, the long-term stability of the device is improved [4].

Results and discussion

This work focuses on the synthesis and application of two novel conjugated thiophene-based polymers integrated with ionic phosphonium salts, providing enhanced solubility in water/alcohol mixtures. The first material - poly{3-(6-tributylphosphoniumhexyl)thiophene-co-3-[5-(4-phenoxy)-10,15,20-triphenylporphyrinyl]hexylthiophene bromide} (**P1buP**, ED_1) - is a copolymer composed of ionic units and tetraphenylporphyrin dye-functionalized segments, while the second - poly[3,4-(6,6'-tributylphosphoniumhexyloxy)thiophene] bromide (**P2buP**, ED_2) - is a disubstituted homopolymer incorporating ionic groups at the end of hexamethylenic side chains, linked to the main polythiophene backbone via ether bridges (*Fig. 1 and 2*). All the synthesized materials were fully characterized by nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR and ^{31}P NMR), infrared (FT-IR) and ultraviolet-visible/photoluminescence (UV–Vis and PL) spectroscopy, as well as thermal analysis (TGA and DSC), cyclic voltammetry (CV), atomic force microscopy (AFM), and external quantum efficiency (EQE). The ionic polymers were then tested as photoactive ED materials in halogen-free (i.e., ethanol) ternary BHJ OSCs, in the presence of an alcohol-soluble serinol-fullerene (**C_{60}-Ser**) derivative as an EA counterpart, the ratio between the three photoactive materials was optimized in order to obtain better performances (*Table 1*). Moreover, to investigate a possible role in the process of device engineering, the alcohol-soluble TPP functionalized copolymer was also tested as cathode interfacial layer in a bicomponent BHJ

OSC made of **P2buP**:**C_{60}-Ser** as active layer (*Table 1*). Finally, to improve and optimize the best performing device, the ionic TPP substituted copolymer was subsequently metalated with Zn and tested in a ternary BHJ OSCs (**P1buP-Zn**:**P2buP**:**C_{60}-Ser** = 0.33:0.67:1 w/w), achieving even higher PCE value (~ 6.0%) but still maintaining an environmentally friendly approach (*Table 2*).

Conclusions

Efficient and completely halogen-free BHJ organic solar cells were fabricated using two polythiophenes functionalized with phosphonium salts at the end of their side chains, giving enhanced solubility in water-alcohol mixtures to the final materials (*Fig. 1*). The two polymers were fully characterized and tested as photoactive donor materials in combination with an alcohol-soluble fullerene derivative (EA) to prepare ternary solar cells (*Table 1*). Results indicate that the ternary cells are effective in complementing absorption spectra, optimizing the electronic energy level gradient, and homogenizing the external surface of the device. Furthermore, when porphyrin is complexed with Zn and the OSCs are tested, the PCE values increases of ~ 20% compared to the cells with not-metalated polymers (*Table 2*). This result is achieved without affecting the solubility and film ability of the active blend. Moreover, to investigate a possible device engineering process, the ionic TPP material was also investigated and tested as an alcohol-soluble cathode interlayer with promising results (*Table 1*).

References

[1] S. Rasool, J. Yeop, *Mater. Fut.*, vol. 2, article 032102 (2023).
[2] A. Soultati, M. Verouti, *Nanomaterials*, vol. 13, pag. 2800 (2023).
[3] L. Chang, M. Sheng, *Org. Electron.*, vol. 90, Article 106063 (2021).

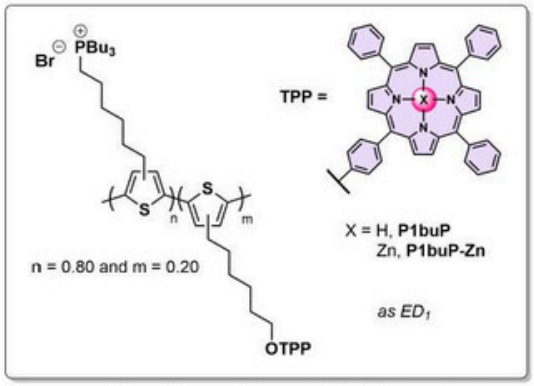


Figure 1: Overview of the dye–porphyrin copolymer.

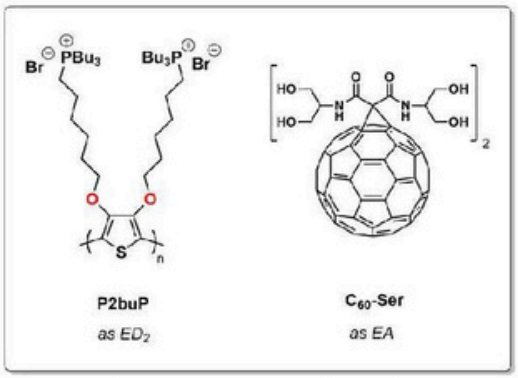


Figure 2: Overview of the other synthesized materials.

Table 1: Properties of BHJ OSCs prepared with alcohol-soluble materials ***P1buP*** *(*ED_1*),* ***P2buP*** *(*ED_2*), and* ***C_{60}-Ser*** *(EA) (average values collected from 5 devices).*

ED_1:ED_2:EA ratio	***J_{sc} ($mA \cdot cm^{-2}$)*** [c]	***V_{oc} (V)*** [d]	***PCE (%)*** [e]
1:0:1	4.4 ± 0.18	0.59 ± 0.10	1.53 ± 0.09
0.67:0.33:1	8.3 ± 0.16	0.60 ± 0.11	2.91 ± 0.12
0.5:0.5:1	11.9 ± 0.19	0.61 ± 0.10	4.45 ± 0.18
0.33:0.67:1	14.7 ± 0.20	0.61 ± 0.12	5.22 ± 0.19
0:1:1	10.9 ± 0.15	0.55 ± 0.14	3.37 ± 0.16
0:1:1 [a]	12.1 ± 0.15	0.65 ± 0.11	4.88 ± 0.15
0:1:1 [b]	13.9 ± 0.21	0.58 ± 0.12	5.03 ± 0.20

[a] With **PFN-Br** as commercial cathode interlayer; [b] With **P1buP** as cathode interlayer; [c] J_{sc} from EQE measurements; [d] Open circuit voltage; [e] Photoconversion efficiency.

Table 2: Comparison of photovoltaic performances of BHJ OSCs prepared with ***P1buP*** *and* ***P1buP-Zn*** *(average values collected from 5 devices).*

ED_1:ED_2:EA ratio	***J_{sc} ($mA \cdot cm^{-2}$)*** [a]	***V_{oc} (V)*** [b]	***PCE (%)*** [c]
1:0:1	4.4 ± 0.18	0.59 ± 0.10	1.53 ± 0.12
1*:0:1	4.8 ± 0.16	0.59 ± 0.12	1.72 ± 0.12
0.33:0.67:1	14.7 ± 0.20	0.61 ± 0.11	5.22 ± 0.21
0.33*:0.67:1	14.9 ± 0.19	0.61 ± 0.10	6.03 ± 0.19

*With **P1buP-Zn** as ED_1; [a] J_{sc} from EQE measurements; [b] Open circuit voltage; [c] Photoconversion efficiency.

FURANIZED CELLULOSE NANOCRYSTALS FOR THE PREPARATION OF DIELS-ALDER RUBBER COMPOSITES

A.Riccioni[1]*, A. Ravicini[2], D. Allevi[2], M. Fumagalli[3,4], R. Bongiovanni[1], V. Barbera[2], A. Vitale[1]

[1] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy
[2] Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milan, Italy
[3] Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, CNRS UMR 5223, Ingénierie des Matériaux Polymères, Boulevard du 11 novembre 1918 43, 69622,Villeurbanne, France
[4] Univ. Grenoble Alpes, CNRS, CERMAV, Rue de la Chimie 601, 38610 Gières, France
e-mail: andrea.riccioni@polito.it

Introduction

In recent years, cellulose nanocrystals (CNCs) have gained growing attention as a biobased material thanks to their high tensile modulus, large surface area, and complete renewability. Moreover, the surface of CNCs can be chemically modified to tailor their physicochemical properties, making them a promising filler in the development of sustainable composites and elastomers. Besides the replacement of traditional fillers, the recyclability of the polymer matrix is another key factor in enhancing the sustainability of composite materials. Dynamic covalent polymer networks offer an attractive solution by combining thermoset durability with thermoplastic reprocessability. One widely used thermoreversible crosslinking strategy exploits the Diels–Alder (DA) reactions. In this perspective, the present work describes the development of a reprocessable rubber composite (Figure 1) based on DA crosslinking and reinforced with furan-functionalized cellulose nanocrystals (F-CNCs).

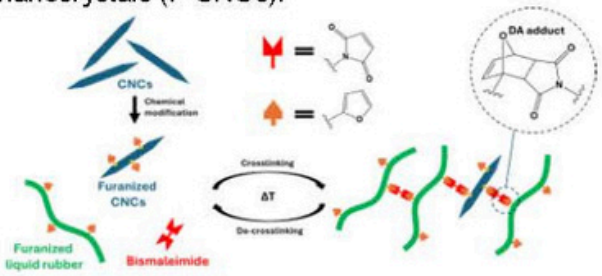


Figure 1. Schematic representation of the Diels-Alder system

Results and discussion

CNCs were extracted from delignified hemp pulp through acid hydrolysis and subsequently functionalized following two different synthetic strategies to introduce furan moieties. The first one was based on reductive amination, while the second involved a coupling reaction (Figure 2). These synthetic approaches required pre-treatment of nanocellulose with sodium periodate or TEMPO, to introduce aldehydes or carboxylic groups, respectively. Successful functionalization was confirmed by FT-IR, SS-NMR spectroscopy and elemental analysis, while the oxidation degree of the intermediate products was estimated using standard titration procedures.

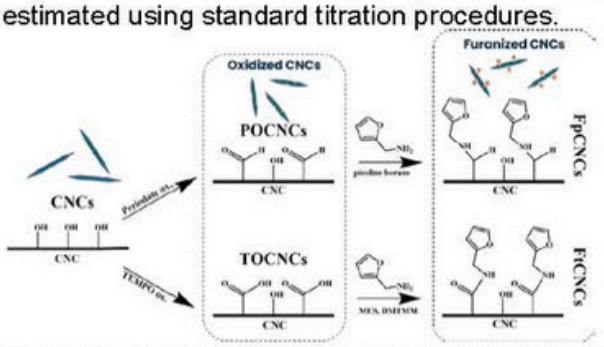


Figure 2. Synthetic routes for the preparation of furanized CNCs

Polybutadiene rubber was functionalized with furan moieties through a two-step process involving the epoxidation of the polymer backbone followed by the grafting of furan groups onto the epoxidized chains. Different composite formulations containing either pristine CNCs or F-CNCs were prepared through thermal crosslinking of furanized polybutadiene rubber in the presence of a bismaleimide crosslinker. The mechanical and chemical properties of the obtained materials were evaluated by DMA, tensile testing, gel content measurements, DSC and FT-IR spectroscopy. Composites containing F-CNCs exhibited higher elastic modulus and stress at break compared to both the unfilled

matrix and the composites with pristine CNCs, highlighting the beneficial role of covalent interfacial interactions promoted by the grafted furan. The reprocessability of the DA-based system was eventually performed through thermomechanical treatment of the shredded crosslinked materials (Figure 3).

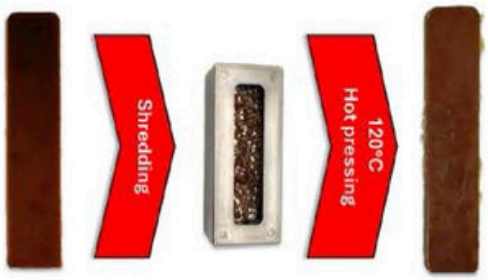


Figure 3. Schematic representation of the thermomechanical recycling of the composite

All the formulations were successful reprocessed and the indroduction of functionalized CNCs did not compromise the effectiveness of the process, confirming the potential of this system for sustainable, recyclable, and high-performance hydrophobic rubber composites.

Conclusions

Furan-functionalized cellulose nanocrystals were successfully synthesized and incorporated into a Diels–Alder crosslinked rubber matrix, yielding composites with enhanced mechanical performance and effective reprocessability. These findings demonstrate the potential of introducing reactive functionalities onto the CNC surface to overcome the limitations associated with their inherent hydrophilicity, improve interfacial interactions with hydrophobic matrices, and maximize their reinforcing effect. Overall, this strategy provides a promising route toward the development of sustainable and recyclable rubber composites based on renewable nanofillers and dynamic covalent networks.

References

[1] H. Kazemi, F. Mighri, D. Rodrigue, *Journal of Composites Science*, vol. 6, no. 7. (2022).
[2] Zheng N, Xu Y, Zhao Q, Xie T. *Chemical Reviews*, Feb 10;121(3):1716-1745. (2021)

Acknowledgments

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SMART POLYMERIC ARCHITECTURES BASED ON PHOTOSWITCHES: FROM ADHESIVES TO RESPONSIVE NANOCARRIERS

R. Rossi[1,2], D. Martella[1,2], M. Abad[3,4], Luis Oriol[3,4], M. Piñol[3,4], C. Parmeggiani[1,2]

[1] Department of Chemistry, University of Florence, Via della Lastruccia 13, 50019, Sesto Fiorentino, Italy
[2] European Laboratory for Non-Linear Spectroscopy (LENS), Via Nello Carrara 1, 50019, Sesto Fiorentino, Italy
[3] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, 50009, Zaragoza, Spain
[4] Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza, Pedro Cerbuna 12, 50009, Zaragoza, Spain

e-mail: rossir@lens.unifi.it

Introduction

The development of smart materials capable of responding to external stimuli is a frontier in polymer science, with photo-responsive systems offering distinct advantages in terms of spatiotemporal control, non-invasiveness, and remote operation. Among various photo-chromic motifs, arylazoisoxazoles (AIZs) have emerged as promising alternatives to traditional azobenzenes. The photochemical behavior of these materials, defined by a rapid *trans*-to-*cis* conversion rate, coupled with the robust thermal stability of the resulting *cis* isomer allows for the induction of isothermal phase transitions and significant shifts in the polarity of the surrounding environment upon light exposure. By leveraging these properties, we present the development of advanced polymeric architectures designed for two critical applications: light-actuated adhesive systems and supramolecularly functionalized nanocarriers for drug delivery.

Results and discussion

The photoresponsive adhesives, designated as P-6-AIZ, were synthesized via free-radical thermal polymerization by incorporating AIZ-based acrylate monomers into the polymer backbone to provide tunable interfacial adhesion on glass surfaces. Single lap-shear tests demonstrated that P-6-AIZ achieves a remarkable adhesion strength of 2.79 MPa. This performance is comparable to commercial cyanoacrylate glues and significantly outperforms previously reported AIZ-based adhesive systems (such as 5-AIZ).[1] Unlike traditional adhesives that require thermal activation or solvent-assisted debonding, these materials utilize the *trans*-to-*cis* photoisomerization of the AIZ units to trigger an isothermal reduction in adhesion strength of over 70% (Figure 1A).[2]

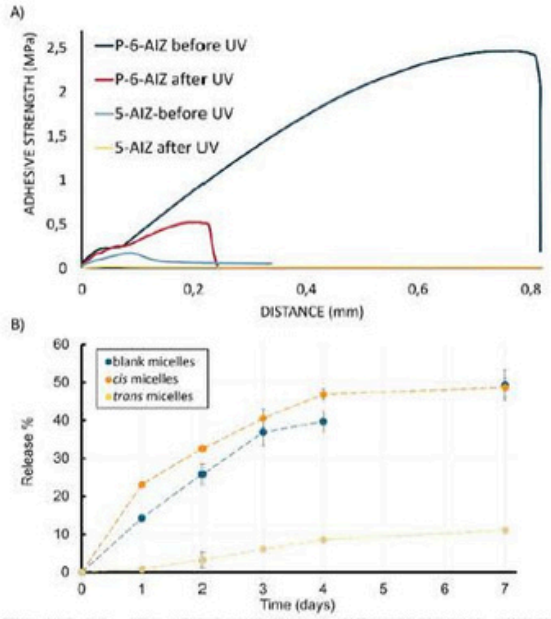


Figure 1. A) Comparison of adhesive strength before and after UV irradiation for the evaluated formulations. B) Release profiles of Nile Red from functionalized micelles in the trans *and* cis *states, if compared to non-functionalized micelles (blank).*

In parallel, we investigated the synthesis of nanocarriers by Polymerization-Induced Self-Assembly (PISA). This methodology provides a one-pot synthetic route for the generation of amphiphilic block copolymers with well-defined architectures, such as nanoworms, micelles or vescicles. After the synthesis of an amphiphilic macro-chain transfer agent (macro-CTA), the PISA was perfomed in an aqueous medium by adding a core-forming hydrophobic block, inducing the formation of monodisperse micelles. The latter were characterized and functionalized through the incorporation of AIZ-thymine derivatives. The supramolecular functionalization

is light-mediated as UV induced *trans*-to-*cis* photoisomerization is required for the AIZ moieties to permeate the micellar corona and anchor to the hydrophobic core via hydrogen bonding. The molecular design of the AIZ-thymine photoswitch is critical to this process: the thymine unit ensures stable anchoring within the core (which is functionalized with a pyridine), while the AIZ moiety enalbles the necessary diffusion into the micellar interior (an absent functionality in conventional azobenzene-thymine derivatives). This system is capable of reversible, light-gated encapsulation and release of hydrophobic cargo (e.g., Nile Red). The structural integrity of the micelles remains preserved throughout the photochemical cycle, while the light-induced shift in environmental polarity ensures a high-fidelity response in the cargo release kinetics (Figure 1B).[3]

Conclusion

By integrating AIZs into polymers through free-radical polymerization and PISA, we have created a versatile platform for dynamic materials. Our findings demonstrate that light-driven control of molecular organization and local polarity is a highly effective strategy for designing the next generation of responsive polymeric systems.

References

[1] L. Kortekaas, J. Simke, D. W. Kurka, B. J. Ravoo, *ACS Appl. Mater. Interfaces*, vol.12, 32054-32060 (2020)

[2] R. Rossi, A. Salvini, B. Pizzo, M. Frediani, D. S. Wiersma, C. Parmeggiani, D. Martella, *Macromol. Mater. Eng.*, vol. 308, 2200504 (2023)

[3] R. Rossi, M. Abad, L. Oriol, M. Frediani, D. Martella, C. Parmeggiani, M. Piñol, *Small*, vol. 21, e11176 (2025)

ENGINEERED POLYMER-BASED COMPOSITES FOR RADIATIVE COOLING SYSTEMS

P. Stagnaro[1a], E. Spotorno[2], L. Conzatti[1a], S. Losio[1b], R. Utzeri[1a], F. Bisio[3]

[1] SCITEC-CNR, [a] Via De Marini 6, 16149 Genova, Italy; [b] Via A. Corti 12, 20133 Milano, Italy
[2] Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy
[3] SPIN-CNR, Corso Perrone 24, 16152 Genova, Italy
e-mail: paola.stagnaro@cnr.it

Introduction

Passive daytime radiative coolers (PDRCs) allow a physical system on the Earth's surface to reduce its temperature, even under direct sunlight, by reflecting the whole solar spectrum and simultaneously emitting thermal radiation toward the cold outer space [1]. The radiative cooling effect occurs when a material shows high thermal emission in the mid-IR atmospheric transparency window between 1250 and 760 cm^{-1} (8-13 μm), and minimizes unwanted absorption both in the solar spectrum and atmospheric scattering range.

By exploiting a highly reflective surface and using materials transparent all across the UV, visible and near-IR range, PDRCs do not require external energy input to achieve net energy radiation to outer space, thus attracting increasing attention for applications such as energy saving, thermal management, sustainable cooling [2].

In particular, PDRC structures composed of a metallic substrate reflecting in the visible range topped by a polymeric coating with high emissivity in the mid-IR are investigated to optimize radiative emission [3].

In this work we fabricated PDRCs composed of silica-loaded polyolefin thin films hot-pressed onto Ag-coated stainless-steel slabs, correlating the photonic response of these systems with their thermodynamic radiative efficiency [4]. The presence of a strong emittance across the mid-IR range was clearly associated to a higher radiative power around room temperature, thereby establishing a clear quantitative criterion for PDRC assessment.

Results and discussion

The PDRC systems here prepared were layered structures made of polished stainless-steel slabs covered by an optically thick silver layer, acting both as mechanical support and highly reflective substrate. On the top of the metallic substrate, a polymer-based film was hot-pressed and acted as the "IR layer". As suitable polymers, commercial poly(4-methyl-1-pentene) (PMP) and cyclic olefin copolymer (COC) were used either in their neat form or as composites containing silica (SiO_2) microparticles to modulate the emissivity in the targeted mid-IR region.

The PMP and COC commercial grades chosen as polymer matrices (Fig. 1) exhibit excellent optical transparency over the solar spectrum, with average reflectivity above 0.95 (Haze ≤ 5%), combined to unique physical properties such as very low water absorbance and high chemical resistance, ensuring excellent durability upon environment exposure. These two polyolefins are indeed successfully employed in demanding applications, such as highly transparent food and drug packaging, automotive components, high-temperature-resistant cling films, baking trays, microwave-safe containers.

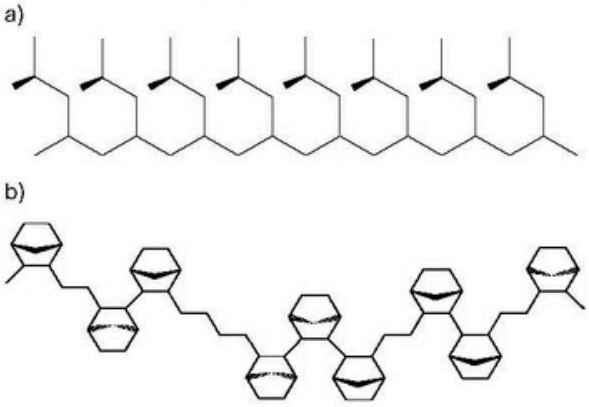


Figure 1. PMP (a) and COC (b) chemical structures.

The silica-loaded composites were prepared by melt mixing and extrusion carried out in a mini twin-screw extruder. Related neat matrices were treated in the same conditions for reference purpose. PMP and COC polymers were loaded with 6 vol.% of either different monodisperse SiO_2 particles with 10 μm (Si-10), 5 μm (Si-5), and 1 μm (Si-1) diameter, respectively, or some their combination in order to tune the optical properties of the polymer-based IR layer. The inclusion of

SiO_2 microparticles has indeed the combined effect of introducing a material with intrinsic optical absorbance/emittance in the mid-IR atmospheric transparency window and taking advantage from finite-size dielectric resonances of the microspheres, that enhance their absorbance in the same spectral window [3].
Scanning electron microscopy (SEM) of cryo-fractured cross-section surfaces of the extrudates evidenced that silica microspheres are homogeneously distributed and finely dispersed within the polyolefinic matrices.
Thermal behaviour of the composites was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Results showed that the adopted melt blending conditions and SiO_2 filler incorporation do not practically affect the characteristic thermal transitions of the matrices. This represents an advantage for the exploitation of the envisaged engineered systems, since processing parameters and conditions typically used for each neat polyolefin matrix can be easily transferred to the corresponding composite materials.
Highly transparent neat polymer and composite films of thickness around 100 microns were achieved by hot-pressing small pellets cut from the extrudates. The prepared films were then adhered onto the stainless steel substrate coated by the silver layer by hot-pressing, achieving a final thickness of the IR layer around 40 microns.
Optical characterization in the mid-IR region was carried out by spectroscopic infrared ellipsometry. As an example, Fig. 2 compares the Ψ parameter spectra acquired for the neat PMP and some silica-loaded composite samples. The former shows only weak and poorly structured features, while a richer set of strong absorbances in the 1250-760 cm^{-1} (8-13 μm) range is found in the presence of silica microparticles.

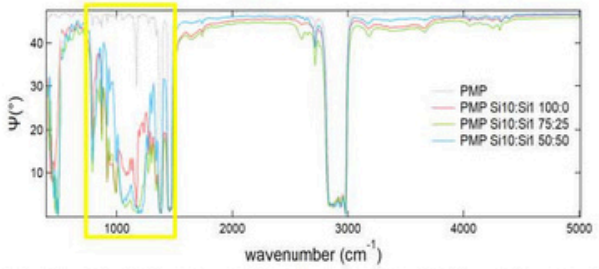


Figure 2. Ellipsometric parameter Ψ for the neat PMP (dashed line) and silica-loaded composite (solid lines) samples between 400 and 5000 cm^{-1}.

The polymeric emissive layer plays a crucial role in maximizing radiative heat dissipation by featuring microstructures that enhance mid-IR emission. A random distribution of inorganic microparticles embedded into a suitable polymer matrix, is a promising approach to obtain economical and large-scale radiative coolers.

To evaluate the PDRCs performance under controlled and reproducible conditions, radiative cooling measurements were carried out in a customized high-vacuum chamber (10^{-6} mbar) equipped with a twin sample holder and a liquid-nitrogen pool placed in front of it. The actual PDRC system and a dummy sample (Ag-coated stainless-steel slab) were individually connected to two separate thermocouples and the corresponding temperatures were acquired under identical experimental conditions. The whole setup was designed to minimize parasitic heat conduction to/from the samples. In such a way, the recorded temperature difference between the PDRC and the dummy sample provides an estimation of the radiative efficiency of the PDRC. Results show that both type of polymer-coated systems (neat polymer matrix and silica-loaded composites) have higher radiative power than the dummy. Moreover, as envisaged, a larger ΔT (7-8 K) was observed for the silica-loaded samples, which exhibited a more efficient radiative emission than those of the neat polymers (3-4 K).

Conclusions

PDRC systems were succesfully fabricated by hot-pressing a polymeric composite layer onto Ag-covered metal substrate slabs. The selected systems were based on highly transparent commercial polyolefins, namely poly(4-methyl-1-pentene) (PMP) or cyclic olefin copolymer (COC), properly loaded with suitably sized silica microspheres, to improve the emissivity in the mid-IR spectral range. In both cases the silica-loaded composite coatings enhanced the optical absorption-emissivity (with respect to the neat parent polymer) in the atmospheric-transparency spectral window. A clear correlation was proven between the engineered optical response in the mid-IR and the radiative efficiency of the systems.

References

[1] A.P. Raman, M.A. Anoma, L. Zhu, E. Rephaeli, S. Fan, *Nature*, *515*, 540–544 (2014)
[2] H. Keawmuang, J. Park et al., *ACS Appl. Mater. Interf.*, *18*, 21363-21423 (2026)
[3] Y. Zhai, Y. Ma et al., *Science*, 355 ,1062-1066 (2017)
[4] E. Spotorno, P. Stagnaro, L. Conzatti, S. Losio, R. Utzeri, F. Bisio, *Macromol. Rapid Commun.*, *e70329* (2026) *DOI: 10.1002/marc.70329*

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ENHANCED HYDROLYTIC DEGRADATION OF PLA GREEN COMPOSITES BY NANOMETRIC ZNO COVALENTLY BOUND ON NATURAL FIBRES VIA ALD

L. Vitiello[1], G. Proietto Salanitri[1], A.A. Scamporrino[1], C. Laferrera[2], G. Impellizzeri[2], L. Gioiella[3], G. Filippone[3], S.C. Carroccio[1]

[1]Istituto per i Polimeri, Compositi e Biomateriali (IPCB) – CNR, Via Paolo Gaifami 18, 95126 Catania, Italia
[2]Istituto per la Microelettronica e Microsistemi (IMM) – CNR, Via Santa Sofia 64, 95123 Catania, Italia
[3]Dipartimento di Ingegneria Chimica, Dei Materiali e Della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio 80, 80125, Napoli, Italia
e-mail: libera.vitiello@cnr.it (Inserire e-mail del corresponding author)

Introduction

The increasing accumulation of plastic waste in the environment has become a major global concern. Conventional petroleum-based plastics are highly resistant to degradation, leading to long-term pollution in terrestrial and aquatic ecosystems. To address this issue, significant efforts have been devoted to the development of sustainable materials derived from renewable resources. Among these, biopolymers have gained considerable attention due to their reduced dependence on fossil resources and their potential biodegradability. However, contrary to common perception, their degradation in natural environments can be extremely slow, limiting their actual environmental sustainability [1]. Poly(lactic acid) (PLA) is one of the most widely used biopolymers owing to its good mechanical properties, processability, and bio-based origin. PLA is commonly employed in packaging, consumer products, and biomedical applications. Despite being considered biodegradable, its degradation under natural environmental conditions is often slow and incomplete. Efficient degradation generally requires industrial composting conditions characterized by elevated temperatures and controlled humidity. Consequently, improving the degradation rate of PLA in real environmental scenarios remains a key challenge for enhancing its overall sustainability. Several strategies have been proposed to accelerate PLA degradation, including the incorporation of additives capable of promoting hydrolytic processes. Among these, zinc oxide (ZnO) nanoparticles have attracted increasing interest due to their catalytic activity and ability to enhance polymer degradation [2,3]. The high surface area of ZnO nanoparticles can facilitate hydrolysis reactions, promoting the breakdown of polymer chains and accelerating material deterioration. Nevertheless, the tendency of nanoparticles to aggregate within polymer matrices can reduce their effectiveness and limit their potential benefits.

A promising approach to overcome this limitation is the use of natural fibres as carriers for nanoparticles. Natural fibres are renewable, biodegradable, and environmentally friendly materials that can improve nanoparticle dispersion while increasing the interfacial contact area with the polymer matrix. By immobilizing ZnO nanoparticles on the fibre surface, it is possible to enhance their distribution throughout the composite and maximize their pro-degradation effect.

In this work, green composites based on PLA and natural fibres functionalized with ZnO nanoparticles were developed. ZnO was covalently anchored onto the fibre surface through Atomic Layer Deposition (ALD), a technique that enables precise and uniform nanoparticle deposition. The functionalized fibres were then incorporated into the PLA matrix to obtain composites with enhanced degradation potential. Hydrolytic degradation tests were carried out under different environmental conditions to assess the effectiveness of fibre-bound ZnO in promoting PLA degradation. The results demonstrate the potential of this strategy for developing biopolymer-based materials with improved environmental responsiveness and controlled degradation behavior.

Results and discussion

Hemp shive fibers (HS), with an average length below 500 µm, were functionalized with nanometric ZnO coatings via low-temperature Atomic Layer Deposition (ALD). Two coating thicknesses, 10 and 90 nm, were deposited, obtaining uniform ZnO layers covalently anchored onto the fiber surface. PLA-based composites were subsequently produced by melt extrusion followed by compression molding using untreated and ZnO-functionalized fibers. Four formulations were investigated: neat PLA as reference, PLA

with 10wt.% untreated HS (PLA-HS), and PLA loaded with 7.5wt.% untreated HS combined with 2.5wt.% ZnO-coated HS with either 10 nm (PLA-ZnO10) and 90 nm (PLA-ZnO90) coating thickness. STEM and TEM analyses confirmed the successful functionalization of hemp shive fibers. Elemental mapping evidenced a uniform and continuous ZnO layer coating the lignocellulosic surface, demonstrating the conformality of the ALD process and strong interfacial adhesion between ZnO and the fibers. Thermogravimetric analysis further highlighted the impact of the inorganic coating on thermal stability. ZnO-functionalized fibers exhibited improved resistance to thermal degradation compared to untreated fibers, consistent with the presence of a protective inorganic layer. TGA analysis further showed a ZnO content of approximately 5 wt.% and 35 wt.% for the 10 nm and 90 nm systems, respectively, confirming controlled inorganic loading via ALD.

Size exclusion chromatography (SEC) of PLA-based materials prior to water immersion revealed a decrease in weight-average molecular weight in composites containing ZnO-functionalized fibers. This suggests that ZnO promotes PLA chain scission already during melt processing, likely through catalyzed hydrolytic reactions activated under extrusion conditions. Therefore, ZnO acts not only as a post-processing degradation promoter but also as an active species during processing. Consistently, MALDI analysis of processed samples showed an increased intensity of PLA oligomers terminated with –OH and –H groups in ZnO-containing systems, confirming enhanced hydrolytic chain cleavage during melt extrusion and a modified end-group distribution compared to neat PLA and PLA-HS.

Hydrolytic degradation was then evaluated by immersing the samples in distilled water for 10, 30, and 60 days under three different conditions: darkness at 30 °C, UV irradiation at 394 nm, and natural light exposure. These conditions were selected to assess the combined influence of hydrolysis and photocatalytic degradation. SEC results showed a progressive reduction in weight-average molecular weight for all formulations as a function of immersion time. However, composites containing ZnO-functionalized fibers, particularly those with 10 nm coatings, exhibited a significantly faster decrease in molecular weight compared to untreated systems (Figure 1).

Notably, the most pronounced hydrolytic degradation was observed under dark conditions at 30°C. In this case, hydroxylated ZnO nanoparticles covalently bound to the hemp fibers are believed to catalyze the rapid hydrolysis of PLA chains, significantly accelerating molecular weight reduction. Conversely, when the system was exposed to UV irradiation at room temperature, the lower thermal contribution limited purely hydrolytic processes, and the degradation behavior was predominantly governed by the photocatalytic activity of ZnO. Under these conditions, photoexcited ZnO promotes oxidative pathways that synergistically enhance PLA chain scission.

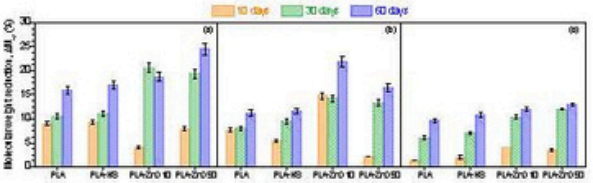


Figure 1. Reduction in weight-average molecular weight (ΔM_w) of the degraded samples after 10, 30, and 60 days of water immersion under three different conditions: darkness (a), UV irradiation (b), and natural light exposure (c).

Conclusions

The present study demonstrates that ALD-functionalized hemp shive fibers are effective carriers for ZnO nanoparticles, enabling controlled dispersion and tunable inorganic loading within PLA composites. ZnO not only enhances thermal stability of the fibers but also actively influences PLA degradation behavior during processing and hydrolytic aging. Both SEC and MALDI analyses consistently show that ZnO promotes chain scission under melt processing conditions and significantly accelerates hydrolytic degradation during water immersion. Furthermore, exposure to UV and natural light enhances degradation through photocatalytic activation of ZnO. Overall, the combination of natural fibers and ALD-deposited ZnO represents a promising strategy to design biopolymer composites with controllable and accelerated degradation profiles, improving their potential environmental sustainability.

References

[1] T.P. Haider et al., *Angew Chem Int*, vol. *58*, 50-62. (2019)
[2] R. Puglisi et al., *Polymers*, vol. 15, 1434 (2023)
[3] M. Qu et al., *J. Appl. Polym.*, vol. 131 (2014)

Acknowledgments

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CAPACITIVE SENSOR BASED ON POROUS LIQUID CRYSTALLINE GEL

V. Spinoso[1], D. Martella[1,2], S. Nocentini[1,3].
[1] European Laboratory for Non-Linear Spectroscopy (LENS), University of Florence, Sesto Fiorentino, Italy
e-mail: vincenzo.spinoso@lens.unifi.it
[2] Department of Chemistry "Ugo Schiff", University of Florence, Sesto Fiorentino, Italy
[3] National Institute of Metrology (INRiM), Torino, Italy

Introduction

Temperature sensing in different environments is a fundamental requirement across biomedical diagnostics, industrial process control, and soft and wearable electronics [1]. Soft capacitive temperature sensors have emerged as particularly attractive alternatives due to their simple architecture, low power consumption, minimal hysteresis, and seamless compatibility with flexible substrates [2–4].

For a parallel-plate capacitive sensor, the operating principle is governed by the equation:

$$C = (\varepsilon_0 \varepsilon_r A)/d$$

where ε_r is the dielectric permittivity, ε_0 is the vacuum permittivity, A is the electrode area, and d is the dielectric thickness. , Thermal transduction inherently relies on the temperature-induced modulation of these physical and geometrical parameters. At present, the performance of current soft capacitive devices is fundamentally bottlenecked by the weak thermo-dielectric response of conventional solid polymer dielectrics, resulting in low sensitivities [2,3].

Thermotropic liquid crystals (LCs), particularly nematic systems such as 5CB, offer a powerful alternative. Driven by their strong temperature-dependent dielectric anisotropy and phase-transitional molecular reorientation, LCs exhibit massive permittivity variations [4–6]. While pure LC-based capacitive sensors can achieve high sensitivity, their intrinsic fluidity inevitably causes functional fluid leakage. This structural instability traditionally necessitates rigid, bulky encapsulation strategies that severely compromise device flexibility and broad integration [7].

To bridge the gap between high thermal sensitivity and structural stability, Liquid Crystal Gels (LCGs) combine the benefits of low-molecular-weight free nematic LCs with the mechanical robustness of crosslinked polymer networks [8]. In this engineered architecture, the crosslinked polymer scaffold acts as a porous matrix that effectively traps the free LC, preventing fluid leakage even in particular conditions, such as direct contact with liquid environments.

We here demonstrate that integrating a free LC within a tailored polymer network enables a synergistic transduction mechanism.

Instead of relying solely on the minor thermal expansion typical of standard solid polymers, LCGs exploit a coupled thermo-responsive effect: temperature variations induce large shifts in the dielectric permittivity (ε_r) of the free LC phase, while the molecular reorientation simultaneously triggers a macroscopic thermal contraction of the porous polymer network (decreasing the thickness, d).

Here, we present a capacitive temperature sensor based on an optimized LCG architectureWe demonstrate that the engineered crosslinked matrix ensures robust mechanical integrity and prevents free LC leakage, allowing the platform to maintain stable, high-fidelity operation over repeated thermal cycles and even under water immersion.

Results and discussion

A Liquid Crystal Gel (LCG) material was synthesized and integrated into a capacitive architecture. The precursor system comprised a polymerizable monoacrylate mesogen (6OBA), a reactive mesogen crosslinker (RM257) required to establish structural integrity, and a non-reactive nematic liquid crystal (5CB) serving simultaneously as the functional stimuli-responsive component and a molecular porogen. The capacitive platform was builded on a glass substrate, which supported a 30 nm gold bottom electrode deposited via sputter coating through a patterned mask. Following capillary infiltration, controlled thermal treatments were utilized to access specific mesophases prior to selective UV crosslinking. Subsequent solvent development yielded a well-defined, anisotropic polymer network that encapsulates the functional LC phase. Finally, a 30 nm gold top electrode was sputter-coated to complete the device fabrication (Figure 1).

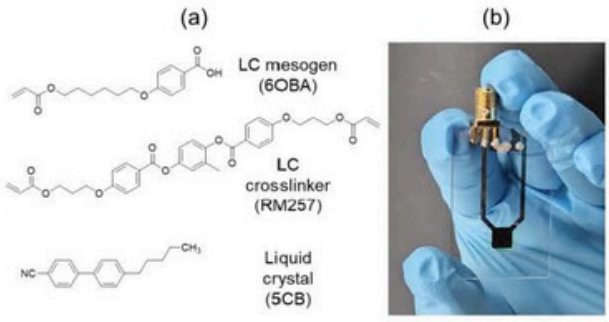


Figure 1: (a) Molecules precursor of the polymer matrix. (b) Assembled capacitive sensor on a glass substrate.

The dielectric and morphological characteristics of the synthesized LCG are fundamentally related to the matrix composition. Systematically varying the concentration of the non-reactive LC fraction within the polymerizable matrix revealed a distinct structure-property trade-off: higher LC contents act as efficient porogens, yielding porous networks with enhanced thermo-dielectric responsiveness, whereas lower LC fractions favor mechanical rigidity. An optimal precursor ratio was identified to establish a polymer scaffold that balances functional actuation with the structural stability of the gel.

Subsequent structural investigations highlighted that the functional response of the LCG is intrinsically governed by the LC phase state of the precursor mixture during the photopolymerization step. Crosslinking the matrix in the isotropic phase resulted in a highly disordered, amorphous polymer network exhibiting negligible thermal responsiveness. Conversely, photopolymerization within a nematic mesophase exhibited positive thermal responsiveness. Specifically, locking in a polydomain nematic alignment, characterized by locally oriented LC domains and topological defects, enables a macroscopic contraction of the porous polymer network upon thermal stimulation. This thickness variation, coupled with the inherent dielectric permittivity shift of the LC phase allows the capacitive device to function effectively as a temperature sensor.

The LCG networks exhibited reversible, hysteresis-free stimuli-responsive behavior over consecutive thermal cycles, characterized by a non-linear sensitivity profile. The temperature-capacitance non-linear sensitivity profile intrinsically amplifies the sensor's response, transitioning from a baseline sensitivity of ~0.25%/°C in the near-physiological regime (37°C) to approximately 1.0%/°C above 70°C. A notable operational feature of this system is its stability under complete aqueous immersion. While classical non-encapsulated LC systems typically suffer from functional fluid leakage when exposed to liquid environments, the crosslinked polymeric architecture effectively traps the free 5CB within its pores. Preventing this leakage is critical, as it avoids parasitic dielectric screening and allows the system to continuously exploit the large temperature-dependent variation in the dielectric permittivity of the free liquid crystal. This performance demonstrates that these engineered liquid crystalline polymer networks can maintain stable signal transduction even in direct contact with water. Under immersion, the device effectively prevented parasitic dielectric screening, preserving an average sensitivity of ~0.80%/°C that approached 1.0%/°C at elevated temperatures.

Conclusion

In this work, we developed and characterized a thermally responsive capacitive actuator based on a liquid crystal gel composite dielectric. Robust crosslinked polymer network was engineered to firmly encapsulate a free nematic liquid crystal (5CB), entirely eliminating the fluid leakage that limits pure LC devices.

The device exhibits hysteresis-free reversibility and environmental resilience. Notably, the stable LC confinement enabling reliable temperature monitoring even under complete aqueous immersion. These LCG composites provide a robust and highly adaptable material paradigm for next-generation soft electronics.

Riferences

[1] Li, Qiao and Zhang, Li-Na and Tao, Xiao-Ming and Ding, Xin, *Advanced healthcare materials*, 6., 1601371.(2017).

[2] Amjadi, Morteza and Kyung, Ki-Uk and Park, Inkyu and Sitti, Metin, *Advanced Functional Materials*, 26., 1678—1698.(2016).

[3] Cohen, Daniel J and Mitra, Debkishore and Peterson, Kevin and Maharbiz, Michel M, *Nano letters*, 12., 1821—1825.(2012).

[4] Jangid, Geetika and Singh, Gautam and Kumar, Sanjeev and Sharma, Kamal Nayan and Pal, Rishi and others, *Advancing Thermal Technologies*, 305—322.(2026).

[5] Balasubramaniam, VM and Sastry, SK, *Journal of food engineering*, 26., 219—230.(1995).

[6] Algorri, Josè Francisco and Urruchi, Virginia and Bennis, Noureddine and Sànchez-Pena, Josè Manuel, Sensors, 14., 6571—6583.(2014).

[7] Urbanski, Martin and Reyes, Catherine G and Noh, JungHyun and Sharma, Anshul and Geng, Yong and Subba Rao Jampani, Venkata and Lagerwall, Jan PF, *Journal of Physics: Condensed Matter*, 29., 133033.(2017).

[8] Shahsavan, Hamed and Aghakhani, Amirreza and Zeng, Hao and Guo, Yubing and Davidson, Zoey S and Priimagi, Arri and Sitti, Metin, *Proceedings of the National Academy of Sciences*, 117., 5125—513.(2020).

PYROLYSIS-DERIVED TELECHELIC POLYPROPYLENE AS A MECHANOCHROMIC PROBE FOR VISUALIZING STRESS REDISTRIBUTION AND CAVITATION IN POLYOLEFIN-BASED MATERIALS

B. Bertoncini [1,2], G. Bancalà [3], C. Adamo [1], M.Carlotti [2], A. Pucci [2]

[1] Chimie ParisTech, PSL Research University, CNRS, Institute of Chemistry for Life and Health Sciences, Paris F-75005, France
[2] Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via G. Moruzzi 13, Pisa 56124, Italy.,
[3] Chemical Product Engineering, Department of Chemical Engineering, University of Groningen, Nijenborgh 3, 9747 AG Groningen, The Netherlands
e-mail: andrea.pucci@unipi.it

Introduction

The development of polymeric materials capable of reporting mechanical deformation through optical signals is attracting increasing interest for applications in structural health monitoring and damage detection. Among the different mechanochromic approaches, systems based on excimer-forming fluorophores are particularly attractive because their optical response directly reflects changes in molecular aggregation induced by mechanical stress. At the same time, the growing importance of polymer recycling motivates the search for new routes to transform waste-derived materials into high-value functional products. In this work, controlled pyrolysis of isotactic polypropylene (iPP) was exploited to generate telechelic oligomers that were subsequently functionalized with pyrene to produce a mechanochromic additive capable of sensing deformation in polymer matrices.

Results and discussion

Controlled pyrolysis yielded oligopropylene chains bearing terminal vinylidene groups, which were converted into pyrene-functionalized telechelic structures. The resulting additive displayed intense excimer emission in the solid state and was incorporated into HDPE, LLDPE, POE, and PCL matrices. The selected polymers provided a broad range of crystallinity, polarity, mechanical properties, and compatibility with polypropylene, allowing the influence of morphology and interfacial interactions on the mechanochromic response to be investigated. The optical response was found to be highly dependent on processing conditions. Samples prepared under conditions that preserved partially segregated polypropylene-rich domains exhibited the strongest mechanochromic behavior because these inclusions acted as stress concentrators during deformation. In LLDPE and PCL matrices, tensile stretching produced a progressive decrease in excimer emission, consistent with the disruption of pyrene aggregates under load. In contrast, POE-based materials showed an unexpected increase in excimer fluorescence during deformation. To understand this unusual behavior, the materials were investigated using confocal microscopy, scanning electron microscopy, small-angle X-ray scattering, and quantum-chemical calculations. The experimental analyses revealed that poorly compatibilized polypropylene-rich domains promoted interfacial debonding and cavitation under tensile stress. The formation and growth of voids around these inclusions increased the local concentration of pyrene moieties, thereby enhancing excimer formation rather than disrupting it. Complementary computational studies supported this interpretation by demonstrating that excimer emission is favored under local packing conditions that increase pyrene proximity and confinement. The combined experimental and theoretical results therefore establish a direct correlation between cavity formation, local dye aggregation, and fluorescence enhancement. As a consequence, the increase in excimer emission becomes an optical signature of cavitation and damage development within the elastomeric matrix (Figure 1).

Conclusions

This study demonstrates a sustainable and versatile strategy for converting pyrolysis-derived polypropylene into a functional mechanochromic additive capable of probing deformation processes in polymeric materials. The pyrene-

functionalized telechelic oligomers enable real-time optical visualization of stress redistribution, interfacial debonding, and cavitation in polymer blends. The strong dependence of the mechanochromic response on matrix morphology and interfacial compatibility highlights the crucial role of local microstructure in force transmission and damage development. Notably, the unusual enhancement of excimer emission observed in polyolefin elastomers was directly correlated with cavitation phenomena, providing a distinctive optical marker for the initiation and evolution of mechanical damage. Combined experimental investigations and quantum-chemical calculations reveal how local packing constraints and fluorophore aggregation govern the observed fluorescence response. Beyond introducing a new diagnostic tool for studying failure mechanisms in soft polymer systems, this work illustrates how pyrolysis-derived polyolefin oligomers can be upcycled into advanced functional materials, opening new perspectives for smart and value-added applications of recycled plastics.

References

[1] B. Bertoncini, G. Bancalà, W. Nowicka, A. Battisti, I. Pusceddu, M. Turelli, J. Neethirajan, G. Portale, R. Duchateau, C. Adamo, A. Pucci, M. Carlotti, *Journal of Materials Chemistry* C (2026). DOI: 10.1039/d5tc04217h

Acknowledgments

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Figure 1:

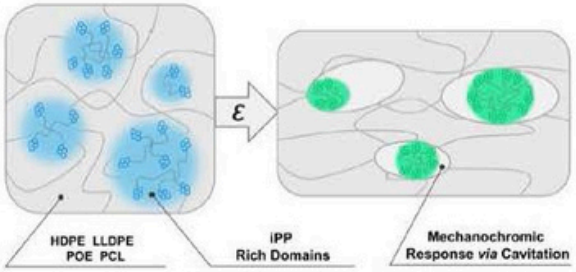


Figure 1. Pyrolysis-derived telechelic polypropylene enables mechanochromic visualization of cavitation and stress redistribution in polymer matrices through deformation-induced changes in pyrene excimer emission..

FROM HYDROPHOBIC TO HIGH-PERFORMANCE WATER FILLED POLYMERIC FILMS: A NEW PARADIGM IN WATER PURIFICATION MATERIALS

D. Riccardi [1], G.Guerra[1], P. Rizzo[1]

[1] Dept. of Chemistry and Biology, INSTM Research Unit, University of Salerno, 84084 Fisciano, Italy; e-mail: prizzo@unisa.it

Introduction

This study presents an innovative approach to water purification based on nanoporous crystalline (NC) polymer films showing high surface area (HSA), focusing on poly(2,6-dimethyl-1,4-phenylene) oxide (PPO).
These materials are characterized by ordered nanoscopic channels capable of hosting organic molecules, making them promising candidates for pollutant removal [1].
A key challenge in this field is achieving both high adsorption capacity and fast sorption kinetics. Traditional dense polymer films offer good capacity but slow diffusion, while aerogels provide fast kinetics but low volumetric efficiency.
The main objective of the work is to overcome this limitation by developing dense polymer films with high surface area and rapid adsorption properties.
A crucial innovation is the preparation of water-filled hydrophobic films without chemical functionalization, achieved through a two step ethanol–water exchange procedure.

Results and discussion

The prepared HSA NC PPO films exhibit remarkable structural features, including surface areas up to about 220 m^2/g, porosity around 20%, and crystallinity near 36%, while maintaining relatively high density [2].
The water-filling process enables high water uptake (>70 wt%) without swelling or altering the polymer structure, significantly enhancing transport properties.
Adsorption experiments using perchloroethylene (PCE) as a model pollutant demonstrate outstanding performance in terms of equilibrium uptake up to ~15 wt%, as well as rapid equilibrium reached within ~60 minutes.
The results show that: pollutant uptake mainly occurs within the nanoporous crystalline channels; sorption kinetics strongly depend on surface area and water filled films accelerate diffusion kinetics [3].
In comparison with other materials water-filled films are more effective than chemically modified (e.g., sulfonated) polymers and their performance exceeds also that of commercial adsorbents such as Tenax.
Additionally, the films show excellent reusability since they showed negligibile loss in contaminant uptake up to 10 cycles, even showing a structural integrity and stability after repeated use.

Conclusions

This work demonstrates a significant advancement in the design of polymer based materials for water purification. The development of water-filled nanoporous crystalline PPO films combines high adsorption capacity, fast kinetics, and structural stability in a single system.
The ability to achieve these properties without chemical functionalization simplifies the production process and enhances material robustness.
Overall, these films represent a highly promising platform for: removal of organic pollutants from dilute aqueous solutions,treatment of drinking water, capture of persistent contaminants, analytical preconcentration applications.
This approach opens new perspectives for efficient, scalable and reusable solutions in environmental remediation and water treatment technologies.

References

[1] M. Golla, M.; B. Nagendra; C. Daniel, P. Rizzo, F. Auriemma; O. Tarallo, G. Guerra, *Eur. Polym. J.* vol. 179 111568 (2022).
[2] B. Nagendra, S. Salman, C. Daniel, P. Rizzo, G. Guerra,(2023). *Materials Advances* vol. *4* 881-889 (2023)
[3] D. Riccardi, P. Rizzo, B. Nagendra, G. Guerra, *ACS Applied Polymer Materials* vol. 8 3279-9287 (2026)

Acknowledgments

Italian Ministry of Education, University, and Research (MUR) is acknowledged for financial support. We acknowledge financial support under the National Recovery and Resilience Plan

(NRRP), Mission 2 “Green Revolution and Ecological Transition,” Component 2 “Renewable Energy,Hydrogen, Grid and Sustainable Mobility,” Investment 3.5“Research and development on hydrogen” (M2C2-3.5), PublicNotice of 23.03.2022 pursuant to Article 1, paragraph 5, letter a), of the Ministerial Decree of 23 December 2021 issued bythe Italian Ministry of Ecological Transition. Project Title:“Tecnologia Elettrocatalitica diretta di converSione di CO2 per LA produzione di e-fuels_TESLA ”_CUP F57G25000060006_Grant Assignment Decree No. 385 adopted on 06/10/2025 by the Italian Ministry of Environmentand Energy Security (MASE).

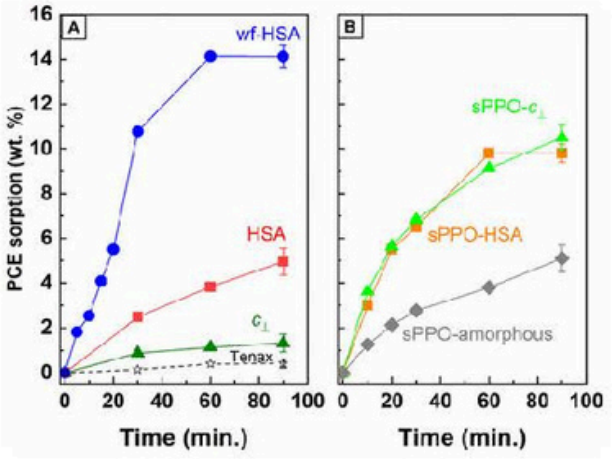


Figure 1. Kinetics of PCE uptake from 50 ppm aqueous solutions: (A) For three hydrophobic NC PPO films: (triangles) c⊥-oriented; (squares) HSA;(circles) water-filled HSA. For comparison, the kinetics of PCE uptake from 50 ppm aqueous solutions by a benchmark commercial adsorbent polymer (Tenax) is also shown (stars). (B) For three hydrophilic sulfonated PPO films: (diamonds) amorphous; (triangles) c⊥-oriented with sulfonated amorphous phase; (squares) HSA with sulfonated amorphous phase.

EMISSIVE BOTTLE-BRUSH COPOLYMERS FOR SOFT OPTO-ELECTRONIC VIA ORTHOGONAL POLYMERIZATION

S. Gabellini, R. Medri, M Ferri, A. Luzi, E. Salatelli, M. Lanzi, D. Caretti , S. Scurti

Dept. of Industrial Chemistry "Toso Montanari", University of Bologna, Via P. Gobetti 85, 40129, Bologna, Italy
e-mail: stefano.scurti2@unibo.it

Introduction

Soft optoelectronics combines light-emitting and light-sensing technologies with flexible and adaptable devices capable of conforming seamlessly to dynamic and complex surfaces, enabling a wide range of applications such as interactive and neuromorphic interfaces, biomimetic robotics, and wearable health sensors. [1-2] Among the materials developed for these applications, semiconducting polymers have shown some of the most promising electrochemical performances. However, the highly planar π-conjugated structures that characterize this class of materials are often affected by aggregation-caused quenching (ACQ) arising from π–π stacking interactions, which severely limit their emissive properties and practical applications. [3] To enhance the photophysical performance of these systems, a macromolecular design strategy based on the incorporation of orthogonal monomers as defective sites within the polymer chains was developed. These monomers can undergo independent polymerization mechanisms, allowing the growth of sterically demanding side chains from the semiconducting backbone to obtain bottle-brush like copolymers. This architecture promotes physical separation of the π-conjugated segments, suppressing ACQ phenomena and enhancing the emissive properties of the resulting materials (Figure 1).

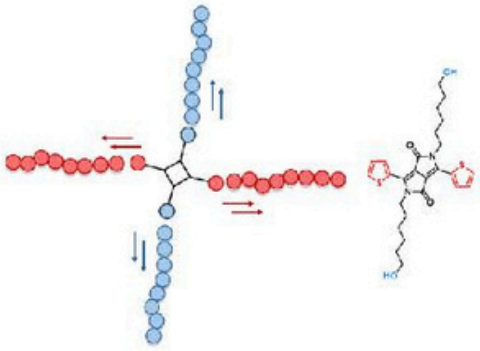


Figure 1: Schematic representation of orthogonal polymerization and monomer synthesized

Results and discussion

To this purpose, an emissive orthogonal monomer based on a diketopyrrolopyrrole (DPP) structure (Figure 1) was synthesized via a pseudo-Stobbe condensation reaction to obtain a heteroaromatic fluorophore containing thiophene units suitable for oxidative polymerization. In a further step, N-alkylation of the DPP core was performed using a hydroxyl-functionalized alkyl chain, introducing a second reactive functionality able to act as an initiator for ring-opening polymerization (ROP). This molecular design enabled the monomer to undergo two independent polymerization processes.

First, polymeric semiconducting backbones were synthesized through Fe(III)-catalyzed oxidative copolymerization with 3-hexylthiophene (3HT). The resulting random distribution of repeating units along the polymer chains increased the conformational entropy of the system, limiting efficient molecular packing and influencing photophysical properties. Different DPP:3HT molar ratios (80:20, 50:50, and 20:80) were investigated to evaluate the effect of defect-site incorporation on the polymer properties. ^{1}H-NMR and DOSY-NMR experiments confirmed the copolymer compositions, while thermal characterization (DSC) revealed the absence of a melting transition compared to the 3HT homopolymer, indicating a reduced constitutional order induced by the random monomer distribution. The obtained copolymers exhibited fluorescence in solution but showed negligible emission in the solid state, consistent with aggregation of the conjugated backbones.

To obtain light-emissive materials, a second polymerization step was performed through a grafting-from approach involving the ROP of ε-caprolactone. The growth of poly(ε-caprolactone) (PCL) side chains promoted the separation of the planar π-conjugated segments, resulting in enhanced photophysical properties, including solid-state fluorescence. The effect of PCL molecular weight was investigated by performing ROP on copolymers with 50:50 and 80:20

DPP:3HT compositions. As shown in Figure 2, grafting PCL chains from the conjugated macroinitiators led to the formation of bottle-brush architectures with fluorescence strongly dependent on macromolecular design. Increasing the PCL chain length enhanced the steric separation of the conjugated segments, resulting in a significant enhance in solid-state emissivity.

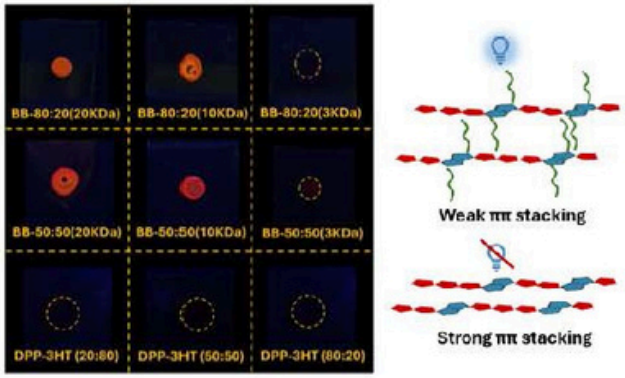


Figure 2: Comparison of solid state emission between the conjugated copolymers at different molar compositions and the bottle-brush (BB) polymer with different PCL molecular weights.

Electrochemical measurements demonstrated the conductive behavior of the prepared materials and their electrochemical stability, both dependent on the polymer architecture. Furthermore, the bottle-brush structures exhibited excellent film-forming ability and good solubility in a wide range of organic solvents. Finally, to develop chemically interactive interfaces, the terminal hydroxyl groups of the PCL side chains were further functionalized. In particular, an anthracene derivative was covalently attached to obtain FRET (Förster Resonance Energy Transfer)-active systems as a proof of concept for the development of interactive chemical biointerfaces.

Conclusions

The development of orthogonal polymerization strategies enabled by the rational design of multifunctional monomers offers a powerful approach to impart emissive properties to π-conjugated systems through the formation of bottle-brush polymer architectures. This macromolecular design effectively suppresses aggregation-caused quenching while preserving the electrochemical properties of the semiconducting backbone.

As a result, both the photophysical and electrochemical performances of the materials can be finely tuned, paving the way for advanced soft optoelectronic devices, interactive interfaces, and sensing applications.

References

[1] Choi, C. et al, *Nat Commun., vol.* 8, 1664 (2017)

[2] Song, G. et al. *Advanced Materials Technologies (2026)*

[3] Weis M., *Applied Sciences, vol* 15(7), 4028 (2025)

Acknowledgments

S.S. position was funded by FSE+ 2021−2027 (RIF. PA: 2023-20090/RER-2-CUP: J19J23000730002). S. G. position was funded by FSE + 2021–2027 (RIF. PA: 2025-23878/RER, pr. 23 CUP: J33C25000520006).

EVALUATION OF THE SELF-HEALING BEHAVIOUR OF MULTIFUNCTIONAL THERMOPLASTIC COMPOSITE LAMINATES

A. Dorigato[1], L. Simonini[1], A. Sorze[1], G. Fredi[1], P. Russo[2], A. Pegoretti[1]

[1] Department of Industrial Engineering, University of Trento, via Sommarive 9, 38123, Trento, Italy
[2] Institute for Polymers, Composites and Biomaterials, National Research Council, via Campi Flegrei 34, 80078, Pozzuoli, Italy
e-mail: andrea.dorigato@unitn.it

Introduction

In recent years, thermoplastic structural composites have attracted increasing interest due to their combination of high mechanical performance, processability, and recyclability. However, their susceptibility to damage, particularly under cyclic loading and impact conditions, still represents a critical limitation. In this context, the integration of intrinsic self-healing functionalities into thermoplastic matrices emerges as a promising strategy to enhance durability and reduce maintenance costs [1]. This contribution summarizes a comprehensive research pathway aimed at the development of self-healing thermoplastic composite laminates based on polyamide 6 (PA6) matrices modified with cyclic olefin copolymers (COC) and compatibilized with ethylene glycidyl methacrylate (E-GMA), reinforced with carbon fibers. Moreover, the self-healing properties of a PLA based matrix modified with polybutylene adipate-co-terephthalate (PBAT) an compatibilized with an epoxy based chain extender (J) were evaluated, also in combination with flax fibers.

Results and discussion

PA6/COC/E-GMA matrix formulation was optimized through a systematic investigation of the effects of compatibilizer content and healing temperature on rheological, microstructural, and mechanical properties. The optimal formulation (PA6/30 wt% COC/5 wt% E-GMA) exhibited significantly improved COC dispersion and interfacial adhesion, enabling high healing efficiencies (up to 82% under impact conditions at 160 °C) [2]. Subsequently, this optimized matrix was employed in the development of short carbon fiber-reinforced composites processed via extrusion and injection molding. In these systems, the addition of COC led to a moderate reduction in quasi-static mechanical properties, accompanied by a significant improvement in impact resistance and self-healing capability. In particular, healing efficiencies up to 80% were achieved in impact tests, and fatigue life was extended by up to 77%, demonstrating the ability of the system to repair microdamage induced by cyclic loading. Microstructural analysis further highlighted the key role of phase morphology and COC mobility in governing the healing mechanisms [3]. Finally, the approach was extended to continuous carbon fiber-reinforced laminates manufactured via film stacking and hot pressing. Despite the additional complexity associated with continuous reinforcement and laminate architecture, the self-healing composites exhibited competitive mechanical properties compared to reference systems and, most importantly, outstanding healing performance. In short-beam shear tests, PA6/COC/E-GMA laminates demonstrated complete recovery of interlaminar shear strength (healing efficiency ~100%), whereas negligible recovery was observed for non-healable laminates. These results were attributed to the ability of the COC phase to effectively flow and fill matrix cracks and delaminated regions during thermal mending [4]. Moreover, fully biodegradable, thermally-activated self-healing composites made of compatibilized poly(lactic-acid) (PLA) and poly(butylene-adipate-terephthalate) (PBAT), reinforced with unidirectional flax fibers (FF), were produced through melt compounding, film-stacking and hot-pressing. The resulting composites had a low void volume fraction (1-3%) and fiber contents of 30-40 vol%. Mechanical characterization showed that PBAT did not significantly alter the tensile response of composites, which remained primarily fiber dominated, with elastic modulus (20.7 GPa) and ultimate strength (283.5 MPa) comparable to neat PLA-based composites. Conversely, flexural and short beam shear (SBS) tests revealed a reduction in flexural modulus (17%), flexural strength (22%) and interlaminar shear strength (39%) with PBAT. This was attributed to the higher hydrophobicity of the PBAT-modified matrix, which increased the static contact angle from 41.3° to 67.4°, limiting the interfacial compatibility of the matrix with the hydrophilic FFs. However, PLA/PBAT-based system demonstrated remarkable self-healing capabilities. Indeed, after thermal mending at 140°C, PLA/PBAT-based composites achieved a

self-healing efficiency of 68.4%, in contrast to the negligible recovery (13%) observed in the neat PLA-based composites.

Conclusions

The results demonstrate that a multiscale design approach, combining matrix formulation and composite architecture, enables the development of structural thermoplastic composites with effective and repeatable self-healing capability.

References

[1] Z.P. Zhang, M.Z. Rong, M.Q. Zhang, *Prog Polym Sci*, vol. 144, 101724 (2023)
[2] D. Perin, L. Botta, D. Rigotti, A. Dorigato, G. Fredi, A. Pegoretti, *Polymers*, vol. 17, 280 (2025)
[3] M. Coser, D. Perin, G. Fredi, L. Aliotta, V. Gigante, A. Lazzeri, A. Dorigato, A. Pegoretti, *Compos Sci Technol,* vol. 268, 111213 (2026)
[4] D. Perin, G. Fredi, P. Russo, A. Pegoretti, A. Dorigato, *Composites A*, vol. 201, 109393 (2026)

FUNCTIONAL POLYMER HYBRID HYDROGELS FOR MULTI-ADSORPTION OF OPPOSITELY CHARGED EMERGENT POLLUTANTS

G. Proietto Salanitri[1], V. Giglio[2], D. Caretti [1], S. C. Carroccio [2]

[1]Department of Industrial Chemistry "Toso Montanari", University of Bologna, Via Piero Gobetti 85, 40129 Bologna (Italy)
[2]CNR-IPCB, Via Paolo Gaifami 18, 95126, Catania (Italy)

e-mail: giuseppe.proietto3@unibo.it

Introduction

The presence of emerging pollutants, including pharmaceutical residues and heavy metal ions, in surface and groundwater represents a critical environmental and public health challenge [1]. Conventional water treatment technologies often fail to address the chemical diversity of these contaminants, particularly when anionic organic molecules and cationic metal species coexist in the same effluent. Among the available remediation strategies, adsorption-based technologies are widely considered suitable for water treatment because of their simplicity, scalability, and cost-effectiveness [2].

Hydrogel-based adsorbents have attracted considerable interest due to their tunable chemistry, high water uptake, and versatility; however, their adsorption capacity and mechanical stability are frequently limited. The incorporation of inorganic nanofillers offers a viable strategy to overcome these limitations.

Physical incorporation approaches suffer from poor nanoparticle dispersion, leaching during use, and disruption of the polymer network, causing structural instability that undermines both performance and safety. To address these issues, we developed functional polymer hybrid hydrogels in which methacrylate-functionalized mesoporous silica nanoparticles are covalently integrated into a cationic polymer matrix via a one-pot polymerization approach. The design exploits the complementary electrostatic functionalities of the two components, the positively charged polymer backbone and the negatively charged silanol-rich surface of the mesoporous silica, to achieve simultaneous adsorption of emerging pollutants of opposite charge within a single, structurally stable material.

Results and discussion

Bare and methacrylate-functionalized mesoporous silica nanoparticles (MSNPs and MSNPs-MA, respectively) were synthesized via a one-pot co-condensation approach, in which the methacrylate-terminated silane was incorporated directly during the sol-gel process [3]. SEM confirmed a well-defined spherical morphology with narrow size distribution for both materials. Successful functionalization of MSNPs-MA was established by ATR-IR, TGA, and EDX.

Both nanoparticle types were subsequently incorporated into a cationic polymer matrix (10% w/w) via one-pot free-radical polymerization. In the case of MSNPs-MA, the surface methacrylate groups participated directly in the polymerization, forming covalent bonds between the inorganic filler and the growing polymer chains, whereas bare MSNPs were confined within the network exclusively through physical entrapment, without interfacial covalent bonding.

SEM analysis of the resulting hybrid hydrogels confirmed the macroporous structure of the composites and showed significant morphological differences between the two systems. In the hydrogel containing covalently integrated MSNPs-MA, nanoparticles were homogeneously distributed throughout the polymer matrix and visibly embedded within the network, indicating

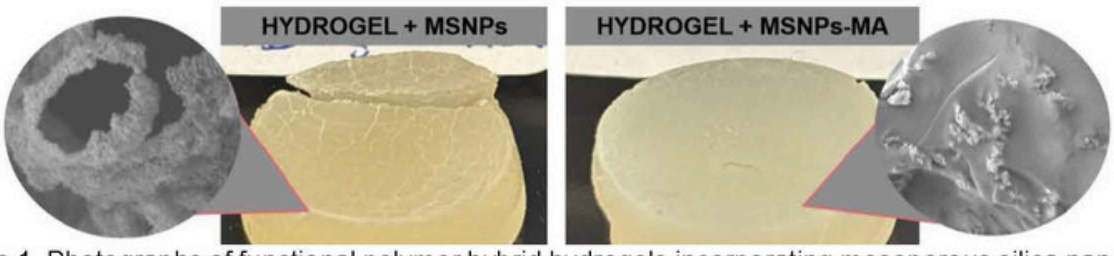


Figure 1. Photographs of functional polymer hybrid hydrogels incorporating mesoporous silica nanoparticles (MSNs) and methacrylate-functionalized MSNs (MSNs–MA). SEM micrographs provide morphological insight into nanoparticle distribution within the hydrogel network.

effective interfacial integration. In contrast, the hydrogel containing physically entrapped bare MSNPs exhibited less uniform filler distribution.
Furthermore, the covalently integrated system displayed greater structural homogeneity and integrity, as the covalent organic–inorganic linkages prevent discontinuities within the network that would otherwise arise from incompatible filler–matrix interfaces.
Preliminary adsorption tests demonstrated the ability of the covalently integrated hybrid hydrogel to simultaneously retain anionic emerging contaminants, including pharmaceutical residues, and cationic heavy metal ions from aqueous solution. Quantitative adsorption isotherms, kinetic profiles, regeneration tests, and selectivity studies in real water matrices are currently in progress to fully assess performance and reusability.

Conclusions

Functional polymer hybrid hydrogels incorporating covalently integrated mesoporous silica nanoparticles were successfully developed via a one-pot polymerization strategy. Comprehensive structural and morphological characterization confirms the formation of a stable organic–inorganic network with homogeneous nanoparticle distribution and absence of leaching. By combining a cationic polymer phase and an anionic mesoporous silica phase within a single material, the hybrid hydrogel enables the simultaneous electrostatic adsorption of emerging pollutants of opposite charge, with quantitative adsorption performance currently under investigation.

References

[1] Nishmitha P.S. et al., *Understanding emerging contaminants in water and wastewater: A comprehensive review on detection, impacts, and solutions*, Journal of Hazardous Materials Advances, 18 (2025), 100755
[2] Bolisetty, S. et al., *Sustainable technologies for water purification from heavy metals: review and analysis*. Chemical Society Reviews, 48 (2019), 463–487
[3] Suzuki K. et al., *Template synthesis of precisely monodisperse silica nanoparticles within self-assembled organometallic spheres*. Nature Chemistry, 2 (2010), 25–29.

SHAPE-CHANGING MULTIPHASE MICROPARTICLES BASED ON LIQUID CRYSTAL EMULSIONS

C. Parmeggiani[1,2], M. Turriani[2], D. Martella[1,2], A. Concellón[3,4]

[1] Dept. of Chemistry, University of Florence, via della Lastruccia 3-13, 50019, Sesto F.no, Italy
2 European laboratory for Non Linear Spectroscopy (LENS), via N. Carrara 1, 50019, Sesto F.no, Italy
3 Instituto de Nanociencia y Materiales De Aragón (INMA), C/ Pedro Cerbuna, 12, 50009, Zaragoza, Spain
4 Dep.of Organic Chemistry,University of Zaragoza, C/ Pedro Cerbuna, 12, 5009, Zaragoza,Spain
e-mail: camilla.parmeggiani@unifi.it

Introduction

Complex multiphase liquid emulsions (i.e., droplets containing two or more immiscible liquid compartments) are versatile soft matter platforms that have been exploited in a wide variety of fields, from drug delivery to sensing, owing to the precise and dynamic control of their morphology. [1]
A higher degree of dynamism can be achieved by employing stimuli-responsive materials as the dispersed phase, with liquid crystals (LCs) representing a particularly powerful choice. [2] LCs are soft materials characterised by long-range molecular order that gives rise to macroscopic anisotropic properties, such as birefringence. When dispersed as colloids, LCs self-assemble into different director field configurations depending on the balance between elastic confinement and interfacial anchoring forces at the droplet surface.[3] Such complex LC emulsions have been explored as platforms for chemical and biological analyte detection, where small perturbations at the interface induce reorientation of the LC director and a measurable optical response. [4]
Few examples have also reported the use of reactive mesogens (i.e., LCs bearing one or more polymerisable moieties) to prepare liquid crystalline networks (LCNs) within emulsion droplets. LCNs are crosslinked materials that deform in a reversible and predictable manner in response to external stimuli. For instance, aligned LCNs can contract macroscopically along the nematic director and perform mechanical work when triggered by different stimuli, and found applicatuion in different fields of research (such as soft robotics, photonics, and biomedicine). [5]

Results and discussion

We introduced a simple and scalable bulk emulsification approach to produce single, double, and triple complex emulsions of reactive liquid crystals, directly addressing the limitations associated with microfluidic fabrication and large droplet sizes in current LC emulsion-based actuators. This strategy enabled the rapid preparation of large quantities of LCN microparticles within a colloidal size regime (10–20 μm). Upon photopolymerization, these emulsions yielded multiphase LCN microactuators that underwent reversible, directional deformation in response to temperature, and, in some cases, also displayed chemoresponsivity through anisotropic swelling in organic solvents. By tuning surfactant composition and crosslinking density, we controlled the internal LC alignment, which in turn dictated the magnitude and the direction of the actuation. The resulting particles exhibited large, fully reversible shape changes, transitioning from spherical to oblate geometries (Figure 1). Importantly, this strategy enabled, for the first time, the fabrication of triple LC emulsions that retained their multi-compartmentalized structure upon polymerization and actively operated as actuators. In addition, the resulting Janus particles exhibited spontaneous gravitational self-orientation, providing a level of collective organization that has not been previously reported. As a proof of concept, we further demonstrated that these multiphase actuators can function as adaptive microlenses, capable of focusing or magnifying projected images under thermal stimulation. [6]

Conclusions

This work therefore establishes a robust and reproducible route for the scalable production of complex multifunctional LCN microactuators, opening new opportunities in adaptive optics, soft robotics, and responsive microsystems.

References

[1] A. Aserin, ed., *Multiple Emulsions: Technology and Applications* (Wiley-Interscience, 2008).
[2] A. Concellón, *Angew. Chem. Int. Ed.*, Vol. 62, 202308857 (2023).
[3] D. S. Miller, X. Wang, N. L. Abbott, *Chem. Mater.* Vol. 26, 496 (2014).

[4] A. Concellón, D. Fong, T. M. Swager, *J. Am. Chem. Soc.* vol. 143, 9177 (2021).
[5] K. M. Herbert, H. E. Fowler, J. M. McCracken, K. R. Schlafmann, J. A. Koch, T. J. White, *Nat. Rev. Mater.*, vol. 7, 23 (2021).
[6] M. Turriani, C. Parmeggiani, D. Martella, A. Concellón, *Adv. Funct. Mater.*, 0:e32069 (2026).

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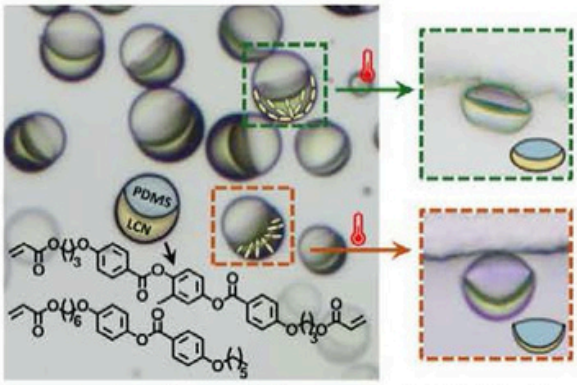


Figure 1. Liquid crystalline network (LCN) micro-particles are prepared from single, dou-ble (Janus), and triple emulsions through a simple and scalable bulk-emulsification strategy. Under heating the particles exhibit robust, reversible, large-amplitude deformations that de-pends both on the morphology and the liquid crystals director field configura-tion. These responses are exploited to realize adaptive microlenses with ther-mally tunable focal plane and magnifi-cation..

FABRICATION OF POROUS MICROPARTICLES BY RAFT POLYMERIZATION

Maya Rovelli, Federica Galmozzi, Michele Mauri and Roberto Simonutti
Department of Materials Science, University of Milan-Bicocca
Via R. Cozzi 55, 20125, Milano Italy

Introduction

Amphiphilic molecules, such as lipids and amphiphilic block copolymers, are well known for their ability to self-assemble in aqueous environments. Upon exposure to water, the amphiphilic molecules organize themselves to minimize the free energy of the system, in such a way that the hydrophilic parts are exposed to water and the hydrophobic parts are sheltered from water. The morphology adopted during the self-assembly process depends on several factors, including temperature, water concentration and the molecular geometry of the amphiphile, the most important factor. The molecular geometric property (packing and curvature) is described by the critical packing parameter p:

$$p = v^*a^*l$$

where v and l are the volume and the length of the hydrophobic chain and a is the optimal surface area of the hydrophilic part at the hydrophilic-hydrophobic interface. The packing parameter determines the preferred curvature of the interface and therefore the type of the self-assembled structure that forms (Figure 1).[1]

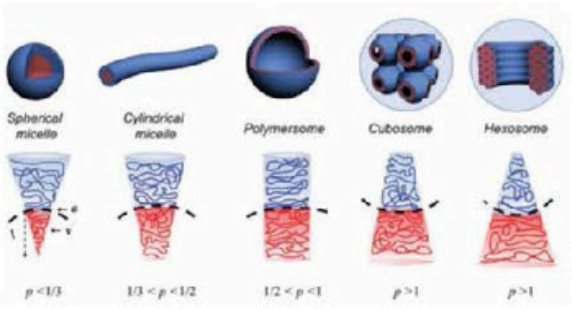


Figure 1: Curvatures and structures determined by the packaging parameter

When p < 1, the interface bends toward the hydrophobic region (positive curvature), leading to normal oil-in-water structures. Conversely, when p > 1, the interface bends toward the aqueous region (negative curvature), favoring inverted structures such as reverse micelles and bicontinuous phases like cubosomes and hexosomes. When p = 1, planar lamellar structures are formed. Polymer cubosomes (PCs) and hexosomes are mesoporous microparticles and possess a long-range ordered, bicontinuous internal porosity; because one of the channel networks remains accessible to the outer environment, they are uniquely suited for encapsulation, release, or templating applications. Compared to their lipid counterparts, which are typically liquid-like, polymer cubosomes exhibit superior mechanical stability. To leverage these advantages, the present work investigated the development and characterization of porous polymeric nanoparticles designed for the effective encapsulation of bioactive agents, controlled delivery and protection of active compounds in biomedical and industrial applications.

Results and discussion

Monodisperse amphiphilic block copolymers based on polystyrene/poly(N,N-dimethyl acrylamide) (PS-*b*-PDMA) and poly(4-vinylpyridine)/polystyrene (P4VP-*b*-PS) were synthesized via RAFT (Reversible Addition-Fragmentation chain Transfer) polymerization using monomers of industrial interest, followed by self-assembly to form nanoparticles [2].
Different hydrophobic/hydrophilic ratios were targeted while maintaining a high proportion of the hydrophobic PS block. In particular, PS-*b*-PDMA copolymers with ratios of 25:1 and 19:1 and P4VP-*b*-PS copolymers with ratios of 1:3, 1:10, and 1:23 were obtained. All polymers were characterized by ^{1}H-NMR to confirm polymer formation and determine reaction yield and average molecular weight, while GPC was used to evaluate molecular weight distribution and the polydispersity index (Đ). Differential scanning calorimetry (DSC) was used to determine the glass transition temperature.
For the PS-*b*-PDMA copolymer, nanoparticles were obtained through self-assembly by the controlled addition of water to the polymer solution after purification by dialysis. In the case of the P4VP-*b*-PS copolymer, a Polymerization Induced Self Assembly (PISA) approach was exploited, thus nanoparticles were already formed at the end of the synthesis, so the self-assembly step was not required. Nanoparticles were characterized by dynamic light scattering (DLS) to determine particle size and by scanning electron microscopy (SEM) to observe morphology and porosity. The porous structure was further investigated by ^{129}Xe-NMR [3]. In Figure 2 the

SEM image of PS_{333}-*b*-$PDMA_{13}$ NPs clearly show the presence of a sponge-like structure with cubic symmetry. The ^{129}Xe NMR spectrum reported in Figure 2 shows the peak corresponding to free xenon at 0 ppm, and the presence of another peak at 22 ppm indicates xenon exchange and the high accessibility of the mesopores.

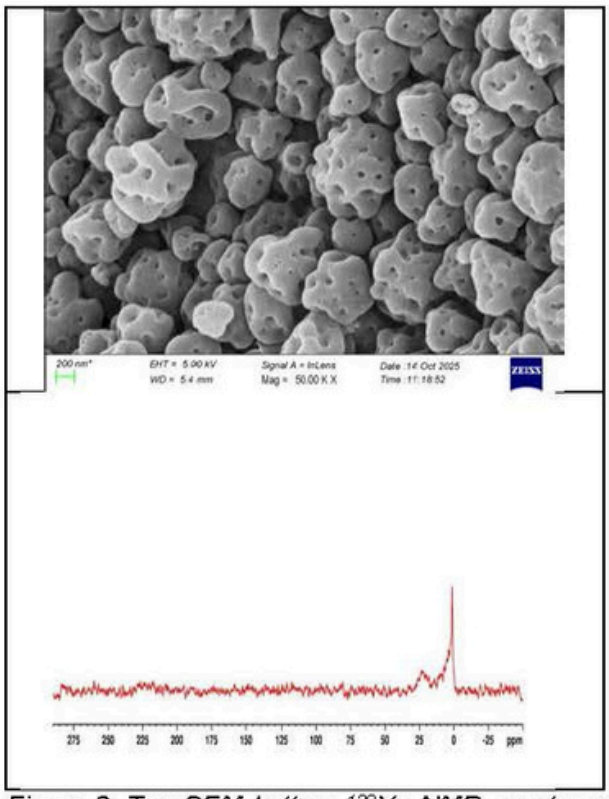


Figure 2. Top SEM bottom ^{129}Xe NMR spectrum of PS_{333}-b-$PDMA_{13}$

Compared to the PS-*b*-PDMA sample, no evident porosity was observed in the SEM images of $P4VP_{70}$-b-PS_{670} NPs (Figure 3). Therefore, ^{129}Xe-NMR was employed to further investigate the accessibility of the NPs. The spectrum (Figure 3) shows the characteristic peak of free xenon at 0 ppm and an additional peak at 212 ppm, which can be attributed to xenon atoms dissolved in the copolymer matrix. This can suggest that a porous structure is present, but xenon exchange does not occur due to the stronger interaction between the aromatic moieties of P4VP and xenon atoms. Since SEM and ^{129}Xe-NMR analyses confirmed an open porosity for the PS_{333}-b-$PDMA_{13}$ NPs, an encapsulation test was performed using curcumin as the molecule to be trapped. Curcumin is photosensitive and in aqueous media undergoes rapid degradation (within 30 minutes) through hydrolysis followed by molecular fragmentation, forming ferulic acid. After the encapsulation, UV-visible spectroscopy was used to determine if curcumin was present inside the nanoparticles or had come into contact with water and degraded. Therefore, UV-Vis analyses were performed on NPs with and without curcumin. By comparing the spectrum obtained with those reported in literature, it can be assumed that curcumin did not undergo degradation.

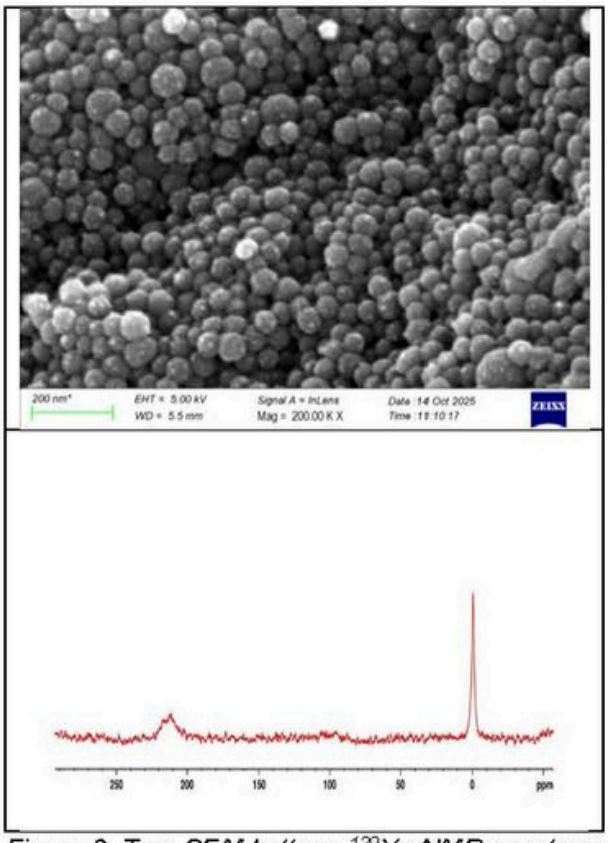


Figure 3. Top; SEM bottom: ^{129}Xe NMR spectrum of $P4VP_{70}$-b-PS_{670}

Finally, to evaluate the NPs as a drug delivery system, in vitro release assays will be performed using the dialysis method to model dissolution kinetics, followed by permeability and cellular uptake studies to assess absorption mechanisms.

Conclusions

RAFT polymerization successfully yielded asymmetric PS-*b*-PDMA and P4VP-*b*-PS copolymers that self-assemble into stable, mesoporous nanoparticles. Extensive characterization confirmed high pore accessibility, while UV-Vis analysis proved that the porous matrix efficiently encapsulates and shields photosensitive curcumin from degradation.

References

[1] Chen, H.; Li, M. H., Macromol. Rapid Commun. 2021, 42 (15).
[2] Truong, N. P.; Jones, G. R.; Bradford, K. G. E.; Konkolewicz, D.; Anastasaki, A.. Nature Reviews Chemistry 2021, 5 (12), 859-869.
[3] Boventi, M.; Mauri, M.; Simonutti, R., Applied Sciences (Switzerland) 2022, 12 (6).

INVESTIGATING BACTERIA-DRIVEN ALGINATE HYDROGEL MATRIX DEGRADATION: A RHEOLOGICAL FRAMEWORK TO DISCRIMINATE BETWEEN CROSSLINKER DEPLETION AND BACKBONE CLEAVAGE

A. Fusari[1], L. Berti [2], S. Solhmirzaei[1], M. Petraretti[2], F. Villa[2], P.Petrini[1], F. Briatico Vangosa[1]

[1] Dept. of Chimica, Materiali e Ingegneria Chimica "G.Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy

[2] Dept. of Scienze per gli Alimenti, la Nutrizione e l'Ambiente, Università degli Studi di Milano, Via Luigi Mangiagalli, 25, 20133 Milano, Italy

e-mail: alice.fusari@polimi.it

Introduction

The development of engineered living materials (ELMs) relies on the encapsulation of microorganisms within hydrated matrices. While hydrogels are widely used due to their non-cytotoxicity, their role is often limited to a passive container. However, moving beyond inert scaffolds to recreate an environment mimicking a native biofilm is crucial to unlock the full functional and metabolic potential of the bacteria, which is otherwise altered or unexpressed in traditional liquid cultures. In nature, when a biofilm faces nutrient starvation, bacteria actively exploit their extracellular polymeric substances as a metabolic reservoir to survive. To investigate whether a similar adaptive behavior occurs within synthetic ELMs, we designed a hydrogel matrix optimized for bacterial viability and subsequently subjected the system to severe nutritional stress. In particular, *Synechocystis* sp. PCC 6803, phtotoautotrophic microorganisms belonging to cyanobacteria philum, were encapsulated (10^6 cells/mL) within a calcium alginate hydrogel matrix formed via internal gelation ($CaCO_3$/GDL in BG-11 medium). Two regimes were imposed: regular nutrient supply and nutrient deprivation to induce stress. Hydrogels' mechanical properties evolution (oscillatory rheometry), and bacterial growth and physiology (cytofluorimetry, microscopy, oxygen mapping) were evaluated over 52 days of culture at room temperature under controlled light conditions.

Results and discussion

Under optimal feeding conditions the hydrogel remains mechanically stable over prolonged periods, and bacteria proliferate without altering the matrix up to 52 days of culture. However, under nutritional stress, while biological analysis shows that bacterial growth initially mirrors the optimal condition, the macroscopic structure of the matrix is severely affected. Rheological monitoring revealed a sharp decline in mechanical properties starting from day 7, with the moduli decreasing by three orders of magnitude in relative short time (Figure 1).

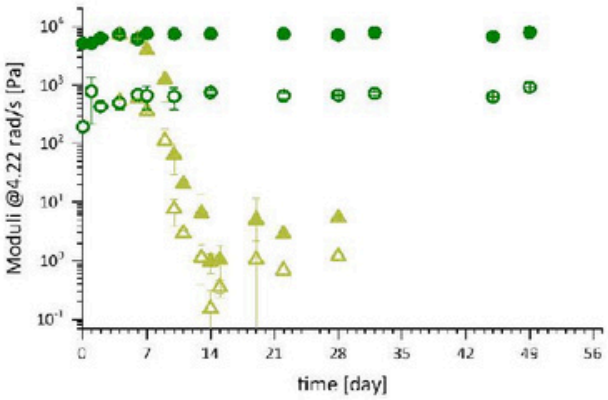


Figure 1. Temporal evolution of storage (full points) and loss (empty points) moduli for hydrogels containing bacteria in optimal feeding condition (dark green dots) and starving condition (pale green triangles).

The microstructural origins of this phenomenon may be attributed to a sequestration of Ca^{2+} ions by the bacteria, with a corresponding reduction of crosslinking density, or to a polymer backbone cleavage. To investigate these hypothesis, and the relative importance of the two causes, we developed a mapping approach based on rheology. Cell-free hydrogels were first formulated from the native alginate using decreasing calcium concentrations (Figure 2). Using this rheological model, it was possible to evaluate the bacteria ion consumption and establish that the very first drop in mechanical properties can be attributed to this phenomenon.

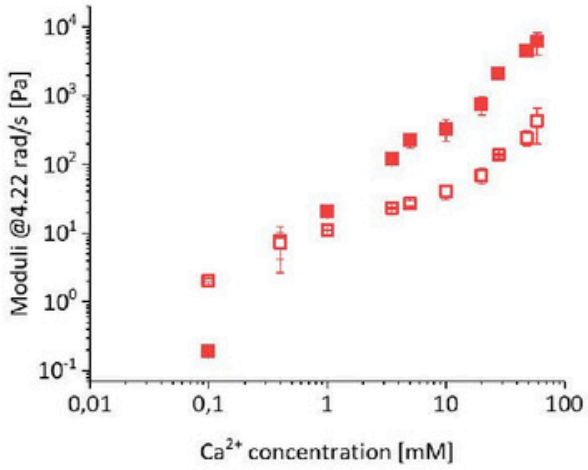


Figure 2. Effect of calcium ions on hydrogel mechanical properties (G' full squares, G'' empty squares).

However, the ion consumption alone fails to explain the system behavior at longer cultivation times (beyond day 10), since continuous calcium extraction should inevitably trigger a transition from hydrogel to viscous solution. In contrast, the rheological data of the degraded starving samples revealed a severe drop in the absolute magnitude of the moduli, but the persistence of an interconnected 3D gel network. The original alginate solution was then subjected to controlled thermal hydrolysis (validated via Mark-Houwink intrinsic viscosity) and crosslinked to form a parallel set of hydrogels, with calcium concentration fixed based on the results of the first mapping (Figure 3).

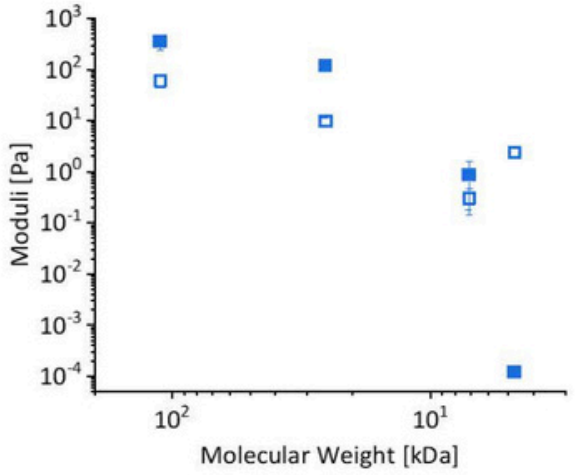


Figure 3. Effect of alginate molecular weight on hydrogel mechanical properties (G' full squares, G'' empty squares).

Given the limited number of tested degradation levels, a purely empirical approach was adopted instead resorting to physics-based modeling, and a rough estimation of the equivalent molecular weight drop over time was obtained. This drastic reduction strongly points toward an active enzymatic cleavage of the alginate chains by the starving cyanobacteria to harvest carbon sources. Remarkably, although this estimation derives exclusively from macroscopic rheological evaluations, it found a direct correspondence in biological assays; preliminary metabolomic analyses successfully confirmed a bacteria metabolic switch, providing a strong biological support to the proposed physical model.

Conclusions

This research leverages macroscopic rheological behavior to decode and quantify how bacteria dynamically alter the surrounding hydrogel structure under nutrient deprivation, successfully decoupling the distinct microstructural phenomena driving the matrix collapse. By combining rheological characterization with advanced biological assays, this study establishes a methodology to investigate bacteria-matrix interactions. Ultimately, it can be expanded to other hydrogel networks and bacterial strains, offering a robust framework for the rational design of responsive microenvironments in engineered living materials.

References

[1] S. Bhusari et al., *Adv. Sci.*, 9, 2106026 (2022)
[2] K. Sauer et al., *J. Bacteriol.*, 184 (4), 1140-1154 (2002)
[3] A. Haug, O. Smidsrod, *Acta Chem. Scand.*, 16, 1569-1578 (1962)
[4] H. Moheimani et al., *Adv. Healthc. Mater.*, 13, 2401550 (2024)

Altri

CONTRIBUTI ORALI

Processabilitá e stampa 3D di materiali polimerici

FROM MARINE PLASTIC LITTER TO 3D PRINTING: OPTIMISING BLENDED POLYOLEFIN FORMULATIONS FOR ADDITIVE MANUFACTURING

Bardelli A.[1], Castellano M.[1], Cavallo D.[1], M. Alloisio[1], Vicini S.[1], Demasi S.[2], Benvenuto L.[2], Mandolfino C.[2], Frascio M.[2], Becherini S.[3]

[1] Dipartimento di Chimica e Chimica Industriale – DCCI, Università di Genova, Genova 16146, Italia
[2] Dipartimento di Ingegneria Meccanica, Energetica, Gestionale e dei Trasporti (DIME), Università di Genova, Genova 16146, Italia
[3] Revet S.p.A., Pontedera 56025, Italia

e-mail: adrianna.bardelli@gmail.com

Introduzione

Il crescente accumulo di rifiuti plastici negli ecosistemi marini rappresenta una delle principali sfide ambientali contemporanee. In questo contesto, il presente studio propone un approccio di economia circolare volto alla valorizzazione delle poliolefine miste (MPO) recuperate dall'ambiente marino come materia prima/seconda per la manifattura additiva. L'elevata eterogeneità di tali materiali, derivante dalla diversa origine e composizione dei manufatti recuperati, rende necessaria l'ottimizzazione della formulazione per garantire adeguate proprietà di processabilità e prestazioni finali. A tal fine, sono state investigate le proprietà termiche, reologiche e morfologiche delle diverse formulazioni di MPO, unitamente alle loro prestazioni meccaniche, con l'obiettivo di valutarne l'idoneità alla realizzazione di componenti funzionali mediante stampa 3D a estrusione diretta di granuli.

Risultati e discussione

Le formulazioni investigate sono costituite principalmente da poliolefine miste (PE/PP) recuperate dall'ambiente marino, opportunamente additivate con antiossidante (Irganox® B215), compatibilizzante (Epolene® E43), un additivo stabilizzante ai raggi UV e due differenti biofiller.

I biofiller utilizzati sono uno a base di $CaCO_3$ (gusci d'uova, ESF) e uno di natura ligno-cellulosica (noccioli d'oliva, OSF), impiegati a diverse concentrazioni. La Figura 1 riporta lo schema delle formulazioni investigate e dei relativi additivi utilizzati.

La caratterizzazione dei materiali è stata condotta mediante analisi termogravimetrica (TGA), calorimetria differenziale a scansione (DSC), microscopia elettronica a scansione (SEM) e

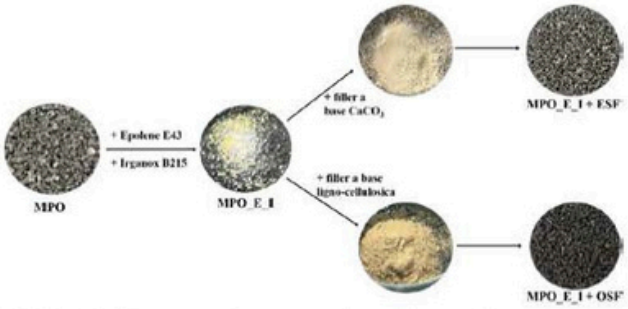


***Figura 1**:Rappresentazione schematica della formulazione dei compositi ottenuti a partire da granuli di MPO.*

prove reologiche in regime oscillatorio, eseguite sia sulle formulazioni iniziali sia dopo 12 cicli di estrusione, al fine di valutarne la stabilità al riciclo meccanico. Successivamente, sono stati realizzati provini normati mediante stampa 3D a estrusione diretta di granuli utilizzando una Delta WASP 4070 High-Definition Pellet (HDP), sui quali sono state eseguite prove di trazione e di flessione a tre punti.

L'analisi TGA ha evidenziato un incremento della stabilità termo-ossidativa nelle formulazioni contenenti Irganox® B215, consentendo inoltre di quantificare il contenuto effettivo di biofiller (nel caso del $CaCO_3$) nella matrice poliolefinica. L'analisi DSC ha confermato una composizione pari a circa 70/30 PE/PP. Inoltre, mediante test condotti in atmosfera ossidativa, è stata determinata la temperatura di induzione all'ossidazione (Oxidation Onset Temperature, OOT), la quale ha mostrato che le formulazioni ottimizzate presentano OOT superiori rispetto all'MPO non additivato, ampliando la finestra di processabilità del materiale.

Le prove reologiche hanno evidenziato un marcato comportamento pseudoplastico e una buona stabilità della viscosità anche dopo ripetuti cicli di estrusione, confermando l'idoneità del materiale alla stampa 3D a estrusione diretta di granuli come evidenziato dai manufatti rappresentativi riportati in Figura 2.



***Figura 2**: Esempi di manufatti ottenuti mediante stampa 3D a partire da granuli di MPO additivati.*

Dal punto di vista meccanico, l'impiego combinato di compatibilizzante e biofiller ha determinato un significativo incremento del modulo di Young, del modulo e della resistenza a flessione e della resistenza a trazione rispetto all'MPO tal quale. Le osservazioni SEM hanno inoltre evidenziato un miglioramento dell'adesione interfacciale e una sostanziale riduzione dei vuoti strutturali, confermando l'efficacia dell'azione compatibilizzante dell'Epolene® E43. Nel complesso, la caratterizzazione integrata ha permesso di individuare una formulazione in grado di coniugare stabilità termo-reologica, buone prestazioni meccaniche e buona stampabilità mediante tecnologia HDP. I risultati dimostrano che, nonostante l'eterogeneità e il degrado tipici delle plastiche recuperate dall'ambiente marino, un'adeguata strategia di stabilizzazione e compatibilizzazione ne consente la valorizzazione in materiali adatti alla manifattura additiva, promuovendo un modello di economia circolare ad alto valore aggiunto.

Conclusioni

Questo studio dimostra la fattibilità della rigenerazione delle poliolefine miste recuperate dall'ambiente marino in materiali idonei alla produzione additiva mediante tecnologia HDP. L'approccio proposto rappresenta una strategia promettente per la valorizzazione di rifiuti plastici eterogenei, contribuendo allo sviluppo di processi di manifattura sostenibile e di modelli di economia circolare.

Ringraziamenti

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In Situ Stereocomplex Formation During Melt Extrusion: An Efficient Nucleating Strategy for Crystallization of High-Molecular-Weight PLA

Rocco Di Girolamo[1], Massimo Christian D'Alterio,[1] Lorenzo Lombardi,[2] Alessandra Cicolella,[1] Antonio Ascione,[1] Sonia Stornaiuolo,[1] Pier Luca Maffettone,[2] Claudio De Rosa[1]

[1]Department of Chemical Sciences, University of Naples Federico II, Naples, Italy
[2]Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Italy

e-mail: rocco.digirolamo@unina.it

Introduction

Poly(lactic acid) (PLA) is one of the most promising bio-based and biodegradable polymers because it combines renewable origin, biocompatibility, good mechanical properties, easy processability, and relatively low production cost. Consequently, PLA has found widespread applications in packaging, biomedical devices, and consumer products. However, its industrial use still present some issues such as slow crystallization kinetics, low heat resistance, brittleness, and modest thermal stability.

PLA is commonly produced by ring-opening polymerization of L- and D-lactide, yielding poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). Blending these enantiomeric polymers promotes the formation of stereocomplex (SC) crystals, whose melting temperature (220–230 °C) is significantly higher than that of PLA homocrystals [1]. As a result, SC formation provides an effective route to improve the thermal stability, crystallization rate, and mechanical performance of PLA. Nevertheless, stereocomplex crystallization is generally favored only in blends of low- or moderate-molecular-weight enantiopure polymers, whereas commercially relevant high-molecular-weight systems exhibit strong competition between stereocomplexation and homocrystallization, limiting SC formation.

Besides improving thermal and mechanical properties, SC crystallites are also highly effective nucleating agents for the α-crystalline form of PLA. Compared with conventional heterogeneous nucleating agents, stereocomplex crystals offer excellent compatibility with the PLA matrix, superior thermal stability, and preserve the fully bio-based and biodegradable nature of the material. Although several inorganic and organic nucleating agents have been proposed to accelerate PLA crystallization, they often require additional compounding steps and may present compatibility or dispersion issues.[2]

In this study, we propose a simple melt-extrusion strategy to induce *in situ* stereocomplex crystallization in high-molecular-weight (M_w > 100 kg/mol) PDLA/PLLA blends, including systems containing stereodefective PLLA with up to 12% D-lactide defects. This composition range extends well beyond the conditions previously reported in the literature for efficient SC formation. The pre-formed stereocomplex crystallites generated during extrusion subsequently act as highly efficient nucleating sites for α-PLA crystallization, eliminating the need for conventional nucleating additives. Moreover, by combining enantiopure PDLA with stereodefective PLLA, the amount of stereocomplex and overall crystallinity can be finely tuned, providing an effective approach to tailor the balance between stiffness, strength, ductility, and processing performance in industrially relevant PLA materials.

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Results and discussion

Different PDLA/PLLA blends were prepared by melt extrusion (Table 1) to investigate the influence of blend composition on PLA stereocomplex formation. The blends differed in the stereoregularity of the PLLA component, the PDLA/PLLA weight ratio, and the extrusion temperature, while the PDLA component was always enantiopure (sample PDLA100). Most blends present a 50:50 PDLA/PLLA weight ratio, while Blend 2 contained a 75:25 ratio of the enantiopure components. Blends 3 and 5 contained only 1 wt% PDLA to promote the formation of trace amounts of stereocomplex crystals and investigate their nucleating effect on the crystallization of the dominant α-PLA phase.

Table 1: Composition, weight ratio, and fraction of stereocomplex phase (f_{SC}) of the PDLA/PLLA blends determined from DSC. The blends vary in the L-lactide content of the PLLA component

(from 88% (sample PLLA88) to 100% (sample PLLA100))

Blend	Samples	Weight ratio	f_{sc} (%)
1	PDLA100-PLLA100	50:50	99
2	PDLA100-PLLA100	75:25	73
3	PDLA100-PLLA100	1:99	2
4	PDLA100-PLLA98	50:50	98
5	PDLA100-PLLA98	1:99	<1
6	PDLA100-PLLA96	50:50	32
7	PDLA100-PLLA92	50:50	2
8	PDLA100-PLLA92	50:50	2
9	PDLA100-PLLA88	50:50	<1
10	PDLA100-PLLA88	50:50	-
11	PDLA100-PLLA88	50:50	-

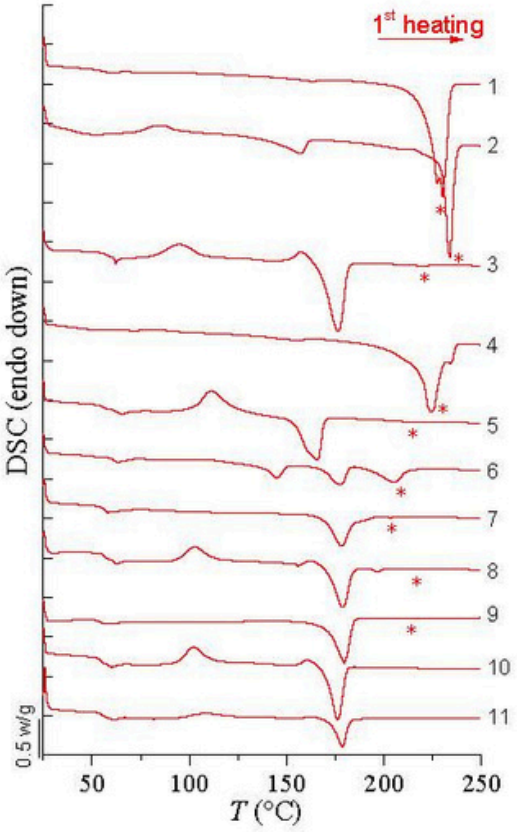


Figure 1. *First-heating DSC thermograms of the extruded PDLA/PLLA blends recorded at a heating rate of 10 °C min⁻¹. The asterisks indicate the stereocomplex (SC) melting endotherms, which are barely detectable in some samples because of the low SC content.*

DSC analysis (Figure 1) confirmed that stereocomplex formation strongly depends on blend composition, stereoregularity, and processing conditions. Blends 1 and 4 (50:50 enantiopure PDLA/PLLA) exhibited almost exclusive SC crystallization, with a melting peak at 225–230 °C. Blend 2 (75:25) also showed predominant SC formation (73%), whereas blends 3 and 5 (1 wt% PDLA) contained only trace amounts of SC. Reducing PLLA stereoregularity progressively decreased SC formation: Blend 6 (96% L-LA) still developed a significant SC fraction (32%), while blends 7 and 8 (92% L-LA) formed only traces of SC. For the most stereodefective systems (88% L-LA), SC crystallization was observed only in Blend 9, whereas blends 10 and 11, processed at higher temperatures, remained amorphous and did not develop SC even after annealing.

The nucleation experiments demonstrate that stereocomplex crystallites significantly enhance the crystallization of the PLA α-form. Blends containing trace or moderate amounts of SC were selected to evaluate their nucleating ability. Blend 3 (1:99 PDLA/PLLA) shows ~2% SC and a nucleation efficiency (NE) [3] of 63.2%. Blend 6 (50:50 with PLLA96) contains a higher SC fraction (f_{SC} = 32%) and exhibits a stronger nucleating effect, with NE slightly exceeding 100%. Blend 8 (50:50 with PLLA92) forms only ~2% SC but still achieves a high NE of 79.1%.Overall, SC crystallites act as highly efficient nucleating agents even at very low concentrations. The nucleation efficiency can be tuned by controlling blend composition and stereodefect content.

Conclusions

The study demonstrates that high-molecular-weight PDLA/PLLA blends (M_w > 100 kg/mol) can successfully form stereocomplex crystals via melt extrusion, even in systems containing up to 12% stereodefects. The SC and α phases coexist, with their relative amounts strongly dependent on blend composition, stereoregularity. In situ-formed SC crystallites act as highly efficient nucleating agents for α-PLA crystallization. An efficient nucleation behavior can be achieved for different compositions, highlighting strong tunability of the system. This allows controlled modulation of crystallinity and thermomechanical properties without sacrificing high molecular weight. Overall, melt extrusion provides a route to design fully bio-based PLA materials with tailored crystallization behavior.

References

[1] H. Tsuji, Macromol. Biosci., 5(7), 569–597. (2005)

[2] T. Ageyeva, J.G. Kovács, T. J.Tábi, *Therm Anal Calorim.* 147, 8199–8211,(2022)

[3] B. Fillon, B. Lotz, A. Thierry, J. C. Wittmann, *J. Polym. Sci., Part B: Polym. Phys.*, *31*, 1395–1405 (1993).

EFFECT OF NATURAL FILLERS AS SUBSTITUTES FOR GLASS FIBERS IN POLYAMIDE 6 COMPOSITES FOR LARGE-FORMAT ADDITIVE MANUFACTURING

A. Sorze [1], F. Valentini [1], N. Soligo [2], L. Pasquardini [3,4], A. Dorigato [1]

[1] Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123, Trento, Italy
[2] Tessilquattro S.p.A., Via Linfano 9, 38062 Arco, Italy
[3] Indivenire Srl, Via Sommarive 18, 38123 Trento, Italy
[4] Department of Engineering, University of Campania Luigi Vanvitelli, Via Roma 29, 81031 Aversa, Italy

e-mail: alessandro.sorze@unitn.it

Introduction

In recent years numerous industries, in the polymer field, have increasingly adopted Large-Format Additive Manufacturing (LFAM) to facilitate cost-effective mass customization and the production of structurally robust, large-scale components for aerospace, automotive, energy and buildings applications. Among engineering polymers suitable for LFAM, glass fibers (GF)-reinforced thermoplastic composites are widely employed in pellet-fed extrusion systems, providing excellent performance. However, the extensive use of GF presents several drawbacks, including increased material density, high processing energy, elevated nozzle wear, and sustainability concerns. Moreover, GF-based composites are not chemically recyclable at the end of their life. This study systematically investigates the potential of natural fillers – including clay, calcium carbonate and silica – as alternative reinforcement for PA6-based composited in LFAM applications in order to guarantee the chemical recyclability of the produced materials [1].

Three different PA6-based composites were produced by melt-compounding at 235 °C. Specifically, formulations containing 10 wt% of organo-modified clay, 10 wt% calcium carbonate and 5 wt% of organo-modified silica were developed and compared with a conventional 30 wt% GF-reinforced PA6 system from rheological, morphological and thermo-mechanical perspectives.

Results and discussion

From rheological analysis, GF-reinforced samples showed the highest viscosity and lowest melt flow index due to the combined effect of high fiber aspect ratio and high filler loading. Clay and silica also displayed an increase in melt viscosity as a result of their agglomerated morphology and higher particle size, whereas calcium carbonate showed a limited effect on rheological properties due the smaller particle size. TGA and DSC analysis revealed that the thermal decomposition and melting behavior of the samples were not significantly affected by the filler addition, with variations observed only in the residual mass at 700 °C (due to filler content) and in the slight increase in crystallinity due to nucleating effect of the filler. The selected compositions were used for preliminarily print LFAM components (Figure 1). Qualitative and morphological analysis revealed a good filler dispersion of natural-reinforced composites and better printing quality compared to GF-reinforced sample. Flexural tests showed that silica and calcium carbonate could provide a more balanced mechanical response both parallelly and perpendicularly to the printing direction, thereby reducing anisotropy.

Conclusions

These results are especially promising considering that the natural fillers were used at significantly lower loadings (≤ 10 wt%) compared to the 30 wt% glass fibers reference, yet they were still able to provide competitive mechanical performance. This highlights the potential of selected natural fillers as viable, lightweight and eco-sustainable alternative to conventional GF reinforcement in LFAM applications.

References

[1] A. Sorze, et al., *Polymers*, vol. 18, 1049 (2026)

Acknowledgments

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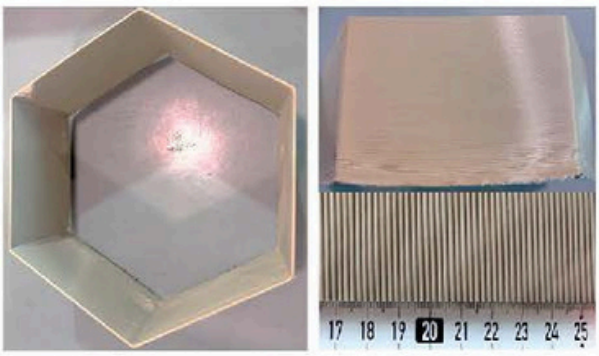


Figure 1. Representative images of a printed LFAM formulation (PA6-10-Clay).

Deadlines:

Submissions must be received no later than June 21, 2026. The abstracts must be uploaded via the platform https://aim.planetweb-it.com after registering with AIM and signing up for the AIM congress, as indicated in the "Registrazione" section.

INFLUENCE OF GRAPHENE ON THE ELECTRICAL AND MECHANICAL PROPERTIES OF SLS-PRINTED PA11

E. Togliatti[1,2], C. Sciancalepore[2,3], F. Toniato[3], R. Giovanardi[1,4], H. Andersson[5], L. Bond[5], Magnus Larsson[6], Magnus Engholm[5], D. Milanese[2,3]

[1] Dipartimento di Ingegneria e Architettura, Università degli Studi di Parma, Parco Area delle Scienze 181/a, 43124, Parma, Italy
e-mail: elena.togliatti@unipr.it
[2] INSTM, Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali, Firenze, Italy
[3] Dipartimento di Ingegneria dei Sistemi e delle Tecnologie Industriali, Università degli Studi di Parma, Parco Area delle Scienze 181/a, 43124, Parma, Italy
[4]Dipartimento di Ingegneria Enzo Ferrari, Università di Modena e Reggio E., Modena, Italy
[5]Department of Engineering, Mathematics and Science Education, Mid Sweden University, Sundsvall, Sweden
[6]2D fab AB, Montörvägen 7, SE-853 50, Sundsvall, Sweden

Introduction

In recent years, there has been a growing demand for multifunctional polymeric materials, particularly in applications requiring a combination of mechanical, thermal and electrical properties. [1] Carbon-based nanofillers have attracted significant interest due to their remarkable physical and chemical properties [2]. Specifically, the integration of graphene into polymer matrices has been demonstrated to enable the creation of nanocomposites with dramatically enhanced performance even at very low filler loadings [3].
Polyamide 11 (PA11), a bio-based polymer derived from renewable resources, is widely used in 3D printing via selective laser sintering (SLS) thanks to its excellent processability.
However, PA11 is electrically insulating and, to overcome this limitation, it can be reinforced with nanostructured graphene, enabling the development of electrically conductive materials for applications such as electromagnetic interference (EMI) shielding, antistatic components, sensors, and smart devices.

The main objective of this work was to study the effect of graphene on the structural, thermal, mechanical and electrical properties of PA11 following SLS processing.
However, due to its naturally white color, the pure polymer exhibited low laser absorption and could not be processed using a commercial SLS printer equipped with a 5 W laser. To overcome this issue, 1 wt.% of biochar was added, by mechanical mixing, to improve laser absorption and enable 3D printing.
For this reason, PA containing 1 wt.% biochar (PA11B), rather than pure PA11, was taken as the reference material for the target material PA11 containing 2 wt.% graphene (PA11G).
Tensile test specimens of model 5A (according to ISO 527 standard) were printed for structural and thermo-mechanical characterizations, that included uniaxial tensile test and dynamic-mechanical analysis (DMA), differential scanning calorimetry (DSC), and Fourier-transform infrared analysis (FT-IR).
For electrical conductivity characterization, which was conducted acquiring voltage-current characteristic curves (DC conditions) for PA11G and impedance spectra for PA11B, disk samples with a 12 mm diameter and 1 mm thickness were printed.

Results and discussion

Morphological analysis of the powders by digital optical microscopy revealed that the biochar particles were clearly distinguishable from the PA11 particles, whereas the graphene was more uniformly dispersed and adhered to the surface of the polymer particles, likely due to the processing method used (Figure 1).

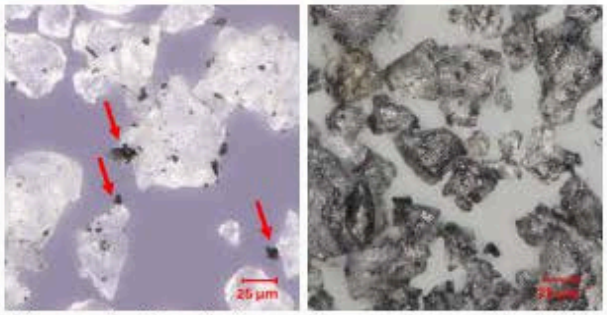


Figure 1 Morphology of powders with 1000x magnification: PA11B (left), PA11G (right)

After SLS, the surface exhibited the typical rough morphology of powder bed fusion and the graphene composite appeared more compact, confirming improved consolidation during 3D printing (Figure 2).

FT-IR analysis confirmed that the chemical structure of PA was retained after the addition of

the fillers and the SLS process. However, a variation in the intensity of CH_2 rocking band (720 cm^{-1}) and of the Amide V peak (683 cm^{-1}) (Figure 3) suggested a rearrangement of the polymer chain packing induced by thermal process [4].

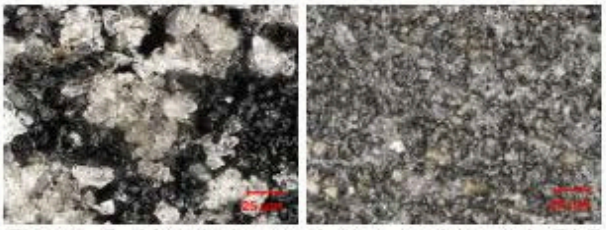


Figure 2 Morphology of the surface of SLS samples with 1000x magnification: PA11B (left), PA11G (right)

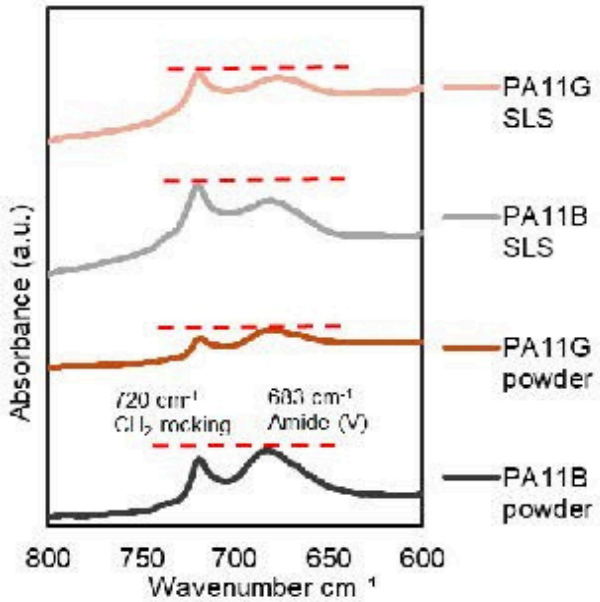


Figure 3 Region of interest of FT-IR scan showing the different intensity of peaks before and after the SLS

In DSC analysis, the first heating scan was considered, representing the effect of the material's thermal history. The pristine powders exhibited a single melting peak characteristic of stable crystalline phase, whereas the SLS printed samples showed a double melting peak, suggesting a more complex structural order. This behavior is coherent with the effect of the SLS process, which involves localized melting followed by non-equilibrium cooling and recrystallization [5]. Overall, the results highlighted a reduction in crystallinity after SLS, indicating a decrease in structural order.

Mechanically, the PA11G displayed increased stiffness but a significant reduction in ductility and toughness, which is typical behavior of polymers reinforced with non-interacting nanomaterials.
This was also corroborated by DMA results, with a higher storage modulus over the entire temperature range. This finding confirmed an increase in stiffness, while the overall thermal behavior remained essentially unchanged.

The most significant difference was observed in the electrical properties, with PA11G exhibiting a reduction in resistivity of approximately ten orders of magnitude compared with PA11B (Table 1). PA11G exhibited ohmic behavior, characterized by a linear current-voltage (I-V) relationship, whereas the inability to perform the DC method on PA11B samples suggested a highly insulating behavior. This result suggested that the addition of 1 wt.% biochar to PA11 did not affect its electrical insulating properties.
In contrast, nanographene effectively promoted the formation of conductive pathways throughout the SLS-processed structure, leading to the achievement of the electrical percolation threshold and the development of a conductive network within the polymer matrix.

Table1 Resistivity values

	PA11G	PA11B
Resistivity ρ [Ωm]	4.7	$2.45 * 10^{10}$

Conclusions

The study demonstrates that graphene is a highly effective filler for enhancing the electrical conductivity and stiffness of PA11-based composites, whereas the biochar-reinforced reference retains the electrical insulating properties of the polymer. Furthermore, the thermal history associated with the SLS process resulted in a decrease in the overall crystallinity of the polymer, suggesting a modification of the structural order within the 3D printed matrix. Overall, this research highlights the potential of graphene as an effective reinforcing filler for the development of sustainable and multifunctional PA11-based composites for advanced technological applications.

References

[1] L. Jolly, A. Tidu, J. J. Heizmann, and B. Bolle, *Polymer (Guildf)*, vol. 43, no. 25, pp. 6839-6851, (2002).

[2] S. Pei and H. M. Cheng, *Carbon N. Y.*, vol. 50, no. 9, pp. 3210–3228, (2012).

[3] V. B. Mohan, K. tak Lau, D. Hui, and D. Bhattacharyya, *Compos. B Eng.*, vol. 142, pp. 200–220, (2018).

[4] M. Daniels, M. Rautenbach, A. du Plessis, and R. Pfukwa, *Macromol. Mater. Eng.*, vol. 309, no. 8, p. 2400071, (2024).

[5] U. F. Gunputh, G. Williams, M. Pawlik, Y. Lu, and P. Wood, *Polymers 2023*, vol. 15, no. 23, p. 4602, (2023).

FUSED FILAMENT FABRICATION OF TPU/PCM COMPOSITES FOR THERMALLY ACTIVE WEARABLE SPORT APPLICATIONS

D. Rigotti[1,2], A. Dorigato [1,2], A. Pegoretti [1,2]

[1] Department of Industrial Engineering, University ofTrento, via Sommarive 9, 38123, Trento, Italy
[2] National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy
e-mail: daniele.rigotti-1@unitn.it

Introduction

Thermal comfort is a key requirement in sport and wearable equipment, especially in applications exposed to cold environments, such as ski-boot liners, insoles, gloves and protective pads. Conventional flexible polymers can provide cushioning, adaptability and mechanical comfort, but they generally do not provide an active thermal-buffering function. Phase-change materials (PCMs) represent an interesting solution because they can absorb thermal energy during melting and release it during crystallization within a relatively narrow temperature range [1]. Their use in smart textiles and wearable systems has already been widely investigated for passive thermal regulation. However, the direct incorporation of solid–liquid PCMs into polymeric matrices may cause leakage after melting. Microencapsulation is commonly used to overcome this limitation, since the PCM is confined within a polymeric shell while preserving latent heat storage capability.

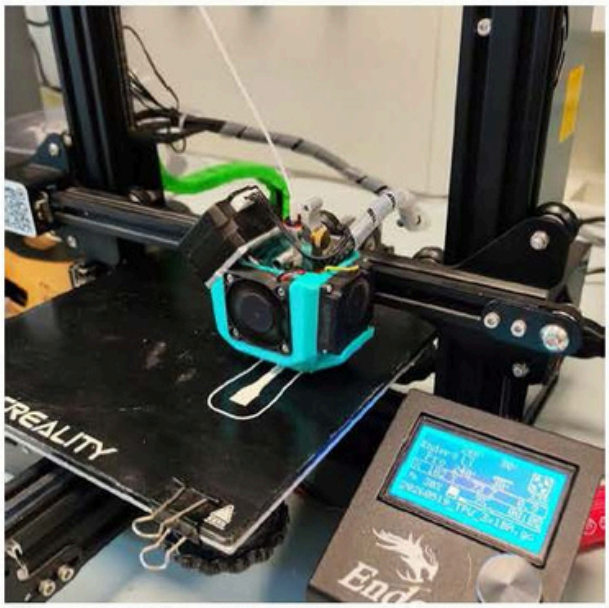


Figure 1. FFF machine during printing.

TPU was selected because of its flexibility, elastomeric behavior and thermoplastic processability, making it suitable for customized wearable components.

Thermoplastic polyurethane blends containing microencapsulated phase-change materials have previously been developed as flexible systems for latent heat storage and release [1]. Their processability by fused filament fabrication (FFF) (Figure 1) was then demonstrated, showing the possibility of producing 3D-printed TPU/PCM components for potential winter sport applications [2]. Further investigations addressed their durability under repeated compressive loading [3], while more recent works explored the introduction of multiwalled carbon nanotubes to improve multifunctionality and thermal transport [4,5].

Results and discussion

The incorporation of microencapsulated PCM provided the TPU composites with significant latent heat storage capability. As expected, the heat of fusion increased with increasing PCM content. Importantly, the 3D-printed samples retained useful thermal storage capability after filament extrusion and FFF processing, reaching approximately 70 J/g for the highest printable PCM content [2]. This indicates that most of the microcapsules survived the thermal and mechanical stresses associated with compounding, extrusion and printing. Morphological observations confirmed that the PCM microcapsules were relatively well dispersed within the TPU matrix, without extensive agglomeration. The printed strands showed acceptable cohesion, although FFF processing introduced voids and local defects between adjacent deposited layers. These defects are typical of extrusion-based additive manufacturing and are particularly relevant for mechanical performance, because they reduce the effective load transfer within the printed structure. Mechanical tests highlighted the main trade-off of the material platform. Increasing PCM content increased stiffness, because the comparatively rigid microcapsules restricted the deformation of the flexible TPU matrix. At the same time, tensile strength and especially strain

at break decreased with increasing PCM content. This reduction was more pronounced in the 3D-printed samples than in compression-molded specimens, due to the combined effect of filler loading and process-induced porosity. Low-cycle compressive fatigue tests showed that repeated loading can strongly affect the mechanical response of the printed composites. At low applied stress, the normalized elastic modulus remained relatively stable. Conversely, under the most severe loading condition, corresponding to 0.5 MPa, a marked decrease in stiffness occurred, mainly during the first cycles. The absorbed mechanical energy followed a similar trend (Figure 2), suggesting irreversible structural rearrangement, local deformation of printed strands and progressive damage within the porous printed architecture.

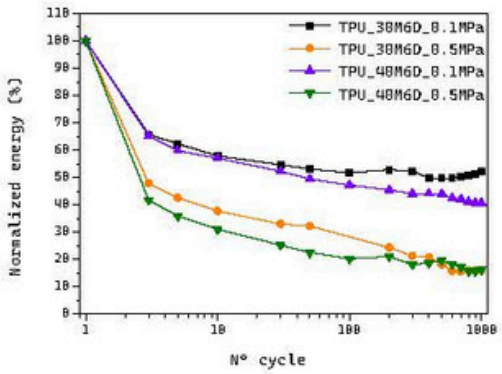


Figure 2. Evolution of normalized absorbed energy from compression fatigue tests on TPU_30M6D and TPU_40M6D samples.

The most relevant result emerged when mechanical degradation was compared with thermal functionality after fatigue. Despite the strong reduction in mechanical stiffness and absorbed energy under severe compressive cycling, the latent heat storage capability remained largely preserved. Melting and crystallization enthalpies were generally retained above approximately 80% of their initial values. This indicates that mechanical damage in the printed structure occurs earlier than loss of thermal function. In other words, the printed architecture may degrade mechanically while most PCM microcapsules remain sufficiently intact to preserve their latent heat storage capability. Carbon nanotube addition represents a possible strategy to improve the thermal transport properties of the TPU/PCM system [5]. Increasing the effective thermal conductivity can accelerate heat transfer through the material and promote faster crystallization during cooling (Figure 3). However, CNT addition also introduces an additional trade-off, because it may further increase stiffness and reduce ductility. Therefore, CNTs should be considered primarily as multifunctional fillers for thermal transport and possible electrical functionality, rather than as simple mechanical reinforcement.

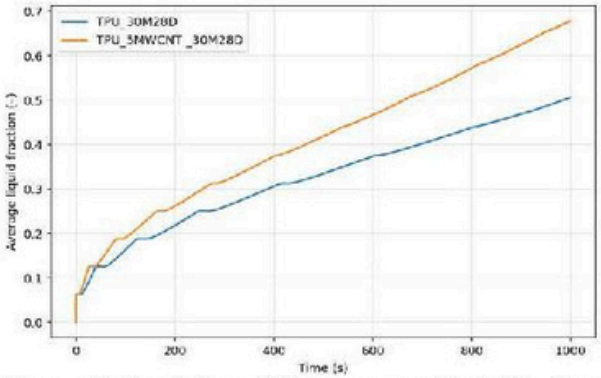


Figure 3. Evolution of the average liquid fraction of PCM during heating from 5 °C to 50 °C for TPU_30M28D and TPU_5MWCNT _30M28D samples.

Conclusions

This work demonstrates the feasibility of processing TPU composites containing microencapsulated PCM by filament extrusion and fused filament fabrication. The printed materials retained significant latent heat storage capability, confirming that FFF is compatible with the production of flexible thermally active structures. The results also show a clear compromise between thermal functionality and mechanical deformability. Increasing PCM content improves latent heat storage but reduces ductility and fatigue resistance, especially in printed samples where interlayer voids contribute to mechanical weakening. Nevertheless, thermal functionality was more robust than mechanical performance under compressive fatigue, with enthalpy retention generally remaining above 80% even after severe cyclic loading.

References

[1] A. Dorigato, D. Rigotti, A. Pegoretti, Frontiers in Materials, vol. 5, 58 (2018)
[2] D. Rigotti, A. Dorigato, A. Pegoretti, Materials Today Communications, vol. 15, 228-235 (2018)
[3] D. Rigotti, A. Dorigato, A. Pegoretti, Journal of Applied Polymer Science, vol. 138, 49704 (2021)
[4] D. Rigotti, A. Dorigato, A. Pegoretti, Applied Sciences, vol. 14, 9614 (2024)
[5] D. Rigotti, A. Dorigato, A. Pegoretti, Journal of Composites Science, vol. 10, 10 (2026)

EXTENDING RUBBER FRACTURE CHARACTERIZATION METHODS TO LAYER ADHESION ASSESSMENT IN 3D-PRINTED TPU

Andrea Caccini[1], Shiva Khoshtinat[1], Manuel Sardinha[2], Maria de Fatima Reis Vaz[2], Sofia Teixeira Freitas[2], Claudia Marano[1]

[1] Department of Chemistry, Materials and Chemical Engineering "Giulio Natta" Politecnico di Milano, Milan MI 20133, Italy

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[2] 2IDMEC, Instituto Superior Técnico, Universidade de Lisboa, Av Rovisco Pais, 1049−001 Lisbon, Portugal

e-mail: andrea.caccini@polimi.it

Introduction

Additive manufacturing is increasingly adopted in engineering applications, owing to its design flexibility, efficient material utilisation, and potential for sustainable production. In the mobility sector, it has recently attracted interest in the manufacture of airless tyres, which offer improved safety and durability compared with traditional pneumatic tyres [1]. Within this context, this study, carried out in collaboration with Instituto Superior Técnico (IST), University of Lisbon, investigates the use of fracture mechanics methods to characterise interlayer adhesion in 3D-printed specimens made of thermoplastic polyurethane (TPU), which is one of the most investigated materials for this application.

Material

The experimental material used is Flexfill TPU 92A, a thermoplastic polyurethane filament (1.75 mm diameter) produced by Fillamentum Additive Polymers. Since the material is highly hygroscopic and prone to print defects, all spools were stored in a climate-controlled cabinet with desiccant salts before and after usage.

Pure shear specimens were fabricated at Lisbon University using a Prusa MK4 printer equipped with a 0.4 mm nozzle and an external cooling system. The specimens were printed in a YZX orientation with a concentric infill pattern and with the following printing parameters:

- Printing Temperature: 235°C vs. 240°C nozzle (with bed temperature fixed at 50°C)
- Layer Thickness: 0.2 mm vs. 0.3 mm
- Cooling Fan: ON vs. OFF

Structurally, the central body of each specimen comprises four filaments along the width (parallel to the printing Y-axis) and two different numbers of total layers that depend on the layer thickness, 102 in the case of a layer thickness of 0.2 mm and 69 in the case of 0.3 mm.

To realise fracture analysis, a 15 mm pre-crack was introduced at the mid-height of one specimen edge. The notch was precisely cut with a razor blade using a custom-made rigid mask designed for the 3D-printed geometry.

Results and discussion

The energy-based fracture parameter J-integral has been calculated as a function of the displacement (d) following with Eq. (1) according to [2]

$$J(d) = \eta \frac{U(d)}{B(W - a(d))} \qquad \text{Eq. (1)}$$

U is the input energy, B is the specimen thickness, $W - a$ is the actual ligament length and η is a dimensionless geometry-dependent parameter, equal to 1 for the adopted specimen geometry.

Higher J-integral values were obtained for the same crack advancement when the layer thickness of 0.2 mm and the printing temperature of 240°C (data not reported).

The evolution of crack propagation as Δa over time (Figure 1) has been evaluated using Tracker software, which enabled the manual tracking of the crack tip position during the test.

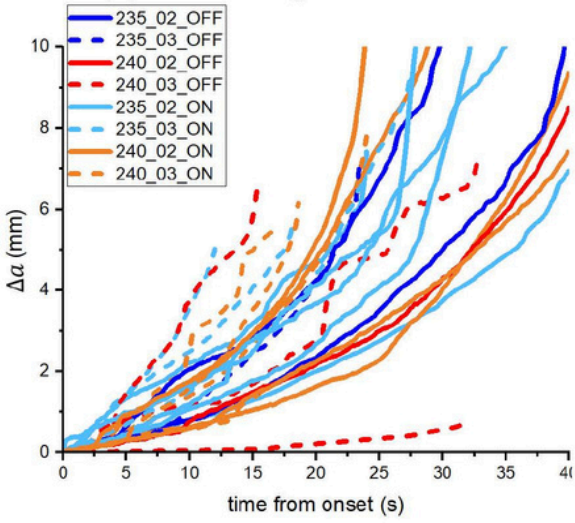


Figure 1: Crack advancement, Δa in time for the different printing conditions

Regardless of the printing parameters, crack propagation is initially slow and then accelerates. A stick-slip behaviour, characterised by discrete

crack advancements, has been observed for thicker layers printed at 235°C with active cooling. Fracture surfaces were observed at a Leica M205C stereomicroscope coupled with an MC 105 HD camera. Four main defect types (coupled pore-protrusion, small crack, diatomee-like and inter-beads gap) were observed: they were found to be more frequent for the lower printing temperature used of 235°C. Full-length surface imagery was compared with propagation curves, as visible in Figure 2, the presence of a defect appears to be correlated to changes in the advancement speed of the crack.

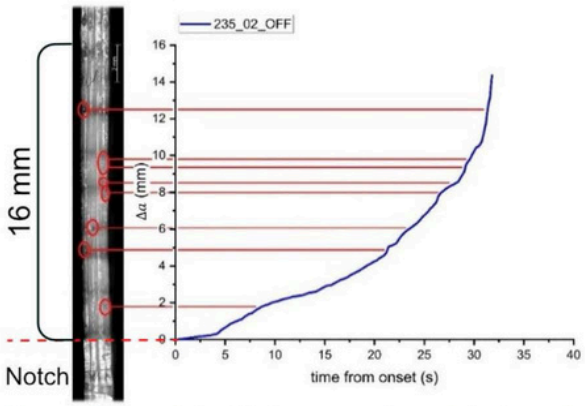


Figure 2: correlation between surface defects and slope changes in Δa -time curve

A wider experimental campaign involving a greater number of specimens is required to validate the correlation between defect characteristics and their specific effects on the material's fracture response.

Figure 3a reports J-integral values at the crack onset: for the printing temperature of 235°C, the lowest values have been obtained, irrespective of the layer thickness, whereas for 240°C, the highest J-integral values were obtained for the lower layer thickness of 0.2 mm.

Figure 3b reports J-integral values at the maximum force, J_{max}, at which the catastrophic failure of the specimen occurred. For the layer thickness of 0.2 mm, higher J_{max} values were obtained. The higher printing temperatures slightly increased J_{max} but introduced wider data dispersion, while external cooling had no significant effect

The data dispersion is likely due to a higher defect density on the fracture surfaces of the specimens printed at 235°C, which prematurely lowers the energy required for crack initiation while leaving the ultimate maximum value largely unaffected.

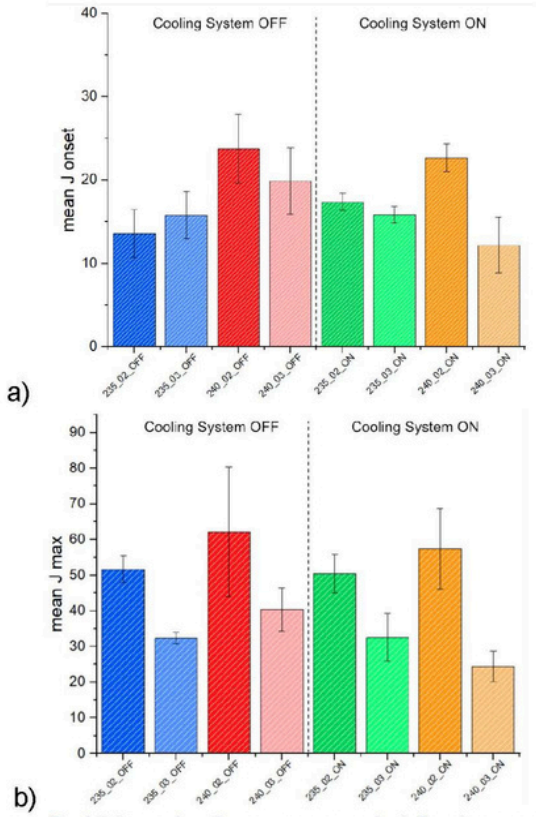


Figure 3: J-integral values measured at fracture onset (a) and at the maximum force (b) for the different printing conditions

Conclusions

A fracture mechanics approach commonly used to measure the fracture toughness of bulk rubber was applied to evaluate the effects of variations in processing conditions on the adhesion between filament layers in a 3D-printed material. The method proved capable of detecting changes in adhesion strength resulting from variations in processing conditions. Furthermore, it enabled the identification of process-related defects at the interlayer interface.

References

[1] R. Shahpasand, A. Talebian, and S. (Sabya) Mishra, *J Clean Prod*, vol. 390, Mar. 2023

[2] J. R. Rice, (1968)

Altri

CONTRIBUTI ORALI

Chimica e fisica dei polimeri

ELECTROSPUN MEMBRANES OBTAINED FROM PLANT PROTEINS AND MALTODEXTRINS FOR THE TREATMENT OF GADOLINIUM-CONTAMINATED WASTEWATER

C. Cecone[1] – F. Alchera[1] – L. Gianoglio[1] – A. Scarciglia[2] – E. Di Gregorio[2] – G. Ferrauto[2] – M. Ginepro[1] – P. Bracco[1]

[1] Department Of Chemistry, University of Turin, Via Pietro Giuria 7, 10125, Turin, Italy
[2] Department Of Molecular Biotechnologies And Health Sciences, University of Turin, Via Nizza 52, 10126, Turin, Italy

e-mail: claudio.cecone@unito.it

Introduction

The widespread use of Gadolinium-Based Contrast Agents (GBCAs) in medical magnetic resonance imaging has led to the contamination of water resources. These compounds can break down in wastewater, releasing free gadolinium ions that are highly toxic and tend to bioaccumulate in living organisms. To address this issue, the study focuses on developing innovative, sustainable, and biodegradable filtration membranes using plant-based materials.

Results and discussion

Zein, a hydrophobic corn protein, and maltodextrins, water-soluble carbohydrates, were used to produce membranes via electrospinning.

After the parameter optimization, several types of membranes were created, showing fiber diameters ranging from 0.7 to 1.2 µm:
i) Membranes made from zein combined with myristic acid.
ii) Membranes made from maltodextrins combined with citric acid.
iii) Membranes made from maltodextrins and zein combined with activated carbon.
iv) Membranes consisting of alternating electrospun layers of zein and maltodextrins, designed to enhance mechanical strength while providing a high removal capacity.

The maltodextrin-based membrane demonstrated the highest efficiency in removing free gadolinium through electrostatic interactions, achieving a removal of 96.1 ± 0.6%. In contrast, the sample with alternating electrospun layers achieved an 83.0 ± 0.3% removal, while the zein-only membrane reached only 24.6 ± 0.5%. However, none of the membranes were able to retain gadolinium in its complexed form (Gadoteridol). To address this, activated carbon was incorporated into the fibers to evaluate its effectiveness in removing Gadoteridol through π-interactions. Flow tests were conducted using a 3D-printed multi-step column. The membranes successfully removed free gadolinium ions from aqueous solutions (up to 75 mL permeated) and simulated urine (up to 45 mL permeated) using just 50 mg of membrane material. However, filtration efficiency significantly decreased in real environmental matrices due to their increased complexity.

Conclusions

Electrospun zein and maltodextrin membranes represent a promising, eco-friendly alternative for treating gadolinium-contaminated water. While they show excellent retention capacity and kinetics in both batch and flow tests, further optimization is necessary to enhance their mechanical strength and efficiency for large-scale applications in complex environmental conditions.

References

[1] X. Gao, G. Han, S. Zhang, J. Ren, Journal of Environmental Management, 2025, 395, 128014
[2] A. Scarciglia, C. Papi, C. Romiti, A. Leone, E. Di Gregorio, G. Ferrauto, Global Challenges, 2025, 9, 2400269
[3] C. Cecone, G. Hoti, M. Zanetti, F. Trotta, P. Bracco, RSC Advances, 2022, 12, 762 – 771
[4] C. Cecone, V. Fiume, P. Bracco, M. Zanetti, Polymers, 2024, 16, 6

FROM AMPHIPHILIC RANDOM COPOLYMERS TO FUNCTIONAL NANO-CHELATORS: A NEW STRATEGY FOR RADIONUCLIDES SEQUESTRATION

M. Turriani [1,2], M. Giomi [1], L. Menichetti [3], D. Petroni [3], F. Casavecchia [3], M. Lessi [1,2,4], E. Rosadoni [1], E. Guazzelli [1,2,4], E. Martinelli [1,2,4]

[1]Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124, Pisa, Italy
[2]National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, Florence, Italy (UdR Pisa)
[3]Institute of clinical physiology (IFC), CNR, Via G. Moruzzi 1, 56124, Pisa, Italy
[4]Center for Instrument Sharing of the University of Pisa (CISUP)), University of Pisa, Lungarno Pacinotti 43/44, 56126, Pisa, Italy

e-mail: marco.turriani@ospiti.unipi.it

Introduction

Amphiphilic (meth)acrylic random copolymers bearing PEG and short fluorinated side chains represent a versatile platform for the fabrication of nanoscale objects through intramolecular single-chain folding in water, resulting in the formation of unimer micelles with dimensions below 20 nm.[1,2] These nanostructures provide a confined hydrophobic environment capable of hosting hydrophobic molecules making them extremely suitable for e.g. drug delivery and bioimaging.[3,4] Furthermore, those materials generally show a lower critical solution temperature (LCST)-like behaviour,[1,2] which could be exploited for the recovery of the polymeric material by hot filtration or centrifugation. In this work, amphiphilic random copolymers PEGMA-co-FA-co-DOTAMA containing a covalently linked DOTA-type chelating agent were synthesized and investigated as thermoresponsive nano-assembled chelating polymers in water for radionuclide sequestration and recovery. These systems could find application in areas of increasing interest, such as environmental remediation, nuclear waste management, and radiopharmaceutical applications.

Results and discussion

PEGMA-co-FA and PEGMA-co-FA-co-DOTAMA random copolymers were synthesized through reversible addition–fragmentation chain transfer (RAFT) polymerization (Figure 1). The covalent incorporation of a polymerizable chelating agent (DOTAMA) allowed for the complexation behaviour of the final materials. Copolymer aqueous solutions were characterized by turbidimetry and dynamic light scattering (DLS)

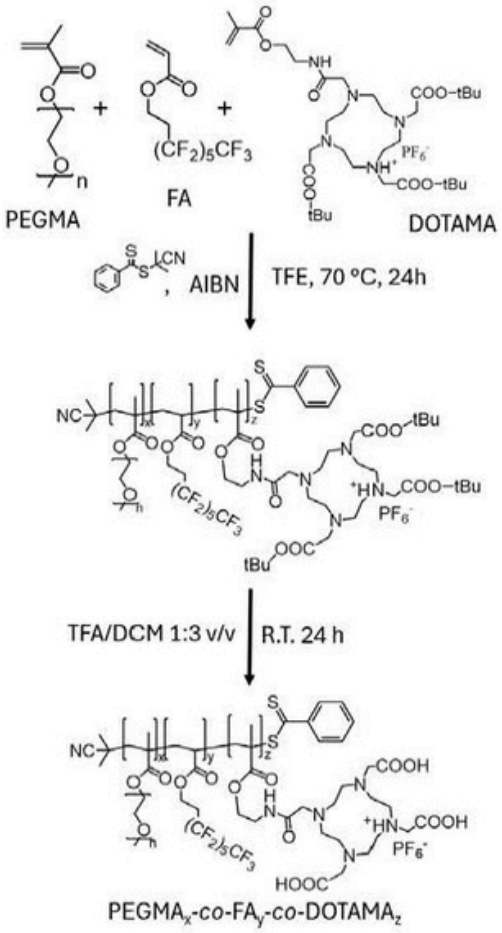


Figure 1. Scheme of PEGMA-co-FA-co-DOTAMA copolymers synthesis

analyses. DLS measurements confirmed the spontaneous self-assembly of PEGMA-co-FA and PEGMA-co-FA-co-DOTAMA copolymers into nanostructures with hydrodynamic diameters

ranging from 7 to 10 nm, consistent with the formation of unimer micelles. Turbidimetric analyses revealed the presence of a cloud-point temperature (T_{cp}) for all polymer samples. The transition temperature could be modulated by varying the oxyethylenic side chain length, providing a convenient tool for tailoring the thermal response of the system. Above T_{cp}, unimer micelles underwent an aggregation into larger particles with dimensions between 100 and 1000 nm (Figure 2). These aggregates could be readily separated from the aqueous phase by hot filtration, highlighting the practical advantages of the thermoresponsive design for material recovery and reuse.

The radionuclide sequestration performance toward ^{68}Ga and ^{99m}Tc was evaluated by radio-thin-layer chromatography (radio-TLC). The chelating polymers demonstrated high complexation efficiency with a radiochemical purity (RCP) approaching 100% by using a 40000:1 mol/mol copolymer/radionuclide ratio at a temperature above 80 °C (Figure 2).

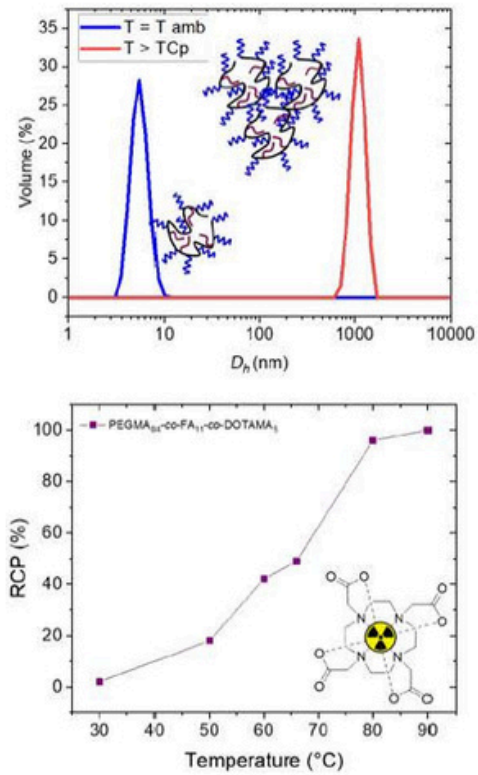


Figure 2. DLS volume size distribution curves of water solution at room temperature and above T_{cp} (above) and RCP vs. temperature curve for the PEGMA$_{84}$-co-FA$_{11}$-co-DOTAMA$_5$ copolymer toward ^{99m}Tc (below).

Conclusions

In this study well-defined amphiphilic chelating copolymers PEGMA-co-FA-co-DOTAMA were successfully synthesized and proved to form self-folded unimer micelles in aqueous solution. Moreover, they were found to exhibit a tuneable LCST-type behaviour and excellent radionuclide sequestration capabilities toward ^{68}Ga and ^{99m}Tc. The chelating properties, combined with the ability to induce aggregation above the cloud-point temperature and subsequently recover the material by hot filtration, represent a significant advantage for practical separation processes, thus highlighting the potential of the copolymers reported here as thermoresponsive platforms for radionuclide sequestration and recovery.

References

[1] E. Guazzelli, E. Masotti, M. Kriechbaum, F. Uhlig, G. Galli, E. Martinelli, *Macromol. Chem. Phys.* 224, 2200360 (2023).

[2] E. Guazzelli, E. Martinelli, G. Galli, L. Cupellini, S. Jurinovich, B. Mennucci, *Polymer*, 161, 33 (2019).

[3] M. Calosi, E. Guazzelli, S. Braccini, M. Lessi, F. Bellina, G. Galli, E. Martinelli, *Polymers*, 14, 774 (2022).

[4] A. Cesari, E. Guazzelli, E. Scaiella, M. Lessi, E. Martinelli, F. Bellina, *Polym. Test.*, 146, 108784 (2025).

Acknowledgments

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A NOVEL MELAMINE-FREE WATERBORNE INTUMESCENT COATING FOR FIRE PROTECTION OF WOOD

Lorenzo Tosato[1], Daniele Caretti[1], Stefano Scurti[1], Elena Minelli[2]

[1]Dept. of Industrial Chemistry "Toso Montanari", Università di Bologna, Via Piero Gobetti 85, 40129, Bologna, Italy
[2]JF Amonn S.r.l., Ponte nelle Alpi, Belluno, Italy
e-mail: lorenzo.tosato2@unibo.it

Introduction

Wood is a renewable and abundant material with numerous advantages, including unique aesthetic characteristic, high strength-to-weight ratio, easy processing, and carbon neutral [1]. However, the high flammability of wood presents a significant safety challenge, in particulary in outdoor applications [2]. For this reason it's very important to protect wood substrates with fire retardant intumescent coatings that works by expanding and creating a dense, porous char layer when expose to fire [3]. Generally, intumescent coatings consist of a polymeric matrix, an acid source, a char former, and a blowing agent that interact each other to form a char layer that expands during a fire. In this work, we focused on the development and scale-up of a waterborne intumescent coating based on urea-formaldehyde binder (UF) without the use of melamine as a blowing agent, due to its classification as a Substance of Very High Concern (SVHC) since 2023. Moving to a synergistic self-intumescent additive, acting simultaneously as carbon, nitrogen, and phosphorus source, we also investigated a modified ammonium polyphosphate based on ethanolamine and polycaprolactone (APP-EA-PCL), evaluating the influence of polycaprolactone chain length on flame-retardant properties.

Results and discussion

The formulation was optimized using standard stabilizing additives and successfully scaled up to 6 kg batches. Four independent batches were produced and evaluated over 1–5 months, demonstrating good storage stability and reproducibility. Free formaldehyde content remained below 0.1 wt.% and showed a decreasing trend during storage. Rheological analysis, Figure 1, showed shear-thinning behavior, with viscosity decreasing significantly at increasing shear rates, ensuring good industrial application properties. The cone calorimeter test (Figure 2-3) revealed excellent fire-protective performance, where for all batches the time to ignition (TTI) is above 200 s. The Total Heat Release (THR) and Fire Growth Rate Index (FIGRA), estimated through an Single Burning Item (SBI) simulator from cone calorimeter data, reached values below 7.5 MJ and 120 W/s, respectively. Considering that SBI is the reference method for the official fire classification of construction products, these results demonstrate excellent flame-retardant performance.To improve the flame retardant properties the APP-EA-PCL, synthetized with different chain length of polycaprolactone, from 5 to 40 ripetitive unite structure, was characterized by ^{1}H-NMR and FT-IR. The thermal stability was evaluated by Thermogravimetric Analysis (TGA), Figure 4. The thermogravimetric profiles indicate an increase in thermal stability above 550 °C for the APP-EA-PCL systems compared to unmodified APP. This behavior is accompanied by a progressive increase in the final residue as the polycaprolactone chain length increases, suggesting a more efficient char-forming ability.

Conclusions

In summary, a melamine-free waterborne intumescent coating was successfully developed and scaled up. The measured viscosity under high shear rate ensure good processability and industrial application. The intumescent coating revealed high fire-protective performance with THR_{600s} and $FIGRA_{0.2MJ}$ below 7.5 MJ and 120 W/s respectively. The next step will involve pilot-scale production, and assessment of the flame-retardant properties of APP-EA-PCL additive to improve the formulation properties.

References

[1] Feixiang Song et al., *Progress in Organic Coatings*, vol. 162, (2013)
[2] Wael Ali et al., *Construction and Building Materials*, vol. 489, (2025)
[3] Nazrun, T. et al., *Fire*, vol. 8, 155, (2025)

Acknowledgments

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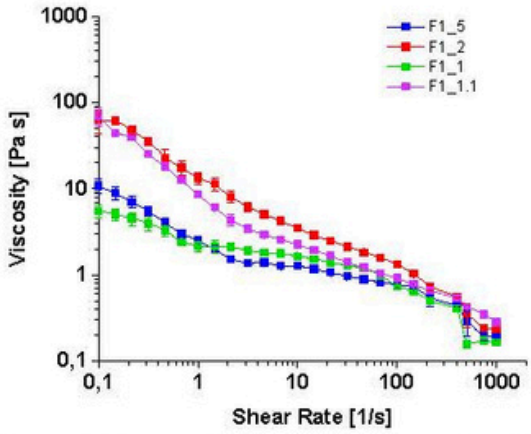


Figure 1. Rheometer test of the same formulation at different shelf life (from 1 to 5 month) in the range between 0,1 s^{-1} to 1000 s^{-1}

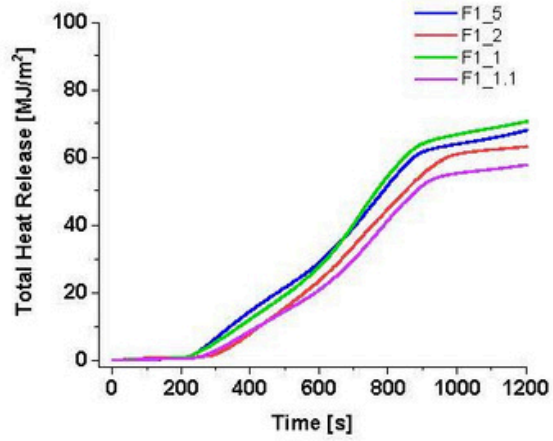


Figure 2. The Total Heat Release (THR) curves obtained by Cone Calorimeter test (ISO-5660-1)

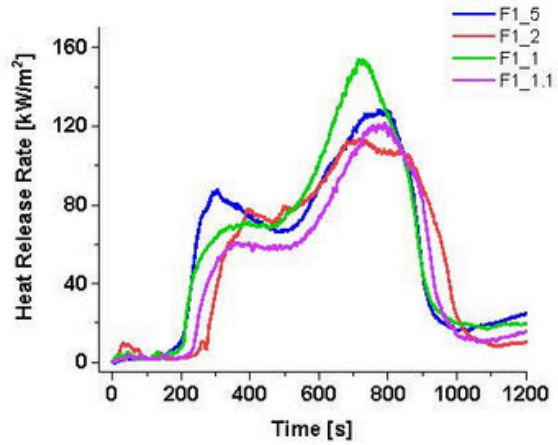


Figure 3. The Heat Release Rate (HRR) curves obtained by Cone Calorimeter test (ISO-5660-1)

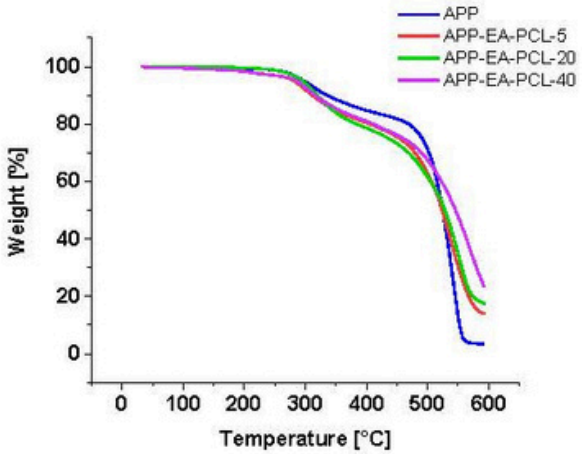


Figure 4. Thermogravimetric Analysis (TGA) of functionalized APP-EA-PCL with different chain length of polycaprolactone

ELECTROSPINNING AND SOLUTION BLOW SPINNING OF WATER-BASED POLYMER SOLUTIONS FOR THE SUSTAINABLE MANUFACTURING OF NANOFIBROUS MATS

J.A. Talamo Ruiz[1], V. Veitengruber[2], M. Retsch[2], L. Pattelli[3], A. Vitale[1]

[1] Department of Applied Science and Technology, Politecnico di Torino, 10129, Torino, Italy
[2] Department of Chemistry, Physical Chemistry I, University of Bayreuth, 95447, Bayreuth, Germany
[3] Istituto Nazionale di Ricerca Metrologica, 10135, Torino, Italy
e-mail: jessica.talamo@polito.it

Introduction

The growing demand for sustainable manufacturing has driven increasing interest in nanofibrous materials produced through environmentally benign processing routes. Owing to their high surface-area-to-volume ratio, interconnected porosity, and tunable structural and optical properties[1], nanofibrous mats are promising for a wide range of advanced applications ranging from filtration to optical and thermal-management structures. Among the available fabrication methods, electrospinning (ES) and solution blow spinning (SBS) are two versatile techniques capable of producing ultrafine fibers from polymer solutions. In particular, in ES, a high voltage is applied to overcome the surface tension of a polymer solution and form a Taylor cone to finally eject a charged liquid jet that undergoes stretching and solvent evaporation, leading to the deposition of a nonwoven fibrous mat[2]. On the other hand, SBS replaces the electric field with a concentric high-velocity gas stream that stretches the polymer solution into a jet. As the jet travels toward the collector, the solvent evaporates leading to fiber formation[3]. Although both techniques rely on the interplay between viscoelastic forces and solvent evaporation, their distinct fiber formation mechanisms result in different morphological outcomes. ES typically produces fibers with greater uniformity and narrower diameter distributions, whereas SBS enables significantly safer production processes at the expense of increased morphological variability[4]. Importantly, both techniques offer the possibility of tuning fiber diameter, porosity, and network architecture, key parameters governing light scattering and the functional performance of nanofibrous materials[5]. Despite these advantages, processing aqueous polymer solutions by ES and SBS remains challenging. The high boiling point and slow evaporation rate of water often prevent complete solvent removal during fiber formation, leading to jet instability, bead formation, or incomplete fiber formation[6]. Consequently, most studies rely on volatile organic solvents or external heating to accelerate solvent evaporation[7], reducing the environmental sustainability of the process.

Here, to isolate the influence of the spinning mechanism on fiber morphology from solution chemistry, identical fully aqueous poly(vinyl pyrrolidone) (PVP) solutions were processed by ES and SBS under optimized conditions. While aqueous systems remain more difficult to process than organic solvent-based solutions, they provide a sustainable platform for assessing how the spinning mechanism alone influences fiber formation and the resulting fibrous architecture.

Results and discussion

Poly(vinyl pyrrolidone) (PVP, Mw = 1,300,000 g mol^{-1}) was dissolved in water with a polymer concentration of 20 wt.%. The same formulation was processed by both ES and SBS to directly compare the influence of the spinning mechanism on fiber formation while eliminating differences arising from solution composition. A SBS laboratory-scale setup equipped with a compressed air system, a coaxial nozzle, a pump and a static collector was employed to fabricate the blown-spun nanofibrous mats (Figure 1a).

For the electrospun mats, an E-fiber electrospinning system with a horizontal configuration (SKE Research Equipment) and composisting of a pump, a syringe system, a conductive-static collector and a high-voltage generator, was used (Figure 1b). Processing parameters such as solution flow rate, tip-to-collector distance, air flow rate and pressure (for SBS) and voltage (for ES) were systematically optimized to obtain a stable spinning process in both cases. The influence of the variation of the parameters was initially assessed through direct observation of the spinning process and verification of the presence of fibers through optical microscopy analysis. Subsequently, morphological characterization of the collected mats was carried out.

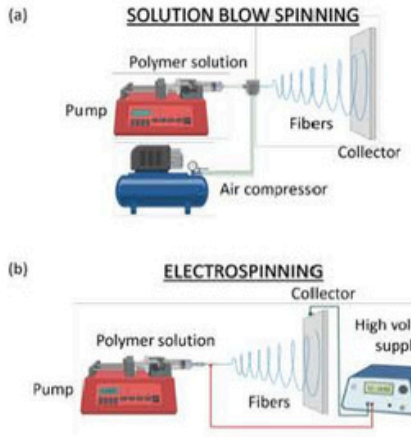


Figure 1. (a) Solution Blow Spinning and (b) Electrospinning set-up used to produce nanofibrous mats.

Scanning electron microscopy (SEM) confirmed that both spinning techniques successfully produced stable, bead-free nanofibrous mats from aqueous PVP solutions, demonstrating the versatility of both processes despite the absence of organic solvents. However, distinct morphological differences in the SBS-produced fibers (Figure 2a) and the ES-produced fibers (Figure 2b) were observed. Quantitative ImageJ analysis confirmed these observations: ES fibers exhibited a mean diameter of ~980 nm with a full width at half maximum (FWHM) of 200 nm, while SBS yielded fibers with a mean diameter of ~430 nm and a broader FWHM of 400 nm. Interestingly, under the optimized processing conditions adopted in this work, SBS produced finer fibers than ES, despite the fact that SBS is often reported to generate larger fiber diameters than electrospinning. This result highlights the strong influence of processing parameters and solution properties on fiber formation, demonstrating that the relative performance of the two techniques depends on the specific processing window rather than on the spinning method alone. The narrower diameter distribution obtained by ES can be attributed to the stabilizing action of electrostatic forces on the charged jet, whereas the compressed-air-driven jet in SBS is inherently more susceptible to aerodynamic instabilities, resulting in broader fiber diameter distributions. Moreover, the electrospun mat consisted of a dense and homogeneous network of smooth, continuous fibers, indicative of stable electrostatically driven jet stretching and targeted fiber deposition.

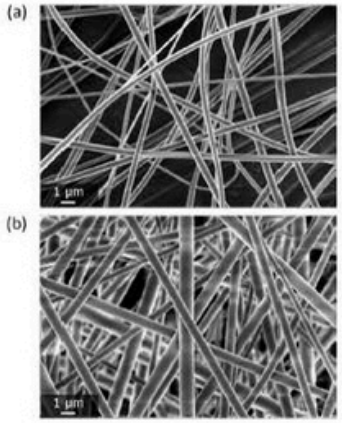


Figure 2. (a) SBS-produced and (b) ES-produced nanofibrous mats.

In contrast, the high-velocity air stream involved in the SBS process promoted highly turbulent aerodynamic forces, leading to a more open and locally heterogeneous network, consistent with the random fiber deposition induced by the turbulent air flow. Despite their different morphologies, these complementary microstructures broaden the range of potential applications of water-based nanofibrous mats, including filtration, optical coatings, and thermal-management systems. In particular, fiber diameters comparable to the wavelength of solar radiation may promote efficient light scattering, making these materials attractive candidates for passive daytime radiative cooling (PDRC)[8].

Conclusions

Both electrospinning and solution blow spinning successfully produced continuous PVP nanofibers using water as the only solvent, demonstrating the feasibility of more sustainable fiber manufacturing without organic solvents. Under the optimized processing conditions investigated in this work, electrospinning provided superior control over fiber uniformity and process stability, whereas solution blow spinning produced finer fibers while offering simpler equipment requirements and greater industrial scalability. The distinct fiber diameters and network architectures obtained by the two spinning techniques demonstrate how the spinning mechanism directly influences the morphology of water-based polymer nanofibrous mats. This tunability provides opportunities to tailor their structural characteristics for a broad range of functional applications requiring controlled porosity and light-scattering behavior, including passive radiative cooling, while supporting the development of more sustainable manufacturing processes.

References
[1] A. Barhoum, K. Pal, H. Rahier, H. Uludag, et. al., Appl. Mater. Today, 17, 1–35 (2019).
[2] M. Ahmadi Bonakdar, D. Rodrigue, Macromol., 4, 58–103 (2024).
[3] G.C. Dadol, A. Kilic, L.D. Tijing, et. al. Mater. Today Commun., 25, 101656 (2020).
[4] M.Á.V. Rodrigues, M.R.V. Bertolo, M.M. Horn, et. al. Int. J. Biol. Macromol., 283, 137806 (2024).
[5] D. Zhang, H. Zhang, Z. Xu, Y. Zhao, Materials, 16, 3677 (2023).
[6] J. Carriles, P. Nguewa, G. González-Gaitano, Int. J. Mol. Sci., vol. 24, 14757 (2023).
[7] A.M.C. Santos, E.L.G. Medeiros, J.J. Blaker, E.S. Medeiros, Mater. Lett. 176, 122–126 (2016).
[8] A. Aili, T. Jiang, J. Chen, Y. Wen, R. Yang, X. Yin, G. Tan, Next Energy, vol. 3, 100121 (2024).

TACTICITY-INDEPENDENT CRYSTALLIZATION AS A DESIGN STRATEGY FOR CHEMICALLY RECYCLABLE SEMICRYSTALLINE POLYMERS

Miriam Scoti, Claudio De Rosa

Dipartimento di Scienze Chimiche, Università di Napoli Federico II, via Cintia 80126, Napoli, Italy

e-mail: miriam.scoti@unina.it

Introduction

Crystallization is a key route to improve the performance of polymeric materials, since the presence of a crystalline phase enhances thermomechanical properties, slows degradation and improves barrier properties. A key requirement for crystallization is the regularity of the molecular structure. However, regularity can be defined at different levels: constitutional regularity, meaning that polymer chains should be made of regular successions of identical repeating units; configurational regularity, that is a regular succession of the configurations of stereogenic centers of steroisomerism, when present; conformational regularity, meaning that chains must adopt a regular conformation, such as a helical or trans-planar conformation, to regularly pack into crystals.

Nevertheless, deviations from perfect regularity do not necessarily prevent crystallization. When defects are present at low concentration, the polymer may be still able to crystallize either including these defects in the crystals or rejecting them in the amorphous regions.

Even more intriguing are cases in which one of these regularity requirements is not fulfilled at all, and yet crystallization still occurs. In particular, polymers able to crystallize despite a high degree of configurational disorder display tacticity-independent crystallization.

This phenomenon is especially relevant because the preparation of stereoregular polymers usually requires enantiopure monomers or highly stereoselective catalysts. The discovery of atactic yet semicrystalline polymers opens a route to semicrystalline, potentially high-performance materials without the need for perfect stereocontrol.

Results and discussion

Although the origin of tacticity-independent crystallization is not yet fully understood, several factors can provide a form of structural "order" that allows stereoirregular chains to crystallize. Classical examples include establishment of secondary interactions, such as hydrogen bonding in poly(vinyl alcohol) or dipolar interactions in poly(vinyl chloride), which can stabilize regular chain conformations and promote packing despite configurational disorder. More recent examples show that tacticity-independent crystallization can also arise from conformational flexibility or from steric effects that allow stereoirregular chains to assume in the crystalline state an overall shape similar to that of the stereoregular chain (shape emulating effect).

A first case is represented by poly(2-thiabicyclo[2.2.1]heptan-3-one) (PBTL), a chemically recyclable polythioester obtained by ring-opening polymerization of a bicyclic thiolactone. Since the monomer contains two chiral centres, different stereochemical sequences can be generated along the chain. Depending on the catalyst and polymerization conditions, stereoregular and atactic samples can be obtained. Remarkably, although the melting temperature decreases with decreasing stereoregularity, the atactic sample also shows a melting transition, indicating that it is semicrystalline. WAXS profiles of both stereoregular and atactic PBTL show a single sharp reflection at about $2\theta = 19°$, demonstrating not only that the atactic polymer crystallizes, but also that it crystallizes in the same crystalline form as the stereoregular one. The crystal structure of PBTL was investigated by combining X-ray diffraction and conformational modelling. Fiber diffraction patterns indicate a chain periodicity of about 12.8 Å. Low-energy conformations compatible with this periodicity were modelled for the different stereosequences, showing that the stereoregular sequence adopts the most favourable conformation. The WAXS profile suggests a pseudo-hexagonal packing with long-range order in the position of the chain axes. For the stereoregular polymer, an orthorhombic unit cell and a chain packing according to $P2_1$ space group provide good agreement between calculated and experimental diffraction data.

A second class of systems is represented by methyl-substituted poly(3-hydroxybutyrate)s (P3HB), namely dimethylated ($P3H(Me)_2B$) and monomethylated (PHMB).

In apolar poly(α-olefin)s, the van der Waals interactions between neighbouring atoms of the side groups induce iso-distortions of the torsion angles from the minimum-energy trans conformation towards the gauche conformation and stabilization of helical conformations with *MIN* symmetry. Moreover, in conventional poly(hydroxyalkanoate)s, including P3HB, crystallization usually favours two-fold helical

conformations, whereas *trans*-planar conformations are typically obtained only upon stretching.

The introduction of methyl substituents in the α-position of P3HB produces an unexpected crystallization behaviour. Semicrystalline P3H(Me)$_2$B and PHMB with different tacticities and melting temperatures can be synthesized, and even the atactic samples are able to crystallize and, remarkably, they crystallize in the same crystal form as the corresponding stereoregular polymers.

In both P3H(Me)$_2$ B and PHMB, conformational energy analysis shows that, among the possible conformations, only the *trans*-planar one is compatible with the chain periodicity obtained from X-ray fiber diffraction. This indicates that, unlike in many polyolefins or unsubstituted PHAs, the presence of methyl side groups stabilizes the *trans*-planar chain conformation instead of helical ones.
The crystal structures of stereoregular and atactic P3H(Me)$_2$B and PHMB have been resolved. Atactic chains have been modelled by randomly connecting *R* and *S* units while maintaining low energy and an overall straight shape. The resulting atactic chain preserves an overall shape closely resembling that of the stereoregular chains, thus allowing the atactic polymers to crystallize in the same crystal structure as their stereoregular counterparts. This behaviour suggests a mechanism of crystallization driven by shape emulation, in which defective chains adopt conformations similar in shape and can therefore be accommodated in similar crystal lattice.

Conclusions

The provided examples show that configurational disorder does not always prevent polymer crystallization.

In some cases, the lack of tacticity can be compensated by other factors, such as secondary interactions, conformational flexibility, or steric effects leading to shape emulation.

For PBTL, ring flexibility allows stereoirregular chains to crystallize in a disordered crystal structure with pseudo-hexagonal packing. For methyl-substituted P3HBs, chains with different tacticities can adopt similar shapes and pack in similar crystal forms.

The general message is that the presence of disorder in semicrystalline polymers can be exploited to tune polymers properties like processability and mechanical strength. The tacticity independent crystallization allows easy synthesis of semi-crystalline polymers with improved mechanical properties without the use of specifically designed stereoselective catalysts.

References

[1] L. Sangroniz, A. Sangroniz, C. Shi, M. Scoti, M. Ximenis, C. De Rosa, E. Y.-X. Chen, H. Sardon, A. J. Müller, *Nature Chemistry*, 18, 625-638 (2026).
[2] C. Shi et al., *Science Advances*, 6, eabc0495 (2020).
[3] M. Scoti, L. Zhou, E. Y.-X. Chen, C. De Rosa, *Macromolecules*, 57, 4357-4373 (2024).
[4] Z. Zhou, A. M. LaPointe, G. W. Coates, *Journal of the American Chemical Society*, 145, 25983-25988 (2023).

Acknowledgments

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STRUCTURE-PROPERTY RELATIONSHIPS IN BIOPOLYMERIC CRYOGELS PRODUCED BY FREEZE-CASTING

G. Pignatiello[1], G. Filippone[1], V. Ambrogi[1], M. Salzano de Luna[1]

[1] Department of Chemical, Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125, Napoli, Italy
e-mail: gioacchino.pignatiello@unina.it

Introduction

Cryogels are a class of highly porous solids, made up of more than 90% air, characterized by low density, high specific surface area and low thermal conductivity. Depending on the material and on the type of microstructure, they find application in the environmental, biomedical, structural, energy, electrical and thermal fields [1]. The control of the cryogel microstructure is a key challenge, since it allows the resulting properties to be tailored to the target application: the presence of macropores, for instance, is detrimental for thermal insulation but beneficial for oil-water separation [2].

In this work, biopolymeric cryogels with controlled microstructure were produced by freeze-casting in order to evaluate their production-structure-property relationships. Sodium alginate, a water-soluble polysaccharide isolated from brown algal species, was dissolved in bi-distilled water under stirring at room temperature at concentrations of 1, 2.5, 5, 7.5 and 10% wt./vol. The solutions were poured into cylindrical plastic molds to obtain a radial geometry, and frozen in cooling baths at -10 °C, -60 °C and -150 °C Macroporous cryogels were finally obtained by lyophilization.

The cooling rate (γ) of the polymer solution during freezing was measured with an Arduino-based system connected to two thermocouples, one placed in the center of the mold and one in contact with the mold wall. Bulk density was determined by a geometric method as the ratio between the mass and the external volume of the cylindrical samples, $\rho = m/(\pi R^2 h)$, and the porosity was calculated as $P = 1 - \rho/\rho_a$, where ρ_a is the density of sodium alginate (1.5 g cm^{-3}). The microstructure was investigated by scanning electron microscopy on gold-sputtered, razor-blade-cut cross-sections observed along the ice-growth direction. Mechanical properties were measured by unconfined uniaxial compression tests up to a strain of 0.75 on cylindrical samples. After cross-linking with an ethanol-based solution of $CaCl_2$, water transport was evaluated by placing the samples in contact with a dyed liquid and measuring its capillary ascent rate, a property of interest for the separation of water from pollutants.

Results and discussion

Cooling tests on the 10% alginate solution were carried out at -10, -60 and -150 °C. All curves show an initial liquid-cooling stage down to the thermodynamic freezing temperature (0 °C), a plateau corresponding to crystallization, and a final cooling of the solid to the bath temperature; supercooling below 0 °C is observed only for freezing at -10 °C. The cooling rate γ, obtained as the slope of a linear fit of the liquid-cooling section, increases with decreasing bath temperature and is higher at the mold wall than at the center of the sample.

The density of the cryogels increases linearly with the alginate weight fraction (f_a) of the starting solution, indicating the absence of structural collapse during freeze-drying, and the porosity exceeds 90% by volume for all samples, consistent with the highly porous nature of these cryogels.

SEM micrographs (Figure 1) show the effect of the process parameters on the final microstructure. Samples frozen at -10 °C exhibit circular pores, whereas those frozen at -60 °C and -150°C exhibit lamellar pores, since the stronger freezing forcing tends to confer greater radiality. At fixed freezing conditions, increasing the alginate fraction increases the thickness of the cryogel walls; moreover, a "star" center appears in the 1% system but not in the 10% one, because at low freezing rates the small forcing of the freezing front produces radiality only when the system is not very dense.

The compression stress-strain curves (Figure 2) can be divided into three domains: elastic, plateau and densification. The samples showing the highest resistance are those obtained with the slowest freezing, and the resistance decreases in order of freezing rate. For the samples frozen at -10 °C (circular porosity), the pore-collapse and densification regions are clearly distinct, whereas for those frozen at -60 °C (lamellar porosity) the two regions merge, since the lamellar walls crush

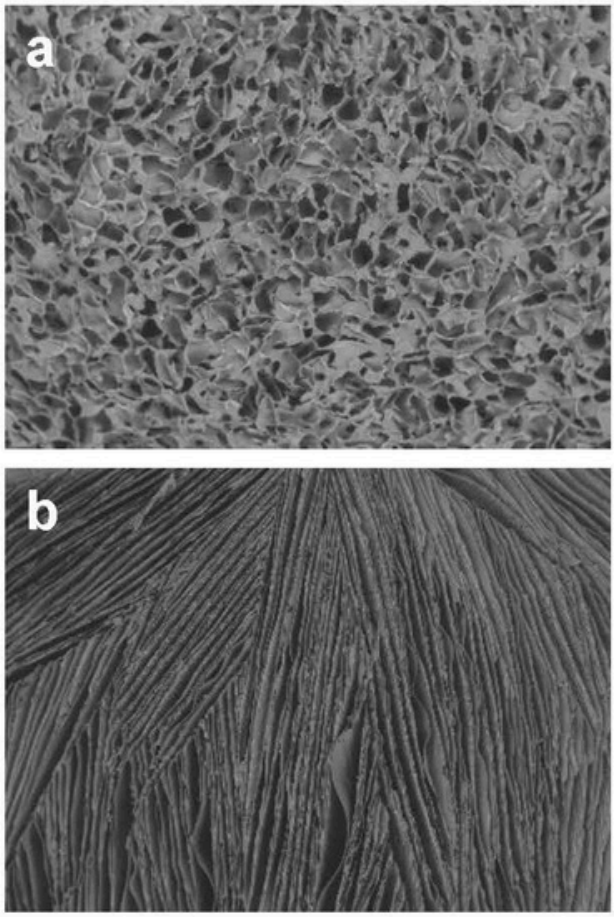


Figure 1. SEM images of 5% alginate cryogel obtained with different cooling rates: freezing at -10°C (a); freezing at -60°C (b).

against each other along extended lines, causing a progressive thickening.

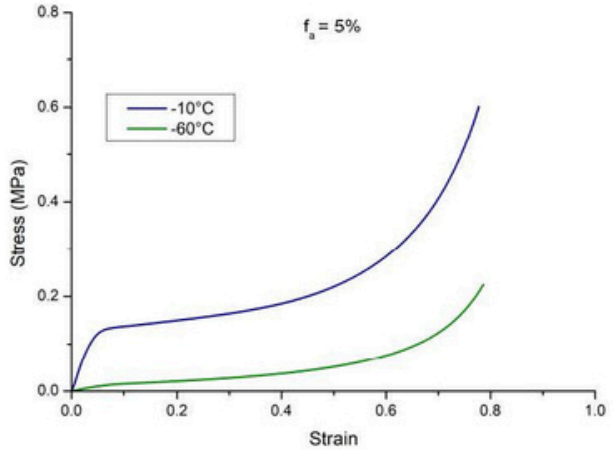


Figure 2. Compression curves of 5% alginate cryogel obtained with different cooling rates: freezing at -10°C and at -60°C.

For biopolymeric cryogels, the compressive modulus E generally depends on density according to the scaling law $E \sim \rho^{\alpha}$. The α values found for the samples obtained with different process parameters range between 2 and 3, in agreement with literature data [3]. Slower-frozen systems, with larger and more circular pores, show a higher elastic modulus and resistance than those obtained by faster freezing, with fine lamellar pores, owing to the presence of stress-bearing pillars of greater entity, which guarantee a greater overall resistance. Finally, water transport experiments reveal that the microstructure also governs the water absorption kinetics: the elongated, aligned pores with very thin walls formed upon rapid cooling are less effective in terms of water absorption kinetics.

Conclusions

Biopolymeric cryogels based on sodium alginate, with radial geometry and controlled microstructure, were produced by freeze-casting. Different cooling rates were obtained by varying the temperature of the cooling bath, which strongly influences the microstructure: the higher the cooling rate, the smaller the pore size and the greater the pore directionality. The resulting microstructure, in turn, governs the compressive behavior and the water absorption kinetics of the material, allowing the production-structure-property relationships of these systems to be established.

References

[1] G. Shao, D. A. H. Hanaor, X. Shen, A. Gurlo, Adv. Mater., vol. 32, 1907176 (2020)
[2] W. Liao, H. B. Zhao, Z. Liu, S. Xu, Y. Z. Wang, Composites Part B: Engineering, vol. 173, 107036 (2019)
[3] S. Zhao, W. J. Malfait, N. Guerrero-Alburquerque, M. M. Koebel, G. Nyström, Angew. Chem. Int. Ed., vol. 57, 7580-7608 (2018)

PRESSURE-INDUCED CRYSTALLIZATION AND POLYMORPHIC TRANSITIONS OF POLYBUTENE-1: HIGH-PRESSURE PVT STUDY

F.Olla[1*], F. Briatico Vangosa[1]

[1]Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
*e-mail: federico.olla@polimi.it

Introduction

Isotactic poly(1-butene) (iPB-1) is a high-performance semicrystalline polyolefin distinguished by its complex polymorphic behavior. The primary technological challenge in its processing stems from the kinetic dominance of the metastable form II. When cooled from the melt at atmospheric pressure, the polymer preferentially crystallizes into form II. Under ambient conditions, this phase undergoes a spontaneous solid-state transformation into the thermodynamically stable and denser form I. This transition from form II to form I, which can take days or weeks, is accompanied by a significant increase in density and a corresponding volumetric contraction (shrinkage) of approximately 4-5%. In commercial applications, such as high-pressure pipes, this delayed shrinkage leads to dimensional instability and internal stresses. Hydrostatic pressure serves as a powerful tool to manipulate these transition kinetics and phase stabilities: it thermodynamically favors the denser modification and dramatically accelerates the conversion from form II to form I. Furthermore, high-pressure crystallization can induce the formation of form I'. In this study, high-pressure PVT dilatometry was employed to systematically characterize crystallization pathways and polymorphic transitions in iPB-1 over the pressure range 10-200 MPa, with the aim of providing a quantitative thermodynamic basis for improving dimensional stability.

Results and discussion

Baseline PVT experiments at 10 MPa confirmed that iPB-1 crystallizes directly from the melt into the metastable form II, exhibiting a melting transition at approximately 115 °C (Figure 1A). Investigating higher pressure ranges reveals a clear structural evolution. In an intermediate pressure window (approximately 75-100 MPa), hydrostatic pressure markedly accelerates the solid-solid transition from form II to form I. As shown in Figure 1A, this leads to a progressive shift in the melting curves, and at 100 MPa the structure is dominated by the denser form I (melting at approximately 130 °C). At higher pressures (above 110 MPa), the melting behavior changes and a faint inflection emerges around 100 °C, suggesting the presence of a small amount of form I' (Figure 1B). Increasing the crystallization pressure further beyond 150-175 MPa, the melting curves converge into a single endothermic step near 100-110 °C, confirming that the system crystallizes predominantly as form I' (Figure 1B). The pressure dependence of the melting temperatures for all three polymorphic forms was quantified using empirical linear relations. By integrating these thermal and volumetric data, phase-resolved V(T,P) maps were assembled for the melt and for forms I, II, and I' using a modified Tait equation (Figure 2). The obtained composite curves reproduce the expected volumetric hierarchy (VI ≤ VI' < VII).

Conclusions

A high-pressure PVT dilatometry study was carried out to elucidate how hydrostatic pressure governs crystallization pathways and relative polymorphic outcomes in isotactic poly(1-butene). From a processing standpoint, the results indicate that applying pressures near 100 MPa during cooling can suppress the persistence of form II and deliver form I immediately, mitigating delayed post-crystallization shrinkage. The assembled phase-resolved V(T,P) maps provide a practical, internally consistent basis for modeling shrinkage, dimensional stability, and processing windows in iPB-1 components.

References

[1] A.M. Chatterjee, J. Macromol. Sci. Rev. Macromol. Chem. Phys., vol. 48, 2008.
[2] B. Wunderlich, Macromolecular Physics, Academic Press, New York, 1973.
[3] C.D. Armeniades, E. Baer, J. Macromol. Sci. Phys., vol. 1, 1967.
[4] T. Nakafuku, T. Miyaki, Polymer, vol. 24, 1983.

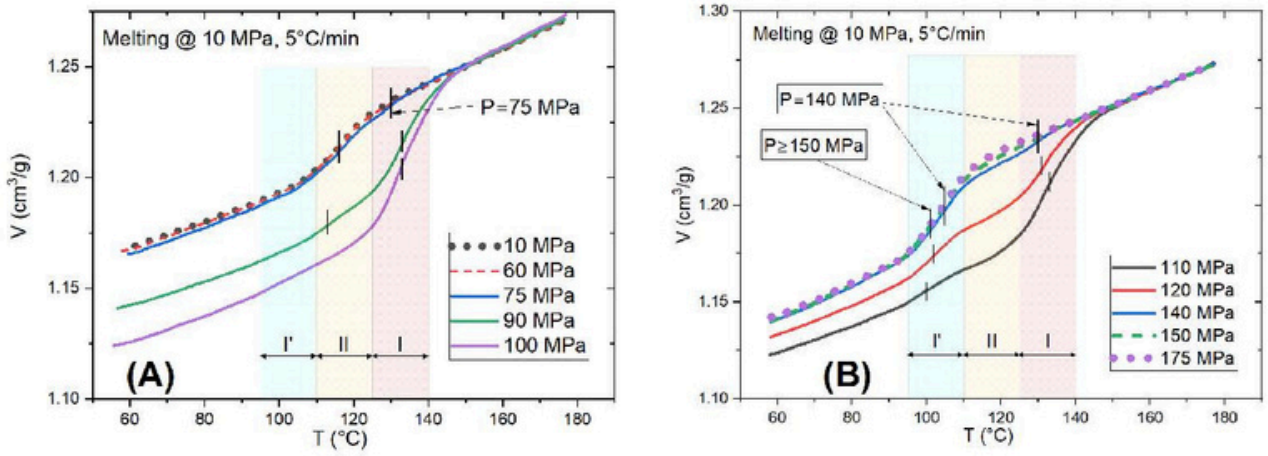


Figure 1: Specific volume evolution during melting at 10 MPa for iPB-1 samples crystallized at different pressures. **(A)** Melting profiles for crystallization pressures up to 100 MPa, highlighting the transition from form II to form I. **(B)** Melting profiles for crystallization pressures from 110 to 175 MPa, showing the emergence and subsequent dominance of form I'.

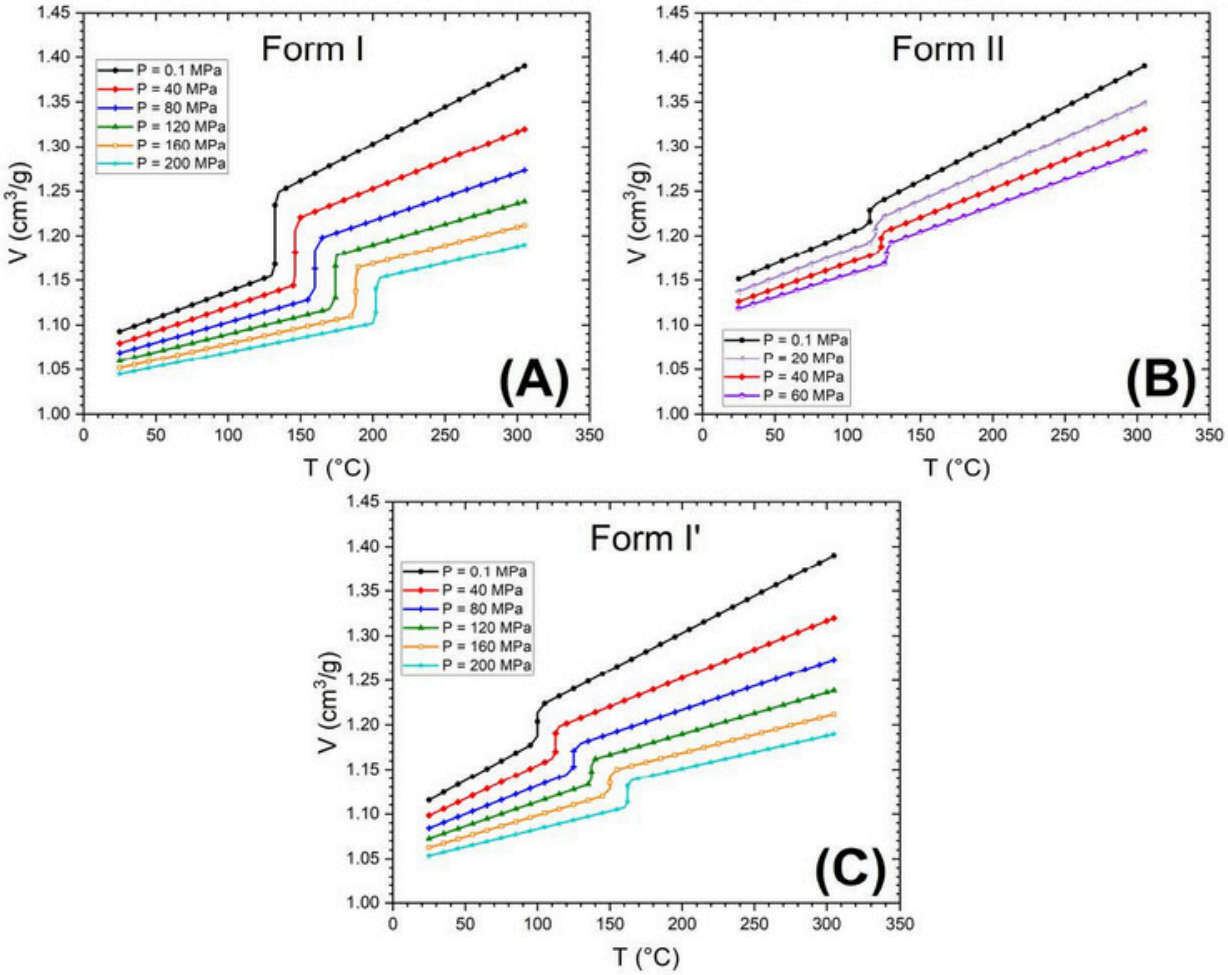


Figure 2: Phase–resolved $V\ (T,\ P)$ curves for iPB-1 polymorphs: **(A)** form I, **(B)** form II, **(C)** form I'.

HEMIN-BASED AMPHIPHILIC RANDOM COPOLYMERS AS BIOMIMETIC AND RECYCLABLE CATALYSTS FOR ARGET-ATRP IN WATER

E. Guazzelli[1,2], M. Turriani[1,3], C. Sissa[4], A. Delledonne[4], M. Fantin[5], A. Antonello[5] E. Martinelli[1,2]

[1] Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy
[2] Center for Instrument Sharing of the University of Pisa (CISUP), University of Pisa, Pisa, Italy
[3] National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy (UdR Pisa)
[4] Department of Chemical, Life and Environmental Sustainability Sciences, University of Parma, 43124 Parma, Italy
[5] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

e-mail: elisa.guazzelli@unipi.it

Introduction

Atom transfer radical polymerization (ATRP) enables the synthesis of well-defined polymers with controlled molecular weight, dispersity, architecture, and chain-end functionality. However, conventional copper-based ATRP catalysts may suffer from toxicity, environmental persistence, cost, and difficult removal from the final polymer product. Bio-derived iron catalysts such as hemin offer a more sustainable alternative, as they can mediate ATRP through the Fe(III)/Fe(II) redox cycle. Nevertheless, hemin is poorly soluble in water, tends to aggregate, and is difficult to recover. In a recent work, oHemin, a thermoresponsive PEGMA/DEGMA-based oligomeric hemin catalyst, showed that polymeric modification can improve water compatibility and enable temperature-triggered catalyst recovery above the cloud point.[1]

Results and discussion

This work explores amphiphilic random copolymers containing short PEG and fluorinated side chains (Figure 1), as polymeric nanoplatforms for stabilizing hemin in water. These systems combine PEGMA-driven water compatibility and thermoresponsiveness with fluorinated moieties that promote self-assembly in water and favor hemin incorporation, mimicking the protective macromolecular environment of metalloproteins. Their LCST-type behavior also offers a route for catalyst recovery above the cloud point by centrifugation or filtration. The copolymers were characterized by NMR and GPC, while their aqueous self-assembly, thermoresponsivity, hemin incorporation, Fe-center electrochemical accessibility, and catalytic activity in ARGET-ATRP of PEGMA500 were investigated by DLS, UV-vis, fluorescence anisotropy, cyclic voltammetry, and polymerization trials, respectively.

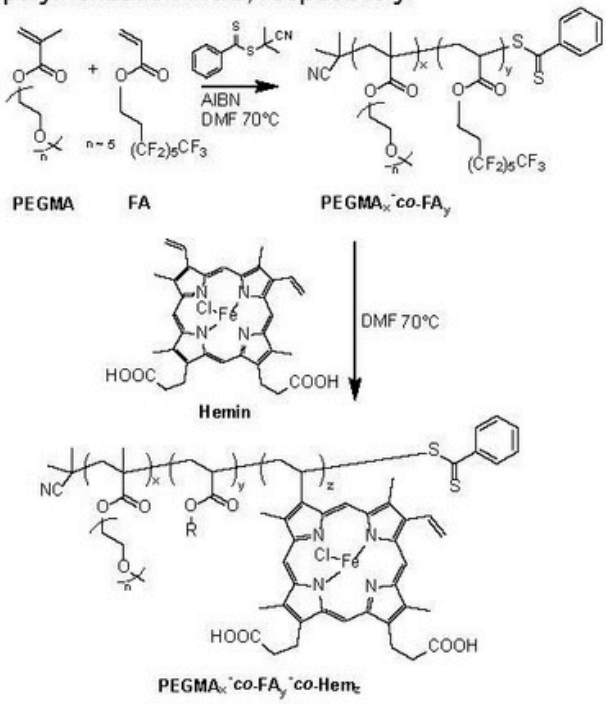


Figure 1. Synthesis of amphiphilic random copolymers PEGMA-co-FA-co-Hem by RAFT polymerization.

In water, the amphiphilic copolymers self-assembled into nanostructured systems, ranging from unimolecular micelles to larger aggregates depending on copolymer structure, molecular weight and temperature. [2-4]. These assemblies provide hydrophobic nanocompartments suitable for hosting hemin. Two stabilization strategies were investigated: covalent incorporation of hemin into the copolymer during RAFT polymerization, aimed at limiting leaching and facilitating recovery, and physical encapsulation

within the self-assembled hydrophobic domains, based on non-covalent interactions with the polymeric microenvironment.
Turbidimetry confirmed LCST-type behavior for the copolymers and hemin-containing systems, enabling dispersion under polymerization conditions and potential recovery above the cloud point by mild heating followed by centrifugation or filtration. Cyclic voltammetry showed that covalently hemin-functionalized copolymers retained an accessible Fe(III)/Fe(II) redox center, and their ability to activate R-Br ATRP initiators, with the high-molecular-weight fluorinated system giving the most promising response. When tested in aqueous ARGET-ATRP of PEGMA500 using ascorbic acid as reducing agent, selected hemin-containing copolymers promoted polymerization up to high conversion. Although further optimization is needed to improve control, these results demonstrate that amphiphilic, random PEGMA-based copolymers can provide a suitable microenvironment for hemin-based catalysis in water.

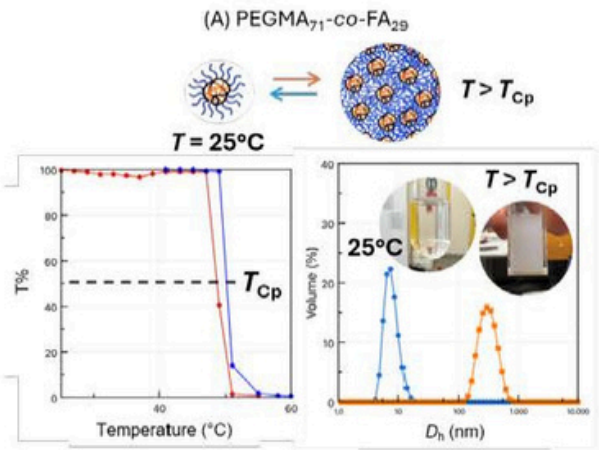


Figure 2. Turbidimetry curves and DLS analysis showing the LCST-type behavior and self-assembly of PEGMA-co-FA copolymers in water.

Conclusions

This work demonstrates that thermoresponsive amphiphilic random copolymers bearing PEG and fluorinated short side chains can be used as polymeric nanoplatforms for stabilizing hemin in water. The copolymers combine several key functions within a single macromolecular structure: aqueous self-assembly, hemin stabilization, LCST-type thermoresponsiveness, and the possibility of catalyst recovery above the cloud point. The high-molecular-weight fluorinated systems were particularly effective in stabilizing hemin under acidic aqueous conditions, supporting the role of the fluorinated hydrophobic side chains in defining the local catalytic microenvironment.
Electrochemical characterization confirmed that the hemin metal center can remain redox-active when incorporated into the copolymer structure and can activate R-Br ATRP initiators in water. ARGET-ATRP experiments of PEGMA500 in water demonstrated catalytic activity up to high monomer conversion. These results support the development of recyclable, bio-inspired nanocatalysts for sustainable controlled radical polymerization in aqueous solution. Future optimization should focus on improving polymerization control, tuning the polymeric environment around the hemin center, and demonstrating efficient catalyst recovery and reuse over multiple polymerization cycles.

References

[1] A. Antonello, G. Lissandrini, M. Brocchini, G. Bellio, D. Badocco, E. Guazzelli, A. A. Isse, E. M. Benetti, E. Martinelli, M. Fantin, *ACS Sustain. Chem. Eng.* **2026**, *14*, 2043.
[2] A. Delledonne, E. Guazzelli, S. Pescina, A. Bianchera, G. Galli, E. Martinelli, C. Sissa, *ACS Appl. Nano Mater.* **2023**, *6*, 15551.
[3] A. Cesari, E. Guazzelli, E. Scaiella, M. Lessi, E. Martinelli, F. Bellina, *Polym. Test.* **2025**, *146*, 108784.
[4] E. Guazzelli, E. Scaiella, A. Cesari, A. Battisti, M. Santi, S. Braccini, D. Puppi, V. Paganini, D. Monti, F. Bellina, E. Martinelli, *Int. J. Pharm.* **2026**, *690*, 126538.

Acknowledgments

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DEVELOPMENT OF CELLULOSE FIBERS RECOVERY STRATEGY FROM SILICONIZED PAPERS

B. Cavallo[1], V. Brunella[1], C. Barolo[1]
[1] Dept. of Chemistry, Università di Torino, Via P. Giuria 7, 10125, Torino, Italia

e-mail: beatrice.cavallo@unito.it

Introduction

Release liners are essential components in the pressure sensitive adhesive industry, as they serve the purpose of protecting labels before their application and facilitate their dispensing. This layer is usually composed of smooth, lightweight yet dense and semi-transparent paper, with good barrier and moisture resistance, called glassine paper[1]. The release properties are provided by a thin coating (~ 1µm) of polydimethylsiloxane (PDMS), as the high flexibility of its chains allow for low surface energy and low energy dissipation upon peeling, resulting in low release forces[2].

However, once the label is dispensed, the liner has ended its purpose and must be discarded. The detachment and removal of the PDSM from the cellulosic fibers present several difficulties in conventional recycling mills, leading to equipment contamination and reduced fiber recovery yields. As a result, most post-consumer release liners end up being incinerated or landfilled, with only limited downcycling opportunities. Considering the large volumes generated annually in Europe, this disposal model represents a substantial loss of valuable fibrous resources and contradicts circular economy principles[3].

In this work, a procedure for removing the silicone coating from glassine paper is proposed, enabling the recovery of fibers and promoting closed-loop recycling of siliconized release liners. Commercial siliconized paper (50g) is disintegrated under thermal and alkaline conditions (70 °C, pH 10) using a hydropulping process. The resulting pulp is treated with 0.2–1 wt.% anionic surfactants to promote the detachment of hydrophobic silicone residues, followed by a flotation step at 40°C to separate silicone-rich particles from the fibers. The cleaned pulp is then used to produce handsheets for characterization. FTIR, EDS-SEM and XRF analyses are used to study chemical composition, morphology and residual PDMS content.

Results and discussion

FTIR-ATR spectra show a clear attenuation of PDMS signatures (Si–O–Si ≈1260 cm^{-1}; Si–CH_3 ≈2960 and 796 cm^{-1}) (Fig.1), while XRF confirms a marked reduction in silicon content after treatment (Table1). SEM-EDS reveals fragmentation of the silicone layer into discrete flakes whose number and size further decrease following flotation (Fig.3). Fiber recovery was quantified as the ration between the weight of the clean pulp obtained after flotation and the weight of the initial pulp, on a dry basis.

Overall, the process removes >80% of the initial silicone and recovers >60% of the cellulose fibers, yielding a clean pulp suitable for papermaking trials.

Conclusions

Once the parameters are optimized to maximize fiber recovery and to maintain a good fiber quality, the scalability of this process will be assessed to evaluate its feasibility for industrial scale

This approach aims to enable closed-loop recycling of release liners, allowing recovery of cellulose fibers and their reintroduction into the papermaking process.

References

[1] CELAB Europe (2023) https://celab-europe.org/case-study-the-recycling-of-paper-based-silicone-release-liners (accessed on June 25, 2026)

[2] Kozlov, I.A., Isaev, A.Y., Lukina, N.F. et al. Pressure-Sensitive Adhesives, Self-Adhesive Materials. Current State of the Art. Part 1.. Polym. Sci. Ser. D 18, 96–103 (2025).

[3] AWA Release Liner Market report (2026) https://awa-bv.com/market_report/awa-release-liner-market-report/ (accessed on June 25, 2026)

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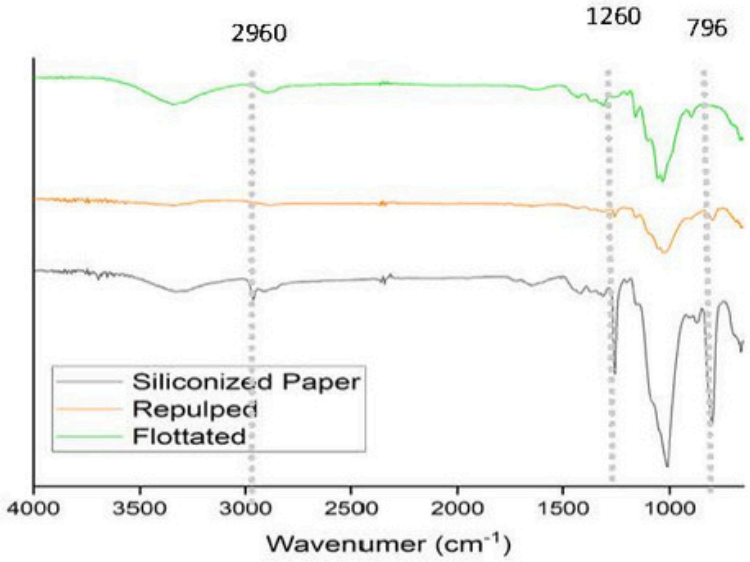


Figure 1. FRIR-ATR spectra of siliconized paper, repulped and floated paper.

Table 1: XRF results / FTIR plots

Sample	Si (g/m^2)
Siliconized paper	1.2
Repulped paper	0.3
Floated paper	0.2

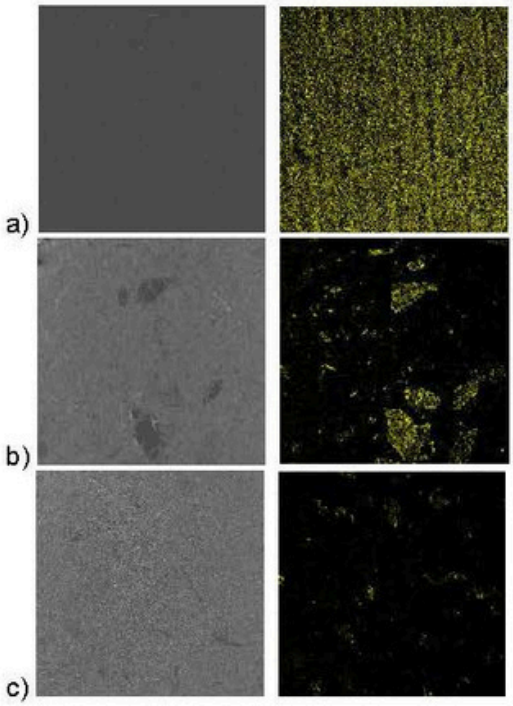


Figure 2. On le left SEM images and on the right EDS maps of the surface of the siliconized paper (a), samples after the disintegration step and (b) and after the flotation step (c). Mag 20X

PBAT/GRAPE POMACE BIOCOMPOSITE FOR FILM BLOWING APPLICATIONS

M. Ceraulo[1,2], M.C. Mistretta[1,2], L. Botta[1,2], Indovino E.[1,2], V. Gelarda[1], M. Leanza [3], M. Rapisarda[3], P. Rizzarelli[3]

[1] Department of Engineering, University of Palermo, Palermo, Italy
[2]National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy
[3] Institute of Polymers, Composites and Biomaterials - National Research Council (IPCB-CNR), Catania, Italy

Introduction

The valorization of agro-industrial by-products within biodegradable polymer systems represents a strategic and necessary pathway toward the development of next-generation sustainable materials, directly aligning with the principles of the circular economy. Among these waste streams, grape pomace (GP)—the solid residue remaining after juice pressing or winemaking—constitutes a massive and underutilized byproduct of the global wine industry.

From a materials science perspective, GP is particularly attractive: it is highly rich in lignocellulosic components that can act as structural reinforcements, and it retains a high concentration of bioactive phenolic compounds, which offer intrinsic natural antioxidant properties. Consequently, GP holds significant promise as a multifunctional biofiller for green polymeric matrices.

While a substantial body of literature has explored the incorporation of grape pomace into bulk biocomposites (such as injection-molded parts or thick sheets), its processability and performance in thin-film applications remain largely unexplored. In particular, utilizing GP within the film blowing process—the standard industrial method for producing packaging films—presents unique rheological and technological challenges that have not yet been systematically addressed.

Results and discussion

To systematically evaluate the performance of this biofiller, a multi-step compounding and manufacturing approach was adopted.

In the first phase of the study, a concentrated masterbatch of GP incorporated into a poly(butylene adipate-co-terephthalate) (PBAT) matrix was formulated. This was achieved using a co-rotating twin-screw extruder (OMC; screw diameter D = 19mm; length-to-diameter ratio L/D = 35). To ensure optimal dispersion of the organic filler and minimize thermal degradation of both the polymer and the bio-additives, a carefully optimized, progressive temperature profile was maintained across the extrusion zones: 145–150–155–160–165–170–180 °C.

The resulting masterbatch was subsequently dry-blended with virgin PBAT pellets in calculated ratios to obtain final biocomposite formulations containing 5 wt% and 10 wt% of grape pomace. These blends were then processed via a laboratory-scale film blowing line to evaluate their industrial processability and melt stability under bubble-forming conditions.

To evaluate the comprehensive performance of the manufactured thin films, a multi-analytical characterization framework was deployed.

The experimental campaign yielded promising insights into the compatibility and functionality of the GP-PBAT biocomposites.

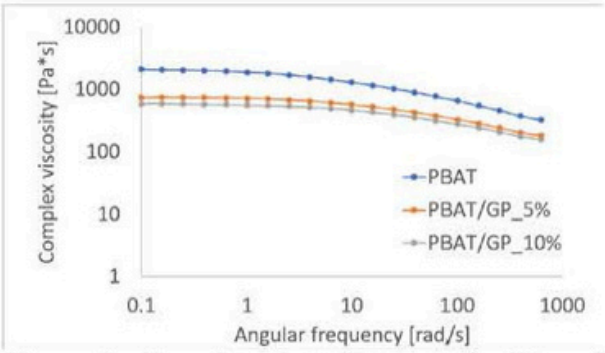


Figure 1. Complex viscosity as a function of frequency

Rheological characterization, specifically focusing on the measurement of Melt Strength (MS) and the Breaking Stretching Ratio (BSR), successfully

validated the filmability of both the 5% and 10% formulations. The melt drawing behavior demonstrated sufficient melt elasticity and bubble stability, indicating that the presence of the biofiller does not compromise the continuous production of thin blown films.
Tensile testing revealed that the introduction of the grape pomace filler did not induce severe embrittlement of the PBAT matrix—a common drawback when introducing rigid natural fillers into flexible polymers. Crucially, the biocomposite films maintained high elongation at break values, preserving the inherent toughness and flexibility required for flexible packaging applications.
Furthermore, the inclusion of the filler significantly altered the material's interaction with the environment. The natural compounds within the GP induced a distinct change in the kinetics of photo-oxidation, altering the UV degradation pathway. Similarly, the biodegradation analysis under controlled conditions showed a modified degradation rate, suggesting that the organic nature of the filler can be leveraged to tune the environmental lifespan of the film.
The collective findings of this study highlight the viable and highly promising potential of grape pomace as a sustainable biofiller in PBAT-based thin films manufactured via film blowing. By successfully balancing melt processability and mechanical ductility, this research demonstrates that high-volume agro-industrial waste can be effectively upcycled into high-value applications.
Ultimately, these results offer a foundational framework for the development of fully biodegradable, eco-friendly packaging films, offering a tangible solution to mitigate plastic pollution while simultaneously creating new value chains within the agro-industrial and winemaking sectors.

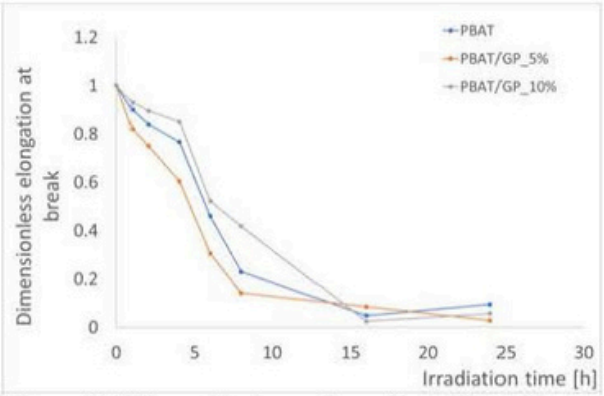


Figure 2. Dimensionless elongation at break as a function of irradiation time

Conclusions

This research highlights that grape pomace can be effectively upcycled from a high-volume winemaking byproduct into a functional, value-added biofiller for biodegradable plastics. These findings offer a scalable, circular-economy framework for the packaging industry, successfully bridging the gap between agro-industrial waste management and the development of next-generation, eco-friendly materials

[1] M. Rapisarda, V. Titone, G. Impallomeni, L. Botta, L. Pulvirenti, M. Leanza, E. Napoli, P. Rizzarelli M. C. Mistretta, Polymer Degradation and Stability 241 (2025) 111551

Acknowledgments
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ANTIOXIDANT AND UV-BLOCKING POLY(BUTYLENE SUCCINATE) FILMS VIA NITROXIDE RADICAL COUPLING FUNCTIONALIZATION

S. Coiai [1*], N. Migliore [1], E. Passaglia [1], R. Spiniello [1], C. Gambarotti [2], F. Cicogna [1]

[1] Istituto di Chimica dei Composti OrganoMetalllici (ICCOM), Consiglio Nazionale delle Ricerche, via G. Moruzzi 1, 56124 Pisa, Italia

[2] Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italia

e-mail: serena.coiai@cnr.it

Introduction

Poly(butylene succinate) (PBS) is a biodegradable aliphatic polyester that offers a promising alternative to conventional fossil-based plastics for short-life packaging applications. However, PBS exhibits limited resistance to thermo-oxidative and photo-oxidative degradation and insufficient UV-shielding capability, which may compromise material durability and product protection. To overcome these limitations, PBS was functionalized via nitroxide radical coupling (NRC) with 3,5-di-tert-butyl-4-hydroxybenzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (BHB-TEMPO), a functional molecule bearing a sterically hindered phenolic antioxidant group (Figure 1). This strategy was designed to covalently introduce antioxidant functionalities onto PBS chains while preserving the main polymer's properties [1].

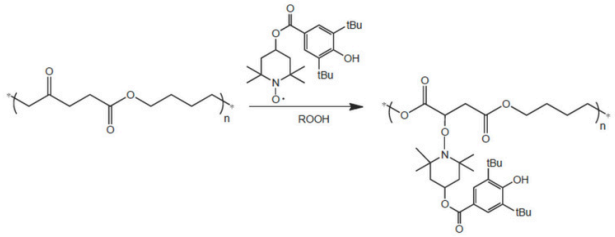


Figure 1. Schematic representation of PBS functionalization by NRC with BHB-TEMPO.

Results and discussion

The functionalization reaction was conducted both in solution and in the melt, using benzoyl peroxide as a radical initiator. UV–Vis and ^{1}H-NMR analyses confirmed the successful grafting of BHB-TEMPO onto PBS chains. The grafting degree increased from approximately 0.01 mol% in solution-modified samples to 0.16 mol% in melt-functionalized PBS, indicating the greater efficiency of the melt NRC process.

SEC showed only minor changes in molecular weight, which suggests effective suppression of radical-induced chain coupling and scission. DSC and TGA demonstrated that the modification did not significantly alter the thermal properties of PBS.

Functionalized films exhibited enhanced thermo-oxidative and UV stability, with the melt-functionalized sample providing the greatest protection. The improved UV-shielding performance was further validated by the β-carotene protection test [2] (Figure 2).

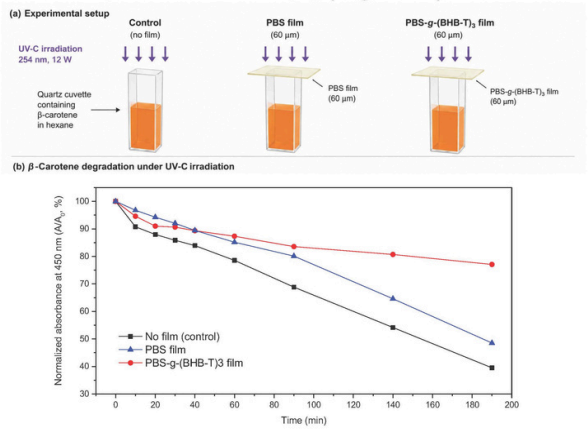


Figure 2. UV-protection test of β-carotene: (a) experimental setup and (b) normalized absorbance at 450 nm during UV-C irradiation.

The functionalized PBS film significantly reduced β-carotene degradation under UV-C exposure, confirming its ability to act as an effective UV barrier.

Conclusions

NRC represents an efficient approach for functionalizing PBS with antioxidant and UV-protective groups. The melt process improves grafting efficiency while preserving the polymer's molecular and thermal properties. The modified materials show improved resistance against thermal and photo-oxidative degradation and offer effective protection against UV-induced degradation of β-carotene.

References

[1] S. Coiai, N. Migliore, E. Passaglia, R. Spiniello, C. Gambarotti, F. Cicogna, *Compounds*, 3, 180-193 (2023).

[2] F. Ge, Y. Ding, L. Yang, Y. Huang, L. Jiang, Y. Dan, *RSC Adv.,* 5, 70473–70481 (2015).

THERMAL METHOD TO RECOVER GLASS FIBERS FROM EPOXY RESIN COMPOSITES

E. Di Francesco[1], N. Parodi[1], R. Freccero[1], A. Pastorino[1], D. Cavallo[1], M. Alloisio[1], M. Castellano[1], S. Vicini[1]

[1] Dipartimento di Chimica e Chimica Industriale (Università di Genova, DCCI, Via Dodecaneso 31, 16165 Genova, Italia).

e-mail: eleonora.di.francesco@edu.unige.it

Introduction

Wind energy has become a leading renewable source, but the disposal of end-of-life turbine blades represents a significant environmental challenge, with an estimated 43 million tons of non-recyclable waste by 2050. Wind blades are mainly composed of glass/carbon fiber reinforced polymers (GFRP/CFRP), making fiber recovery essential for sustainable recycling. Among current recycling methods, mechanical grinding is widely used but degrades fiber integrity, while chemical treatments preserve fiber properties but are difficult to scale up. Thermal recycling, particularly pyrolysis, is considered the most promising industrial solution, although it damages fibers and leaves char residues. [1] This work presents preliminary results of a project investigating induction heating as an alternative thermal recycling method. Compared with pyrolysis, induction heating offers higher energy efficiency, improved safety, and rapid heating, reducing fiber exposure to high temperatures. [2] This is expected to better preserve the mechanical properties of recovered glass fibers while maintaining the scalability and versatility required for industrial applications.

Results and discussion

Samples were collected from a blade specimen of end-of-life wind turbine Vestas V47. The materials were characterized through DSC, TGA, FTIR and XRF results, taking into account the information listed in the technical data sheet provided by the manufacturer. The results showed that the material is mainly composed by epoxy resin bisphenol A-based reinforced with glass fibers.

A pyrolysis treatment (instrument: CARBOLITE model, vertical tube furnace) was performed to evaluate the effect of this thermal process, on 1x1x0,5 cm samples size, under nitrogen gas flux of 100 mL/min, controlled by a flowmeter. The furnace was heated from room temperature to 500 °C using two different heating profiles: the first with a ramp of 5 °C/min for 95 minutes and the second with a ramp of 20 °C/min for 25 minutes. After the furnace reached the desired temperature, it was maintained for approximately 10 min to complete the pyrolysis. The reactor and the samples required 8 h to cool down to room temperature.

The percentage of organic residue in the pyrolysis product was determined by subtracting the glass fiber content, estimated by calcination. Treatments performed with both heating ramps yielded a resin removal of approximately 83–84%. In both processes, products are mainly solid (figures 2a and 2b), due to the presence of a cross-linked structure and stable aromatic units, which promote the formation of a dense carbonaceous residue. Fibers recovered from both pyrolysis treatments are anchored to the solid char derived from epoxy resin degradation, and their removal implies the formation of a "fluffy" appearance ascribable to fiber breakage (figure 2c).

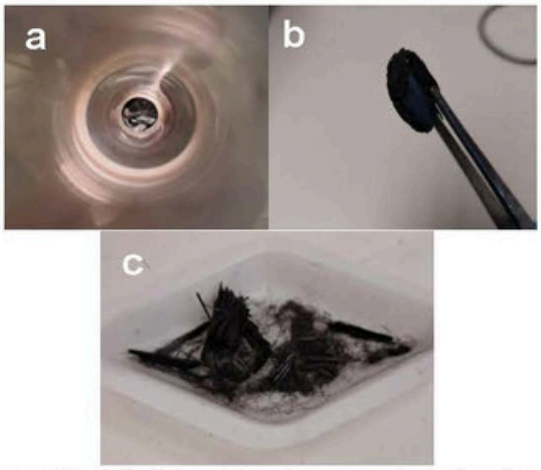


Figure 2. a) Solid residue from pyrolysis treatment at 500°C, 5°C/min. b) Solid residue from pyrolysis treatment at 500°C, 20°C/min. c) Fibers recovered from the solid residue of pyrolysis treatment at 500°C. 20°C/min.

The thermal treatment through induction heating was performed with an instrument model: VEVOR 15 kW, Ultra High Frequency Induction Heating Machine 30-100 KHz, on 1x1x0,5 cm samples size, covered with aluminum foil and then put inside a closed quartz tube (20 cm length, 25 mm diameter, 1 mm thick) which was passed through a round coil (figure 3).



Figure 3. Set-up of induction heating treatment

During 250 seconds of treatment at 400A, the aluminum cover (6 layers of sheets) reached the red heat temperature but not its melting point. Temperature range associated with the red coloration of this metal is between 500°C and 650°C. Thermal conductivity of aluminum is significantly higher than that of the polymeric material. This large difference means that while the metal heats up quickly, the sample requires much more time to reach similar temperatures through conduction. Considering an average heating time of 3-5 minutes, it is estimated that the sample did not reach temperatures up to 550 °C. Induction heating of GFRP in contact with a conductor comes out to produce a compact and easy-to-handle sample, achieved with very short processing times (figure 4). The epoxy resin reached its degradation temperature within 3-5 minutes, representing a significant reduction in time compared with previous pyrolysis experiments. In all samples heated for 250 s at 400 A the percentage of resin removal was around 93-95%. Fibers recovered from the induction heating can be easily separated.

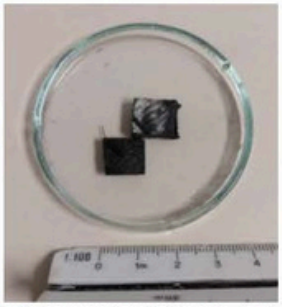


Figure 4: Solid product from induction heating treatment at 400A for 250s.

Vapors created from thermal degradation of the resin get condensed very quickly. Moreover, the sample and the metal require only 10 minutes to cool down to room temperature once the magnetic field is switched off. Aluminum has been chosen as conductive material, since it can be used repeatedly after thermal or chemical cleaning. Considering that it is a passive metal, it spontaneously forms a thin protective alumina layer upon exposure to oxygen. This feature prevents further oxidation of aluminum and consequently allows it to retain its electrical conductivity. Scanning electron microscopy (SEM; instrument model: Zeiss EVO 40) was used to observe the surface of recovered fibers. The organic residue appear to be uniformly distributed on fiber surfaces (figura 5a). Fibers have been incorporated into a mixture of EPIKOTE RIMR 135 and EPIKURE RIMH 134, an epoxy resin bisphenol A-based and a cross-linker. Subsequently, the composite obtained was cross-cut, and the sections were examined by SEM to analyze the fiber–resin interface (figure 5b). Results are promising, as they clearly indicate good adhesion between the surface and the matrix.

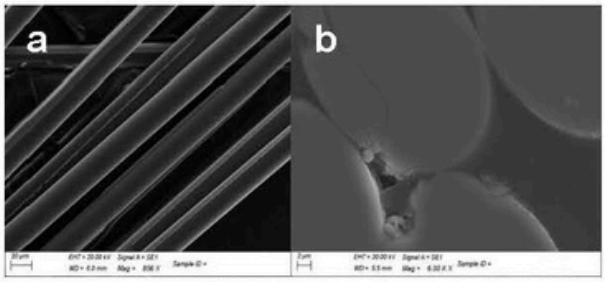


Figure 5. a) Fibers after induction heating treatment at 400A for 250s (856x). b) SEM image of fiber-resin interface (6000x).

Conclusions

This study proposes induction heating as an alternative method for GFRP recycle. Compared to pyrolysis, it significantly reduces processing time and improves the quality of the recovered fibers. Future work will focus on process scale-up and the reuse of recycled fibers in new composite materials.

References

[1] S.J. Pickering, 4-Thermal methods for recycling waste composites. Management, Recycling and Reuse of Waste Composites (2010) 65-101

[2] R. Rudolf, P. Mitschang, M. Neitzel, Induction heating of continuous carbon-fibre-reinforced thermoplastics. Composites Part A-Applied

Acknowledgments

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INFLUENCE OF FAST PYROLYSIS BIO-OIL-DERIVED PHENOLIC-RICH FRACTION ON PLLA UV STABILITY

D. Duraccio[1], M. Di Maro [1], G. Gomez d'Ayala [2], G. Dal Poggetto[2], Taina Ohra-aho[3], Elmeri Pienihäkkinen[3], Petri Widsten[3], Giulio Malucelli[4]

[1] Istituto di Scienze e Tecnologie per L'Energia e La Mobilità Sostenibili CNR Sede Secondaria Strada Delle Cacce, 73 10135 Torino, Italy
[2] Istituto per i Polimeri, Compositi e Biomateriali (IPCB) Via Campi Flegrei 34, Comprensorio "A. Olivetti" 80078 Pozzuoli (Na), Italy
[3] VTT Technical Research Centre of Finland Ltd., Tekniikantie 21, 02150 Espoo, Finland
[4] Politecnico di Torino - Dipartimento di Scienza Applicata e Tecnologia, Viale Teresa Michel 5, 15121 Alessandria, Italy
e-mail: mattia.dimaro@stems.cnr.it

Introduction

Poly-L-lactic acid (PLLA) is a thermoplastic polymer derived from renewable resources, which is emerging as an alternative polymer matrix with a wide spectrum of applications in medicine, packaging, agriculture, electronics, and the automotive industry [1,2]. It possesses good mechanical properties, can be easily melt-processed and also mechanically recycled. However, given its biodegradable nature, it is inherently more prone to photodegradation than conventional polymers (i.e. polypropylene, polyethylene) derived from fossil fuels [3].
In this work, we investigated the ability of phenolic-rich fraction obtained by fast pyrolysis bio-oil (PRF-BO) from logging residues to mitigate the effects of ageing on PLLA when exposed to UV irradiation. The ageing was evaluated by assessing changes in the structure, morphology, thermal, and mechanical properties of a PLLA blend containing 2 wt.% PRF-BO.

Methods

Fast pyrolysis bio-oil (FPBO) was produced from logging residues using a circulating fluidized bed pilot unit operated with the feed capacity of 20 kg/h biomass feedstock. A detailed description of the unit and fractionation procedure can be found elsewhere [4]. The water insoluble phenolic-rich fraction was separated from FPBO via water addition, using a water/organics ratio of 1:1. PRF-BO was collected from the bottom of the separation vessel for further use. Based on the NMR results, shown in Figure 1, PRF-BO shows different phenolic hydroxyls in which the p-hydroxyphenyl-, cathecol- and guaiacyl-type phenolic OH beared the important active sites. 2wt.% of PRF-BO was then added to PLLA by melt mixing using a Brabender W50E internal mixer (175°C and 100rpm). Unfilled PLLA was processed at the same conditions as reference. The materials were labeled as PLA0 for the unfilled polymer and PLA2 for the blend containing 2wt.% of PRF-BO. PLA0 and PLA2 were compression-molded using a Collin P200T laboratory press at 170 °C (100 bar for 5 min) to obtain several plates suitable for the ageing process.

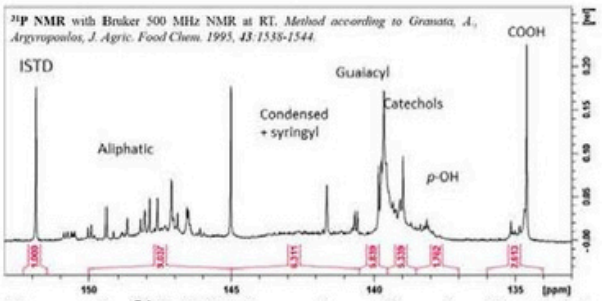


Figure 1. ^{31}P NMR spectra of water insoluble phenolic rich fraction.

The ageing process was conducted in a climate chamber equipped with a mercury UV lamp (λ > 250 nm) under dry conditions (RH = 0%, T = 40 °C) for two different times (t_1 = 180 h; t_2 = 560 h). PLA0 and PLA2 were analyzed by Gel Permeation Chromatography (GPC) to evaluate the change in molecular weights (M_w, M_n and IV) of PLLA as a result of ageing process. The analysis was carried out using a GPC Omnisec system equipped with a triple detector and a Phenogel (Phenomenex) column set after dissolution in $CHCl_3$.
Structural analysis was performed by X-ray diffraction (XRD) in Bragg-Brentano geometry using a PANalytical X'Pert PRO diffractometer with CuK_α radiation (λ = 0.15418 nm), operating at 45 kV and 40 mA, to analyze the change in crystallinity of PLLA during the ageing.
Mechanical tests were conducted with an Instron 5966 dynamometer in tensile configuration. The test was performed at RT at a constant crosshead speed of 2 mm/min until break.

Results and discussion

Slab images of PLA0 and PLA2 after 180 and 560h of UV-treatment are reported in Figure 2. From a visual standpoint, PLA0 sheets exhibit an increase in surface roughness and a transition from a transparent to a white color, indicating an increase in the material's crystallinity. PLA0 also appears extremely brittle when cut. These effects are considerably less pronounced in PLA2 after UV-ageing: the sample is significantly less brittle and does not change its color.

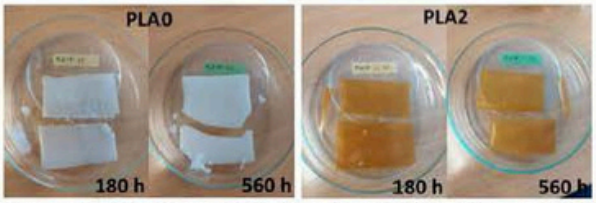


Figure 2. PLA0 and PLA2 after 180 h (t_1) and 540 h (t_2) of UV exposure.

The increase in crystallinity of PLA0 is confirmed by the XRD results. In Figure 3, the amorphous PLA0 crystallizes already after 180h (7 days) in the α-form of PLLA [5]. Conversely, PLA2 remains amorphous even after 560h irradiation.

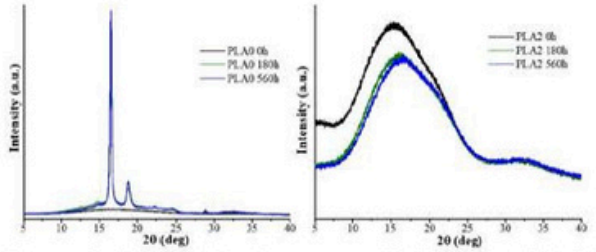


Figure 3. XRD diffractograms of PLA0 and PLA2 before and after the UV-ageing.

PLA0 and PLA2 before UV exposure exhibit a significant difference in molecular weights (Table 1), suggesting that the presence of PRF-BO aleardy acts as a stabilizing agent during melt mixing.

Table 1. Molecular weights of a of PLA0 and PLA2 before and after ageing process.

Sample	M_n (Da)	M_w (Da)
PLA0	87277	112511
PLA0 t_1	9717	18511
PLA0 t_2	3962	10761
PLA2	109007	131904
PLA2 t_1	78263	108841
PLA2 t_2	58448	106985

After UV irradiation, both M_n and M_w of PLA0 drastically decrease as time of exposure increases. After 580h irradiation, M_n and M_w decrease by about 90-95% with respect to those measured at t_0. Conversely, in the presence of PRF-BO, the decrease in molecular weight is significantly attenuated, evidencing the protective effect exerted by PRF-BO.

The mechanical properties of PLA0 and PLA2 before and after ageing are collected in table 2. The ability of PRF-BO to slow down the degradation of PLLA is supported by the mechanical properties of the filled material. More specifically, PLA0 after ageing becomes very brittle already after 180h, so that it is not possible to prepare specimens suitable for mechanical tests. In contrast, PLA2 shows a slightly reduction in mechanical parameters (i.e., Young's modulus and elongation at break) but exhibits significantly better mechanical properties than PLA0.

Table 2. Mechanical properties of PLA0 and PLA2 before and after ageing process.

Sample	E (MPa)	ε_b (%)	σ_b (MPa)
PLA0	2972 ± 115	5.9 ± 3.0	38.0 ± 4.8
PLA0 t_1	n.d.	n.d.	n.d.
PLA0 t_2	n.d.	n.d.	n.d
PLA2	2651 ± 106	3.8 ± 0.7	38.7 ± 3.1
PLA2 t_1	2785 ± 122	2.0 ± 0.2	39.4 ± 2.5
PLA2 t_2	2150 ± 121	2.0 ± 0.2	32.2 ± 2.3

Conclusions

Preliminary results of this work indicate that UV ageing of PLLA causes a decrease in molecular weight, an increase in crystallinity and a dramatic drop of the mechanical properties already after 7 days of exposure. The presence of 2 wt.% of PRF-BO drastically slows down the ageing of PLLA, allowing it to maintain its mechanical properties for up to 23 days.

References

[1] S. Navin, A. Mondal. *Polymer Bulletin* 81.13 11421-11457 (2024).
[2] P. Brachi, G. Ruoppolo, M.G. Faga et al. *Sci Rep* (2026).
[3] H. Jiang et al. *Environ Geochem Health* 46-163 (2024).
[4] E. Pienihäkkinen et al., *J. Anal. Appl. Pyrolysis* 176-106239 (2023).
[5] D. Duraccio et al., *Polymers* 18-871(2026).

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Polyethylene Glycol-Assisted Film Stacking of Polylactide/Bacterial Cellulose Nanocomposites for Sustainable Food Packaging

Zonta E.[1,2,3], Mantovani S.[1,2], Fredi G.[1,2]

1 Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123 Trento, Italy.
2 National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy.
3 Bioniks srl, Via della Segheria 1/H, 37141 Montorio (VR), Italy.
e-mail: giulia.fredi@unitn.it

EXTENDED ABSTRACT

Introduction

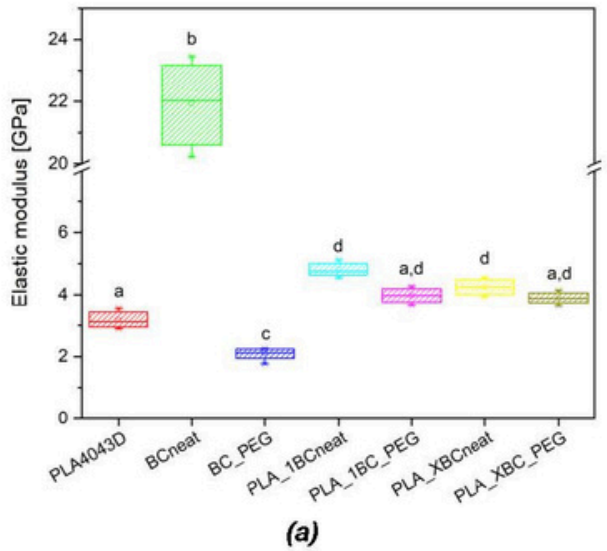
Cellulose is the most abundant renewable biopolymer and an attractive platform for sustainable packaging. Bacterial cellulose (BC), produced as a highly pure nanofibrillar network, combines high specific strength, biocompatibility and biodegradability. However, preserving its reinforcing ability when it is coupled with thermoplastic matrices remains challenging, because dried BC can be brittle and the drying-induced hornification can densify the nanofibre network and limit polymer infiltration. In this work, film stacking was selected as a solvent-free route to assemble laminated polylactide (PLA)/BC nanocomposites, while polyethylene glycol (PEG) impregnation was investigated as a simple treatment to plasticize BC and promote adhesion with the PLA matrix.

Experimental

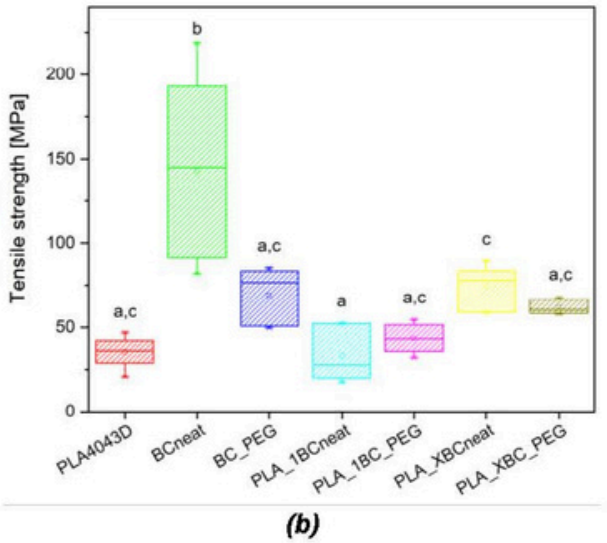
BC sheets supplied by Bioniks srl were dried and impregnated with PEGs of different molecular weights and concentrations. Neat or PEG-treated BC layers were alternated with PLA films and consolidated by hot pressing to obtain single- and multi-layer laminates. The composites were characterized by tensile testing, scanning electron microscopy, thermal and optical analyses, gas permeability measurements, water absorption and preliminary industrial composting tests.

Results and discussion

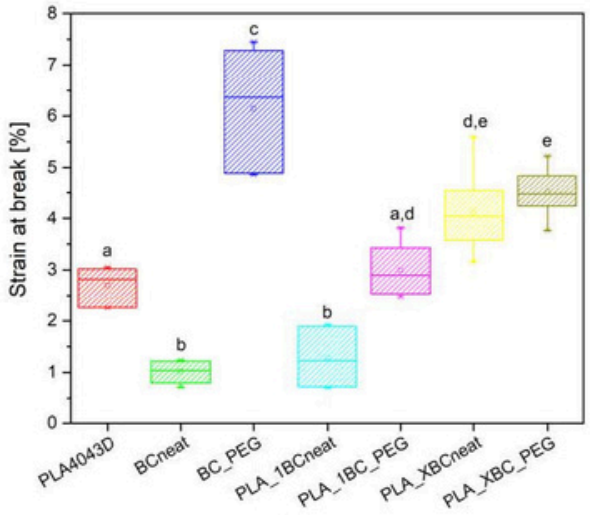
PEG impregnation markedly improved the handling and deformability of dried BC, giving up to a six-fold increase in strain at break compared with neat dried BC. SEM observations indicated that PEG-treated BC favoured PLA penetration into the nanofibrillar network and generated a continuous, well-bonded BC/PLA interface with limited fibre pull-out or defibrillation. The improved interface translated into higher stiffness and strength than neat PLA, together with enhanced ductility in optimized multi-layer laminates (Figure 1).



(a)



(b)



(c)

Figure 1. *Results of the tensile tests on neat PLA, neat BC, PEG-impregnated BC, and the prepared laminates with one or more ("X") BC layers. (a) Elastic modulus; (b) tensile strength; (c) strain at break.*

The gas barrier response was also strongly affected by the presence of BC. All composites showed lower O_2 and CO_2 permeability than neat PLA, even when only one BC layer was used, confirming the efficiency of the nanocellulose network as a tortuous path for gas transport. Optical analyses showed that PEG-treated BC better preserved transparency, while all composites provided a UV-barrier effect, an advantage for light-sensitive food products. Water uptake was significantly reduced with respect to neat BC, with preliminary data showing about 95-99% lower hygroscopicity, and composting tests confirmed the compatibility of the laminates with industrial compostable packaging scenarios.

Conclusions

This study demonstrates that PEG impregnation is an effective strategy for integrating bacterial cellulose into PLA laminates by film stacking. The treatment improves BC processability and interfacial adhesion, enabling biodegradable nanocomposites with enhanced mechanical performance, reduced gas permeability, UV-shielding behaviour, low hygroscopicity and compostability. These properties indicate strong potential for sustainable food packaging, particularly where mechanical integrity, transparency and protection from oxygen and light are simultaneously required.

References

[1] T.C. Mokhena et al., Carbohydrate Polymers, 273, 118507 (2021).
[2] E. Zonta et al., ACS Omega, 11, 8283-8296 (2026).
[3] M. Hervy et al., Composites Part A, 107, 155-163 (2018).

Acknowledgments

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Biopol4Soil - BIODERIVED POLYMERIC GRANULES AND NON-WOVEN FABRICS FOR SUSTAINABLE AGRICULTURE: BIODEGRADABILITY AND PHYTOTOXICITY EVALUATION

L. Gianoglio[1,3] – A. Boarino[2,3] – C. Cecone[1,3] – S. Celletti[2,3] – M. Zanetti[1,3] – E. Padoan[2,3]

[1] Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125, Turin, Italy
[2] Department of Agricultural, Forest and Food Sciences (DISAFA), University of Turin, Largo Paolo Braccini 2, Grugliasco, 10095, Turin, Italy
[3] SUSPLAS@UniTo, Sustainable Plastic Scientific Hub, University of Turin, Via Pietro Giuria 7, 10125 Turin, Italy

e-mail: luca.gianoglio@unito.it

Introduction

The valorization of natural resources is a cornerstone of the ecological and energy transition. Beyond their conventional use as food additives and pharmaceutical excipients, maize-derived maltodextrins and proteins (e.g., zein) have demonstrated remarkable potential as sustainable building blocks for synthesizing functional polymeric materials, in both granular and fibrous forms. Processing these natural biomolecule matrices without toxic organic solvents enables environmentally benign applications in the agricultural and water remediation sectors, such as heavy metal trapping, organic contaminant removal, and the controlled release of bioactive compounds. Despite these promising functional capabilities, the direct application of such biopolymers in agronomic soils requires thorough validation of their environmental persistence, stability, and ecocompatibility. To bridge this knowledge gap, the Biopol4soil project investigates the agricultural applicability of two innovative biobased material classes developed via green synthetic protocols: (i) neutral and cationic cross-linked maltodextrin granules and (ii) electrospun fibrous nonwoven fabrics (NWFs) composed of maltodextrin and zein. Evaluating their biodegradation kinetics in soil environments and ensuring the total absence of phytotoxicity in the soil-plant system are essential prerequisites for their safe deployment for soil remediation or as soil conditioners.

Results and discussion

Water-insoluble polymeric granules were synthesized via epoxide ring-opening cross-linking of commercial maltodextrin (Glucidex 2®, GLU2) using 1,4-butanediol diglycidyl ether (BDE) while the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) or glycidyltrimethylammonium (GTC) allowed the functionalization of the polymers with cationic groups, yielding three functional formulations (GR1: GLU_BDE, GR2: GLU_DABCO_BDE, GR3: GLU_GTC_BDE). The synthesis exhibited high atom economy with mass balances over 80%. Morphological characterization revealed polydisperse granules (10–200 µm) with smooth external surfaces lacking macro- or mesoporosity. FTIR-ATR confirmed quaternary ammonium shoulder bands at 1590 cm^{-1} while TGA and DSC indicated amorphous polymeric networks with high thermal stability (Tonset > 260 °C) and ~20% stable carbon residue at 700 °C. Elemental analysis measurements confirmed the presence of quaternary ammonium function for GR2 and GR3 with a nitrogen content of 0.59 wt.% and 0.45 wt.%, respectively. Remarkably, all granules demonstrated extraordinary water retention capacities after 12 h of immersion (GR1: 622%, GR2: 734%, GR3: 694%), highlighting their potential as agricultural hydro-retention additives to mitigate soil water stress and nutrient leaching. Biodegradation studies in simulated soil solutions (ISO 14851) over 8 weeks showed progressive weight loss for all granule formulations, confirming microbial accessibility. For fibrous NWFs (NWF1: pure maltodextrin; NWF2: maltodextrin + zein), soil incubation tests (ISO 17556) were conducted across two contrasting soil matrices: a sub-alkaline soil (pH 7.7, microbial biomass 226 mg/kg) and an acid soil (pH 4.7, microbial biomass 62 mg/kg). In sub-alkaline soil, degradation was extremely rapid, resulting in complete degradation of both NWF1 and NWF2 within 2 weeks, supported by respirometric CO_2 cumulative emission metrics. Conversely, in low-biomass acid soil, degradation proceeded at a controlled, slower rate, revealing a distinct

structural effect: the incorporation of zein hydrophobic proteins in NWF2 significantly retarded biodegradation compared to pure maltodextrin fibers.

Conclusions

The Biopol4soil project aims to demonstrate that bio-derived cross-linked maltodextrin granules and electrospun maltodextrin/zein non-woven fabrics can combine functional performance with agronomic safety. Their high water retention capacities, tunable biodegradation kinetics responsive to soil microbial biomass and protein content, establish them as promising, highly sustainable, eco-compatible multifunctional materials. These biopolymers offer a viable, green alternative for soil conditioning, water retention enhancement, and sustainable environmental remediation in modern agriculture.

References

[1] A. Boarino, N. Carrara, E. Padoan, L.R. Celi, H.A. Klok, Macromolecular Bioscience, 2025, 25(8), 2500042
[2]S. Celletti, R. Fedeli,M. Ghorbani, S. Loppi, Science of the Total Environment, 2023, 856, 159163
[3]C. Cecone, G. Costamagna, M. Ginepro, F. Trotta,RSC Advances, 2021, 11, 7653–7662.
[4]C. Cecone, G. Hoti, M. Zanetti, F. Trotta P. Bracco, RSC Advances, 2022, 12, 762–771.

Acknowledgments

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CHARACTERIZATION OF HYDROLYZED POLYESTERS FROM AGRO-WASTE: EFFECT OF EXTRACTION CONDITIONS ON COMPOSITION

C. Meo [1], E. Buratti [2], M. Calosi [1], I. Dedieu [3], A. Montanari [3], T. Barbieri[3], M. Bertoldo[1]

[1] Dept. of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy
[2] Dept. of Environmental and Prevention Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy
[3] Tomapaint Srl, via Roma 4, S.Ilario D'Enza, 42049, Reggio Emilia, Italy
e-mail: cristina.meo@unife.it

Introduction

In recent years, research on sustainable coatings has garnered growing interest as a response to the issues associated with fossil-based polymers commonly used in industrial coatings, including the depletion of petrochemical resources, pollution from plastics and microplastics, and greenhouse gas emissions linked to their disposal. In this context, biobased polymers derived from renewable sources represent a promising alternative, especially when they are produced by valorizing agro-industrial byproducts in accordance with the principles of the circular economy [1]. Among the biomasses of interest, tomato processing by-products play a particularly significant role. Tomato peels contain high amounts of cutin, which can account for up to 40–80% of their dry weight [2]. Cutin is an amorphous, cross-linked natural polyester consisting mainly of C16 and C18 polyhydroxylated fatty acids linked by ester bonds. The main monomers include derivatives of dihydroxyhexadecanoic acid and hydroxy-epoxyoctadecanoic acid [1] [2]. The most interesting aspect of cutin is its high hydrophobicity. Thanks to this property, cutin exhibits low permeability to water and water vapor, providing plant surfaces with effective protection against moisture loss. In addition to its excellent barrier properties, cutin combines biodegradability, good thermal stability, and adequate mechanical properties, making it a particularly promising candidate for the development of sustainable coatings for various substrates, including paper, glass, and metals [1] [2]. Until now, cutin had not been utilized due to the difficulty of extracting it, given its high insolubility, but in recent years, a few technologies have been developed to obtain cutin monomers from tomato agricultural waste on an industrial scale, for example, through alkaline hydrolysis of the biopolyester and subsequent acidic precipitation of the hydrolyzed cutin (HC) monomers. The composition of the resulting C16–C18 monomer mixture depends both on the plant source and on the hydrolysis conditions, since some low-molecular-weight oligomers may also be present in the mixture of ω-hydroxy acids [1]. Despite growing interest in these recovery technologies, the detailed composition of these mixtures and the influence of hydrolysis parameters on the various components have not yet been systematically investigated.

Therefore, the aim of this study is to analyze the effect of the main parameters of the alkaline hydrolysis process (temperature and time) on the composition of the monomer mixture derived from tomato cutin, evaluating how different operating conditions influence the nature and relative percentage of the C16 and C18 components obtained.

Results and discussion

The spectroscopic analysis of previously freeze-dried cutin samples using NMR and IR-ATR spectroscopy showed that the characteristic peaks of cutin are common to all samples, regardless of the hydrolysis temperature and reaction time applied, which varied by approximately 20 °C and 60 min, respectively. In particular, in the ^{1}H-NMR spectrum, a triplet at 3.36 ppm is observed for the CH_2 groups attached to the terminal OH group, and at 2.18 ppm, the triplet of the CH_2 group in the α-position to the carboxylic acid (C=O) is detectable; finally, the multiplets present between 1.20 ppm and 1.45 ppm are attributed to protons bonded to the carbon atoms of the saturated chain [2]. ^{13}C NMR spectroscopy shows a prominent peak at 175.3 ppm that can be assigned to the carbon of carboxylic acid groups. The peaks at 70.3 and 61.5 ppm are assigned to carbons bearing secondary and primary hydroxyl groups, respectively [2]. In the ATR spectrum, at 1703

cm⁻¹, an intense band associated with the carbonyl stretching of the carboxyl group (C=O) is observed, along with a shoulder at 1730 cm⁻¹ attributable to the ester carbonyl group, indicating the presence of incompletely hydrolyzed cutin oligomers. To investigate the composition of the samples in greater detail, GPC analyses were performed to study the molecular weight distribution, along with DSC analyses and acid-base titration of the COOH groups.
The last analysis allowed us to determine the COOH content in the cutin mixtures, which ranged from 2.23 to 2.93 mmol/g across the different samples. The COOH content was correlated with the temperature and treatment time of the tomato peels (Figure 1), revealing an increase in the amount of COOH as both evaluated parameters increased, indicating greater efficiency of the basic hydrolysis process.

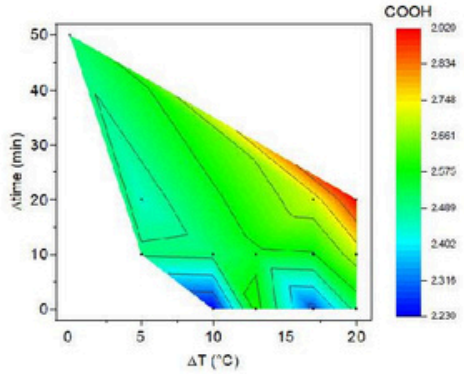


Figure 1: *XYZ contour plot of the average COOH values in the samples (Z) as a function of the tested temperatures (X) and extraction times (Y).*

From the GPC analyses, the chromatogram obtained for the various samples revealed three peaks (Figure 2a) which, in order of elution, were associated with the presence of oligomers ($t_R \approx$ 14.2), dimers ($t_R \approx$ 14.5), and monomers ($t_R \approx$ 15.0). It was observed that the percentage of the three components varied depending on the extraction conditions (Figure 2b); specifically, the amount of dimers was nearly constant, the amount of monomers varied within a range of 46 - 71%, and the amount of oligomers varied between 12% and 40%.
DSC analyses of all the samples studied showed at least one melting peak (around 55°C) with the correlated crystallization peak, thus indicating the presence crystallizable components. A glass transition temperature (Tg) is also visible at around -33°C for all the samples.

Conclusions

This study focused on the in-depth characterization of the mixture of cutin monomers. Combined NMR and IR-ATR analysis confirmed the presence of functional groups characteristic of cutin in all the samples studied, without revealing the formation of new chemical species following hydrolysis treatments. Acid-base titration revealed an increase in the content of carboxyl groups as treatment time and temperature increased, indicating greater efficiency of the alkaline hydrolysis process. GPC analyses showed a molecular weight distribution consisting of oligomers, dimers, and monomers, with a significant variation in the ratio between these species depending on the operating conditions. DSC analyses also revealed the presence of a crystalline phase in all samples, characterized by similar melting temperatures. Overall, the results demonstrate that hydrolysis parameters influence the composition of the mixture derived from tomato cutin, providing useful insights for optimizing the extraction and valorization of this biopolymer for sustainable applications.

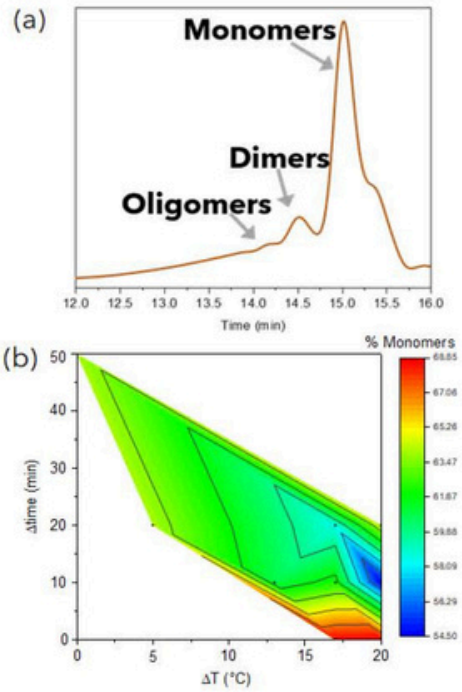


Figure 2: *GPC analysis. (a) Three chromatographic peaks corresponding to oligomers, dimers, and monomers. (b) XYZ contour plot of the average percentage of monomers in the samples (Z) as a function of the tested temperatures (X) and extraction times (Y).*

References

[1] E. Buratti et al., *ACS Sustain. Chem. Eng.* **2024**, 12, 6856-6869,
[2] E. Buratti et al., *Progress in Organic Coatings*, **2026,** 213,109946

Acknowledgments

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INFLUENCE OF GLOCHIDS AND COMPATIBILIZER ON THE RHEOLOGICAL, MECHANICAL AND BIODEGRADATION BEHAVIOUR OF PBAT AND PLA BIOCOMPOSITES

M.C. Mistretta[1], L. Botta[1], E. Indovino[1], G. Lalia[1], P. Rizzarelli[2], M. Rapisarda[2], M. Leanza[2], M. Bianchi[3], A. Dorigato[3]

[1] Dept. of Engineering, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italia
[2] Institute of Polymers, Composites and Biomaterials - National Research Council (IPCB-CNR), Via Paolo Gaifami 18, Catania, Italia
[3] Department of Industrial Engineering (DII), Via Sommarive 9, 38123, Trento, Italia
e-mail: mariachiara,mistretta@unipa.it

Introduction

Biocomposites derived from biodegradable polymers and agro-food residues are a promising development in sustainable material technology. Among these residues, glochids (from Opuntia ficus-indica) are a plentiful and inexpensive lignocellulosic filler that can increase stiffness, reduce environmental impact and add value to a waste stream that is usually discarded during fruit processing. Incorporating them into polymer matrices supports circular economy strategies and enables the development of biodegradable composites with tunable mechanical and functional properties. However, limited compatibility between matrices and fillers often leads to weak interfacial adhesion and reduced performance [1, 2].

This study investigates PBAT and PLA as matrices to clarify the role of glochids as a bio-filler in different polymer systems, alongside a compatibilizer designed to improve matrix–filler interactions. Findings indicate that both glochids and the compatibilizer behave differently in PBAT and PLA.

Results and discussion

PLA/G and PBAT/G biocomposites, with and without compatibilizer, were prepared through melt blending in a Brabender mixer, using two different percentages of fillers: 10% and 20%. The sample codes and respective compositions of the biocomposites are shown in the Table 1 and 2.

Table 1: Samples code and compositions of PBAT biocomposites

Sample	G (wt%)	J (phr)
PBAT	0	0
PBAT_J	0	1
PBAT+G_10	10	0
PBAT+G_20	20	1
PBAT+G_10_J	10	0
PBAT+G_20_J	20	1

Table 2: Samples code and compositions of PLA biocomposites

Sample	G (wt%)	J (phr)
PLA	0	0
PLA_J	0	1
PLA+G_10	10	0
PLA+G_20	20	1
PLA+G_10_J	10	0
PLA+G_20_J	20	1

GPC analysis were carried out on PBAT, PLA, PBAT_J and PLA_J in order to evaluate molecular weight after the addition of the compatibilizer.

All of the biocomposites produced were characterized in terms of morphology, rheology, mechanical properties (via tensile testing), dynamic-mechanical behavior in order to evaluate the effect of adding glochids and a compatibilizer. Furthermore, biodegradation kinetics were assessed in the presence of both the filler and the compatibiliser.

The SEM image of the PBAT biocomposite shows good dispersion and interfacial adhesion.

The compatibiliser appears to increase interfacial adhesion.

In PLA biocomposites, however, interfacial adhesion appears to be poorer.

Rheological results show that viscosity increases in both PBAT and PLA biocomposites as the glochid content increases Fig. 1 and Fig. 2.
The addition of Joncryl significantly increases viscosity, particularly in PLA-matrix biocomposites.

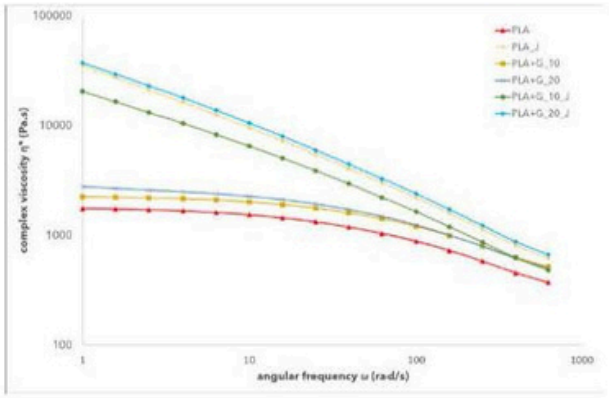


Figure 1. Complex viscosity as a function of frequency of pure PLA and glochid-filled biocomposites

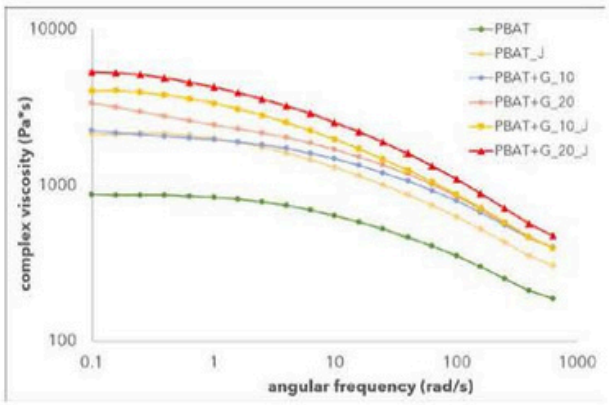


Figure 2. Complex viscosity as a function of frequency of pure PBAT and glochid-filled biocomposites

GPC results show that, following the addition of the compatibiliser, the molecular weight of PLA increases exponentially, whilst that of PBAT remains virtually unchanged; thus confirming the data obtained from the flow curves.
The mechanical results show that the addition of glochids stiffens and embrittles the biocomposites.
The addition of compatibilizer mitigates the embrittlement of the biocomposite especially for PBAT biocomposites.
Soil burial tests shows that weight loss increases as the glochids content increases and that glochids increases the biodegradation rate.
Joncryl slightly reduces the rate of biodegradation.

Conclusions

In this study, PBAT- based and PLA-based biocomposites were prepared using prickly pear glochids, both with and without a compatibilizer. All the results obtained showed that the addition of the compatibilizer has a greater influence in the case of PBAT, whilst it appears to act primarily as a chain extender in the case of PLA.
The addition of the compatibilizer alters the biodegradation kinetics; however, these remain acceptable due to the presence of the filler.

References

[1] L. Botta, M.C. Mistretta, G. La Mattina, F. Gargano, G. Liguori, Polymer Composites, 46 (13), (2025).
[2] F. Marchetta, L. D'Arienzo, L. Di Maio, L. Botta, M.C. Mistretta, P. Rizzarelli, M. Leanza, P. Scarfato, Composites Communications, (2025).

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CIRCULAR VALORIZATION OF POST-CONSUMER POLYURETHANE FOAMS THROUGH MECHANICAL RECYCLING AND SUSTAINABLE COMPOSITE DESIGN

J. Martignetti [1], L. D'Arienzo [1], L. Incarnato [1,2], P. Scarfato [2,3]

[1] Dept. of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132 – 84084 Fisciano (SA), Italy
[2] INSTM, National Interuniversity Consortium of Materials Science and Technology, Via G. Giusti, 9 – 50121 Florence, Italy
[3] Dept. of Civil Engineering, University of Salerno, Via Giovanni Paolo II, 132 – 84084 Fisciano (SA), Italy
e-mail: pscarfato@unisa.it

Introduction

The transition toward a circular plastics economy requires the development of innovative routes for the recovery and re-engineering of thermoset polymer wastes. Flexible polyurethane (PU) foams, widely employed in the bedding sector, represent a particularly challenging waste stream because their crosslinked structure prevents conventional melt reprocessing [1]. Rather than considering these materials as end-of-life products, they can be regarded as valuable secondary raw materials for the production of new functional systems.

In this work, post-consumer PU foams were mechanically recycled and transformed into densified panels and sustainable composites by combining cryogenic grinding, compression molding, and the incorporation of volcanic ash as a mineral filler. The study aims to demonstrate how waste-derived resources can be converted into value-added materials with enhanced thermo-mechanical performance, contributing to circular and sustainable polymer engineering.

Materials and methods

Commercial flexible polyurethane foams characterized by different viscoelastic properties were collected from post-consumer mattresses and subjected to cryogenic grinding using liquid nitrogen. The resulting powders were processed through compression molding in a hydraulic press to obtain densified panels. Both single-foam formulations and blends of different foam types were investigated.

The influence of particle size, molding temperature, pressure, and residence time on the properties of the recycled materials was systematically evaluated. Furthermore, volcanic ash was incorporated as a low-cost and abundant mineral filler to develop recycled PU-based composites.

The produced materials were characterized through optical and microscopic observations, FT-IR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), tensile testing, and puncture resistance measurements.

Results and discussion

The compression molding process successfully generated compact panels with good cohesion among the recycled foam particles. FT-IR analyses suggested that residual isocyanate functionalities may promote the formation of additional urethane and urea linkages during thermo-compression, contributing to interparticle bonding.

Mechanical performance was strongly influenced by the composition of the starting foams. Tensile modulus values ranged from approximately 2.5 to 18 MPa, while puncture resistance varied between 470 and 1220 J m^{-2}, demonstrating the possibility of tailoring material properties through appropriate foam selection and blending (Figure 1).

The incorporation of volcanic ash produced a further enhancement of material performance. In particular, the addition of about 10 wt% filler resulted in improved thermal stability and mechanical properties, indicating an effective reinforcing action of the mineral phase (Figure 2). The simultaneous valorization of polyurethane waste and volcanic ash represents an additional sustainability advantage of the proposed approach.

Conclusions

The results demonstrate the feasibility of transforming post-consumer flexible polyurethane foams into value-added materials through a simple mechanical recycling route. The combination of cryogenic grinding, compression molding, and sustainable mineral fillers enables the production of recycled panels with promising

thermo-mechanical properties for technical applications such as protective packaging, insulation elements, and cushioning systems.

References

[1] Karrech A., et al. A systematic review on the recycling of polyurethane materials. Cleaner Engineering and Circular Economy, 2025.

Acknowledgments

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This research was financed by the 'Accordi per l'innovazione' program (MISE – D.M. 31 December 2021) - 'STUDIO E SVILUPPO DI TECNOLOGIE PER IL RECUPERO E RIUTILIZZO DEI COSTITUENTI IL MATERASSO' (CUP: B49I23002740007)."

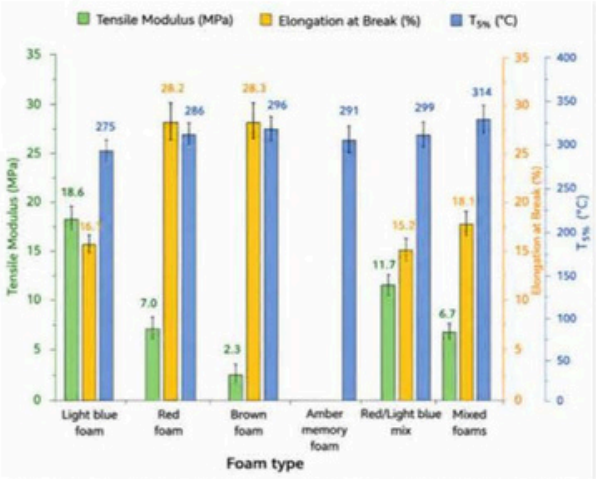


Figure 1. Effect of foam type on the properties of recycled PU panels.

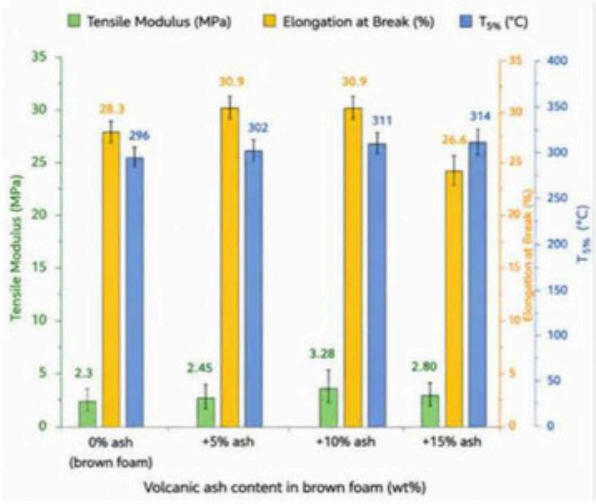


Figure 2. Effect of volcanic ash content on the properties of brown foam panels.

ITACONIC ACID: A SUSTAINABLE PLATFORM ALTERNATIVE TO ACRYLIC ACID IN RADICAL POLYMERIZATION

Tsvetevelina Georgieva, Michele Mauri and Roberto Simonutti

Department of Materials Science, University of Milan-Bicocca
Via R. Cozzi 55, 20125 Milano, Italy
e-mail: roberto.simonutti@unimib.it

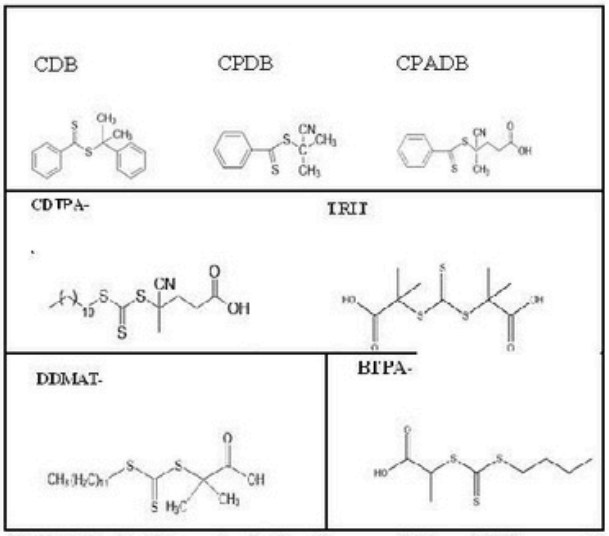
Introduction

Acrylates based polymers offer excellent chemical versatility, outstanding film-forming properties, and optimal reactivity, making them the industry standard for coatings and adhesives. However, their production heavily relies on non-renewable fossil sources, and the resulting polymers exhibit poor biodegradability. Consequently, current research is strongly driven toward sustainable bio-based alternatives—such as itaconic or methylsuccinic acids—to mitigate environmental impact without sacrificing performance. Itaconic acid, obtained via sugar fermentation, is endowed with two orthogonal functionalities: a double bond capable of undergoing radical polymerization, and carboxylic groups that can either participate in polycondensation reactions or be esterified similarly to acrylic acid. [1] Despite being considered one of the most promising alternatives to acrylates, the use of itaconic acid is still limited especially in radical polymerization due to slow polymerization kinetics and formation of low-molecular-weight polymers due to steric and electronic effects [2]. In our approach RAFT (Reversible Addition-Fragmentation Chain Transfer) polymerization is employed as a strategy to overcome these limitations, as this synthesis allows to produce polymers with controlled molecular weight and composition [2]. Various Chain Transfer Agents (CTAs) and initiators are used to test polymerizations conducted at different temperatures and reaction times, in order to identify the optimal reaction conditions. As monomers we focused on dimethyl itaconate (DMI), whose polymers has Tg in range of 80-100 C, dibutyl itaconate (DBI) forming a polymer with Tg around -10 °C, with possible film-former characteristic, and itaconic anhydride (IA).

Results and discussion

The structure of used CTAs is reported in Scheme 1, instead as initiators AIBN and Vazo 70 were exploited. In the case of DMI, bulk polymerizations were conducted at 60 °C for 72 hours, using AIBN as the initiator.

,



Scheme 1. *Chemical structures of the CTAs used: Dithiobenzoates, CDB: Cumyl dithiobenzoate, CPDB: 2-Cyanopropan-2-yl dithiobenzoate, CPADB: (4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid). Trithiocarbonates, CDTPA: (4-Cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid), TRIT: (S,S'-Bis(αα'-dimethyl-α'-acetic acid) trithiocarbonate, DDMAT: (2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid), BTPA: (2-(Butylthiocarbonothioylthio)propanoic acid.*

Table 1 DMI polymerization data

CTA	Conversion %	Mn GPC (Da)	Đ
CPADB	42.20	9223	1.41
CPDB	60.32	7827	1.34
CDB	24.24	6070	1.12
BTPA	69.79	17714	1.45
DDMAT	87.62	10235	1.76
CDTPA	84.73	11210	1.9
TRIT	90.82	47497	1.46

As shown in Table 1, for the PDMIs obtained using dithiobenzoates, an decrease in the polydispersity index (Đ) is observed with increasing conversion,

ranging from 1.41 to 1.12, which indicates highly effective control. Conversely, when using DDMAT and CDTPA, the D values exceed 1.5, indicating a partial loss of control. Furthermore, the PDMI obtained with TRIT exhibits an Mn value higher than the theoretical calculated value. Also for DBI, bulk polymerizations were conducted at 60 °C for 72 hours, using AIBN as the initiator.

Table 2. DBI polymerization data

CTA	Conversion %	Mn GPC (Da)	Đ
CPADB	0	0	0
CPDB	15.46	2514	1.52
CDB	9.09	0*	0*
BTPA	55.75	19891	1.30
DDMAT	71.99	14839	1.57
CDTPA	55.16	8855	1.89
TRIT	70.05	85736	1.33

As shown in Table 2, the PDBIs obtained exhibited a polydispersity index (Đ) ranging from 1.33 to 1.52, indicating highly effective control, whereas with CDTPA, the D values exceeded 1.5, indicating a partial loss of control. Furthermore, the polymerization conducted using CDB was repeated three times; however, the yield of the resulting polymer was too low for GPC analysis. Additionally, the PDBI obtained with TRIT displayed an Mn value higher than the theoretical calculated value. It is possible that the limited conformational mobility of PDBI compromises the reliability of GPC data. Consequently, AF4 (asymmetric field flow flow fractionation) analyses are underway to address this issue. Glass transition temperatures, Tg, measured by DSC, range between -5 °C and 15 °C. The molecular weights and thermal characteristics confirm the film-forming nature of the resulting polymers.
Preliminary results show that Vazo 70, a low temperature initiator, leads to a significantly faster polymerization due to its higher capacity to provide sufficient radicals. Specifically, after three hours of reaction at 60°C, a conversion of 10% is reached with V-70, whereas the conversion with AIBN is only 5%."
The reactivity of the itaconate monomers in RAFT polymerization was also tested synthesizing block copolymers. In fact poly(dimethyl itaconate) was exploited as macro CTA. Specifically, poly(dimethyl itaconate-co-di-*n*-butyl itaconate) block copolymers were synthesized, displaying characteristic thermoplastic elastomer properties. This confirms the macro-CTA's capability to form block copolymers.

Subsequently, an amphiphilic poly(dimethyl itaconate-co-itaconic acid) block copolymer was successfully synthesized. A PDMI-BTPA macro-CTA was utilized as the first block, while the second block was formed via hydrolysis of itaconic anhydride into the corresponding itaconic acid. Following the self-assembly of the copolymer, monodisperse polymeric nanoparticles with sizes ranging between 20 and 30 nm were developed, as confirmed by SEM and DLS analyses (Figure 1).

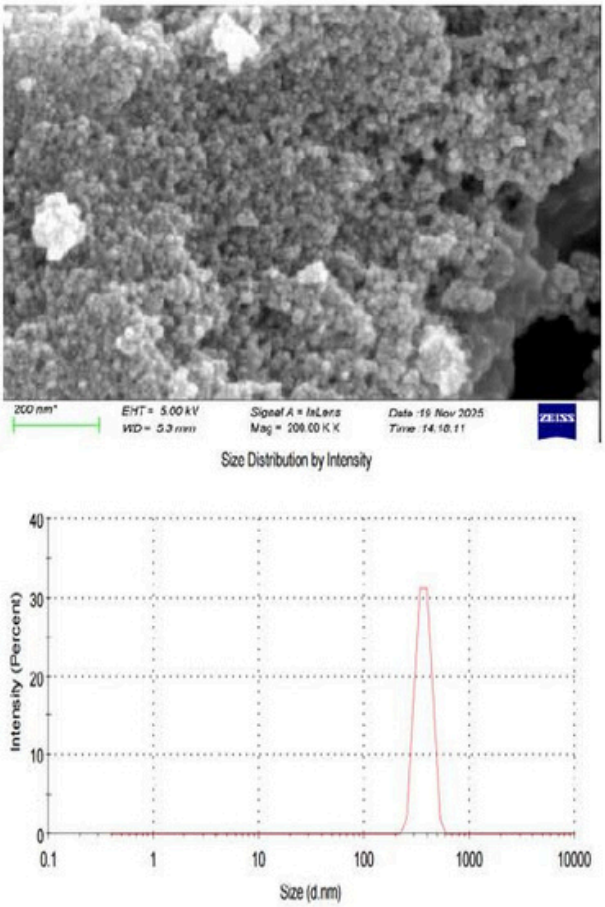


Figure1. Top SEM image, bottom DLS correlogram of PDMI$_{110}$-b-PIA$_3$ nanoparticles.

Conclusions

A careful choice of CTAs allows RAFT polymerization of itaconic monomers to effectively overcome kinetic limitations, yielding controlled, film-forming polymers and functional block copolymers that self-assemble into well-defined, monodisperse 20–30 nm nanoparticles.

References

[1] Robert, T.; Friebel, S., Green Chemistry.2016, 18, 2922–2934.
[2] Sollka, L.; Lienkamp, K.. Macromolecular Rapid Communications 2021, 42 (4), 2000546.

BIOBASED VITRIMERS USING EUTECTIC HARDENER SYSTEMS

S. Zeynalova[1], R. Bongiovanni[1], A. Vitale[1], S. Dalle Vacche[1]
[1] Politecnico di Torino, Department of Applied Science and Technologies
Corso Duca degli Abruzzi 24, 10129 Turin, Italy
e-mail: sakina.zeynalova@polito.it

Introduction

The transition towards a circular economy necessitates the development of polymeric materials that combine the high performance of thermosets with the recyclability of thermoplastics. Vitrimers, a class of covalent adaptable networks (CANs), are considered as a promising solution. While traditional thermosets are permanently crosslinked and cannot be reprocessed, vitrimers rely on dynamic covalent bonds, which allow the reprocessing of the material. In response to a suitable external stimulus, these bonds undergo exchange reactions, such as transesterification, allowing the network to be reshaped [1].
One of the most sustainable approaches to the development of CANs is the use of bio-based components with minimal environmental impact. Biobased epoxy resins are a clear example of such components. This study investigated a blended epoxy resin system consisting of cashew-derived epoxy resin [2],Cardolite Lite 514HP, and diglycidyl ether of vanillyl alcohol (DGEVA) from wood lignin [3]. To overcome the solubility limits of solid dicarboxylic acids, a green eutectic hardener (a mixture of malic acid and ethyl lactate in a molar ratio of 1:1) was used to cure the vitrimer. The application of eutectic hardeners for epoxy resins has already been demonstrated in the literature [4], but is not yet widely used, and is therefore of particular interest. Zinc trifluoromethanesulfonate (zinc triflate, $Zn(OTf)_2$) was incorporated as a catalyst to facilitate dynamic transesterification, imparting vitrimeric behavior and reprocessability to the network.

Results and Discussion

Cardolite Lite 514HP-DGEVA (Figures 1 and 2) blends were prepared at various component ratios: details of the prepared formulations are summarized in Table 1.

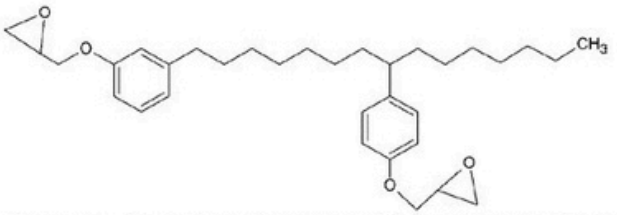


Figure 1. Chemical structure of Cardolite Lite 514HP

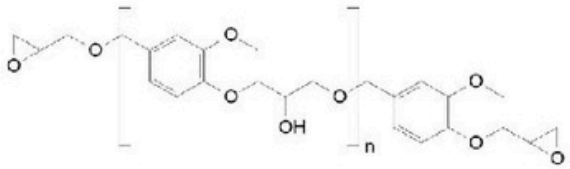


Figure 2. Chemical structure of DGEVA

Moreover, malic acid, a bio-based carboxylic acid, was used as the curing agent to promote epoxy–acid crosslinking and the formation of dynamic ester linkages. To facilitate its incorporation and ensure a homogeneous distribution within the resin mixture, malic acid was used as a deep eutectic mixture with ethyl lactate. The curing behavior and network formation of the resulting materials were investigated via differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR), while their mechanical performance was assessed by tensile testing. Additionally, gel content measurements were conducted to assess crosslinking density and evaluate network integrity.
The results indicate that the proposed bio-based formulations can successfully generate crosslinked vitrimer networks while offering opportunities to tune their properties through the resin composition.

Table 1: Composition of the materials

Cardolite Lite 514HP, wt %	DGEVA, wt %	R (COOH/ epoxy)

100	0	1 / 1.2
90	10	1 / 1.2
70	30	1 / 1.2
50	50	1 / 1.2

Conclusions

The integration of two distinct bio-based epoxy resins provides an effective strategy for tailoring the properties of the investigated vitrimeric system. By adjusting the Cardolite-to-DGEVA ratio, it is possible to systematically shift the crosslinking temperature (T_{curing}) as well as the Tg, and thus the operational service temperature. Furthermore, the use of a eutectic mixture composed by biobased and biodegradable chemicals can overcome the issue of using environmentally unfriendly curing agents, and decrease the energy input required for curing epoxy resins with carboxylic acids. These results highlight the potential of combining renewable epoxy precursors with environmentally benign curing systems for the development of sustainable vitrimer materials with tunable properties. Subsequent research will focus on assessing vitrimeric behaviour via stress relaxation and reprocessing, incorporating cellulose fibres, and investigating the 3D printability of the materials using Liquid Deposition Modelling.

References

[1] D. Berne, S. Laviéville, E. Leclerc, S. Caillol, V. Ladmiral, C. Bakkali-Hassani, *ACS Polymers Au*, 5, 214–240 (2025).
[2] E. Albertini, S. Dalle Vacche, R. Bongiovanni, I. Bianco, G. A. Blengini, A. Vitale, *ACS Sustainable Chemistry & Engineering*, 13, 2120–2131 (2025).
[3] S. Guggari, F. Magliozzi, S. Malburet, A. Graillot, M. Destarac, M. Guerre, *ACS Sustainable Chemistry & Engineering*, 11, 6021–6031 (2023).
[4] J. Tellers, M. Jamali, P. Willems, B. Tjeerdsma, N. Sbirrazzuoli, N. Guigo, *Green Chemistry*, 23, 536–545 (2021)

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POSTERS

Materiali polimerici ibridi e (nano)compositi sintesi, caratterizzazione e applicazioni

GRAPHENE OXIDE FUNCTIONALIZATION OF BACTERIAL CELLULOSE: EFFECTS ON THE STRUCTURE AND ADSORPTION PERFORMANCE

Erika Caianiello [1], Federico Olivieri[1], Martina Aulitto[2], Rachele Castaldo[1], Roberto Avolio[1], Maria Emanuela Errico[1], Patrizia Contursi[2], Gennaro Gentile[1], Mariacristina Cocca[1]

1. Institute for Polymers, Composites and Biomaterials National Research Council of Italy, via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy
2. University of Naples Federico II, Biology Department, via Cinthia 26, 80126, Napoli, Italy

e-mail: erikacaianiello@cnr.it

Introduction

Water is essential for human life, however, rapid growth in industries such as textile, paint, pharmaceuticals, and personal care has led to the release of organic pollutants into water bodies. These pollutants include dyes, solvents, surfactants, and organometallic compounds. Many of these persist in the environment and pose serious risks to ecosystems and human health, due to their toxicity, mutagenicity, carcinogenicity, and strong resistance to breakdown [1]. Several treatment technologies have been explored, including oxidation, coagulation, membrane filtration, biological degradation, and adsorption. Among these, adsorption is often seen as the most effective because of its simplicity, high efficiency, low cost, and minimal secondary pollution [2-4]. However, conventional methods often face challenges with highly stable and non-biodegradable dyes, which shows a need for better adsorbents. In this situation, cellulose-based materials have gained attention as sustainable alternatives thanks to their renewability, biodegradability, and chemical stability [5]. Among these, bacterial cellulose (BC) is particularly interesting due to its highly crystalline, three-dimensional nanofibrous structure and large surface area, but it has limited attraction to anionic [6, 7]. Graphene oxide (GO) has been widely studied as an effective adsorbent for both cationic and anionic contaminants, but its practical use is limited by recovery issues. To address this, GO can be combined with cellulose matrices to improve both stability and adsorption performance [8-10].

In this study, bacterial cellulose was examined for its ability to remove organic pollutants from water. BC was synthesized under static conditions as layers and under stirred conditions as cellulose beads, with graphene oxide added during cultivation to create hybrid materials. BC biofilm and BC-GO beads were chemically, morphologically, and thermally characterized, and their adsorption performance was tested for the removal of Rhodamine 6G (R6G), Methyl Orange (MO), and 2,4-dichlorophenol (DCP) using UV-Vis spectroscopy.

Results and discussion

SEM characterization shows that the characteristic interconnected nanofibrous structure of cellulose fibers remains intact in all samples. Moreover, in BC-GO beads, the homogeneous distribution of graphene oxide sheets within the nanofiber network confirms efficient incorporation of the nanofiller.

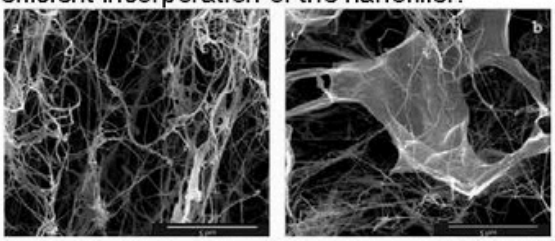


Figure 1 SEM images of BC (a) and BC-GO (b)

TGA was performed to compare the thermal stability of BC and BC–GO and to assess their composition based on the residual weight. Both materials decompose at temperatures above 250 °C, whereas BC-GO exhibits a higher residual mass due to GO incorporation.

Adsorption tests were performed using R6G, DCP, and MO as model pollutants with different charges, and the equilibrium data were fitted using the Freundlich and Langmuir models.

The results show that BC-GO beads demonstrate higher efficiency in comparison with pristine BC. Additionally, GO allows removing contaminants that are not adsorbed with only BC. For R6G, the adsorption capacity for BC was found to be 13 mg/g, while that for BC-GO was significantly higher, being 245 mg/g when C_0 was 250 mg/L. The adsorption capacity for DCP for BC was found to be 14 mg/g when C_0 = 250 mg/L, while for BC-GO, it was 130 mg/g under the same

condition. In the case of MO, no significant adsorption of BC was observed, which was anticipated, while the removal by BC-GO was up to 22 mg/g at C_0 = 250 mg/L.

Conclusions

In conclusion, the results demonstrate that bacterial cellulose-based materials, specifically, BC-GO nanocomposites, are promising sustainable adsorbents for water purification. The addition of GO improves the adsorption capacity of bacterial cellulose, making possible the removal of positively charged, neutral, and negatively charged organic substances. Moreover, the interconnected three-dimensional porous structure of BC–GO beads suggests potential applications in micro- and nanoplastics capture. Further research will be focused on studying the structure of the composites, optimization of their sorption efficiency, stability, reusability, and activity in the complex water matrices to better understand the mechanisms of adsorption and help in developing sustainable adsorbents for emerging contaminants.

References

[1] Iqbal, M. Z., Pal, P., Shoaib, M., & Abdala, A. A., *Desalination and Water Treatment*, 68, 226–235 (2017)

[2] Burevska-Atkovska, K., Olivieri, F., Avolio, R., Castaldo, R., Cocca, M., Errico, M. E., Gentile, G., Grozdanov, A., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 700, 134720 (2024)

[3] Guerritore, M., Olivieri, F., Avolio, R., Castaldo, R., Cocca, M., Errico, M. E., Lavorgna, M., Silvestri, B., Ambrogi, V., Gentile, G., *Microporous and Mesoporous Materials*, 335, 111864 (2022)

[4] Li, B., Zhang, Q., Pan, Y., Li, Y., Huang, Z., Li, M., & Xiao, H., *International Journal of Biological Mac-romolecules*, 163, 309–316 (2020)

[5] Maglione. A., Olivieri, F., Avolio, R., Castaldo, R., Cocca, M., Errico, M. E., Ambrogi, V., Gentile, G., *ACS Applied Materials & Interfaces,* 17 (26), 38619-38634 (2025)

[6] Abdelhamid, H. N., & Mathew, A. P., *Frontiers in Chemical Engineering*, 3, 790314 (2021)

[7] Dao, N. T., Bui, H. T., Kim Le, P. T., Le, K. A., Tuong Tran, A. T., Nguyen, K. D., Mai Nguyen, H. H., & Ho, P. H., *ACS Omega*, 8(37), 33412–33425 (2023)

[8] Castaldo, R., Lama, G. C., Aprea, P., Gentile, G., Lavorgna, M., Ambrogi, V., & Cerruti, P. *Microporous and Mesoporous Materials*, 260, 102-115 (2018)

[9] Castaldo, R., Avolio, R., Cocca, M., Errico, M. E., Lavorgna, M., Šalplachta, J., Santillo, C., & Gentile, G., *Chemical Engineering Journal*, 430, 133162 (2022)

[10] Ramesha, G. K., Vijaya Kumara, A., Muralidhara, H. B., & Sampath, S., *Journal of Colloid and Interface Science*, 361(1), 270–277 (2011)

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• "Production of bacterial cellulose from agrifood residues by Kombucha culture: enhancing cellulose productivity and tailoring its techno-functional properties for advanced applications - BACK APP", PRIN2022 founded by European Union—Next Generation EU, C.I. 2022AEXJL7 - CUP B53D23005780006.

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RESIDUAL ANTIOXIDANT ACTIVITY OF WINERY BY-PRODUCT BIOFILLERS IN LDPE AND HDPE COMPOSITES

F.Cicogna[1*], E. Passaglia[1], A. Nanni[2], M. Buono[2,3], M. Colonna[3], A. Fortunelli[1], S. Coiai[1]

[1] Istituto di Chimica dei Composti OrganoMetallici (ICCOM), Consiglio Nazionale delle Ricerche, Via G. Moruzzi 1, 56124 Pisa, Italia
[2] AgroMateriae srl, Via Granarolo 177/3, 48018 Faenza (RA), Italia
[3] Dipartimento di ingegneria civile, chimica, ambientale e dei materiali, Università di Bologna, Via U. Terracini 28, 40131, Bologna, Italy
e-mail: francesca.cicogna@cnr.it

Introduction

In recent years, environmental and health concerns related to the use of fossil-based additives to polymers have stimulated research toward more sustainable strategies to enhance the performance of conventional polymers. In this context, the incorporation of agro-industrial residues as biofillers represents a promising approach to improve material properties while promoting waste valorization.

Particular attention has been devoted to biomasses deriving from food production and waste, which are rich in bioactive molecules having antioxidant, UV-blocking, and antimicrobial activity. Among these, polyphenol- and tannin-rich biomasses, such as winery by-products, represent a natural reservoir of antioxidant compounds that, acting as radical scavengers, can enhance the thermo-oxidative stability of polyolefins, such as low-density and high-density polyethylene (LDPE and HDPE), during processing and service life. Bioactive molecules are usually extracted from biomass before their incorporation into polymer matrices to maximise their activity [1]. Alternatively, biofillers can also be added to polymer matrices without extractions. This strategy simultaneously exploits the structural role of the lignocellulosic fraction and the intrinsic bioactivity of residual polyphenols and tannins, offering a multifunctional and more sustainable alternative to conventional synthetic stabilizers [2]. Our study aims to evaluate whether residual biofillers from grape seeds after oil extraction still maintain some antioxidant and UV-blocking activity. Indeed, grape seed biofillers contain residual tannins that are known to have antioxidant and UV-blocking properties.

Results and discussion

Two winery by-product biofillers derived from grape seeds after oil removal and containing 3 wt.% (WGS B1) and 5 wt.% (WGS GV3) of tannins were compared with tannins extracted from quebracho (Fintan Q, containing 70.5 wt% of tannin), chestnut heartwood (Fintan ENC, containing 75 wt.% of tannin), and grape seeds (AQTAN, containing 81.8 wt% of tannin). For comparison, Irganox 1010 and Irganox B225 were also used in this study. All samples were analysed by TGA (under air and nitrogen) and ATR-FTIR to determine their thermal stability and the nature of the main functional groups. The DPPH test, carried out to evaluate the antioxidant properties of biofillers and commercial tannins compared to Trolox, a water-soluble analogue of vitamin E, shows that biofillers retain antioxidant activity.

The two biofillers and commercial tannins were melt-mixed by extrusion at 180°C with LDPE and HDPE. Different amounts of fillers were added to the polylefins to maintain the tannin quantity constant in the final composites (0.8 wt.% of tannin). Analogously, two composites of LDPE and HDPE containing 0.8 wt.% of the two Irganox antioxidants were also prepared. Composites were characterised by DSC and TGA (under nitrogen and oxygen), and preliminary results show that biofillers can increase the thermal stability of composites. The antioxidant role of biofillers was further confirmed by thermal aging of composite films at 110°C in a vented oven.

Conclusions

Preliminary studies show that the residual biofillers, after grape seed oil extraction, WGS B1 and WGS GV3, still maintain antioxidant activity, as demonstrated by the DPPH test. Interestingly, their antioxidant activity was also transferred to LDPE and HDPE that were protected from thermal aging at 110°C.

References

[1] Saini, R.K.; Khan, M.I.; Kumar, V.; Shang, X.; Lee, J.H.; Ko, E.Y. Antioxidants 2025, 14, 650
[2] Nanni, A.; Parisi, M.; Colonna, M. Polymers 2021, 13, 381.

UPCYCLING HAZELNUT BY-PRODUCTS INTO FUNCTIONAL ELASTOMERIC COMPOSITES FOR SUSTAINABLE SPORTS SURFACES

L. Conzatti[1a], R. Utzeri[1a], L. Visentin[1b], F. Zaccheria[1b], M. Guidotti[1b], I. Nedi[2], G. Lesage[2]

[1] Institute of Chemical Sciences and Technologies "Giulio Natta" (SCITEC), CNR: [a] Via De Marini 6, 16149 Genova, Italy; [b] Via C. Golgi 19, 20133, Milano, Italy
[2] MONDO S.p.A., P.le E. Stroppiana 1, 12051, Alba (Cn), Italy
e-mail: lucia.conzatti@cnr.it

Introduction

The growing demand for sustainable materials and the transition toward a circular bioeconomy are driving the development of bio-based alternatives to conventional additives used in elastomer compounds [1]. In particular, the rubber industry is increasingly focused on replacing petroleum-derived process oils, mineral fillers and synthetic antioxidants with renewable and low-impact ingredients, while maintaining high performance requirements, especially for demanding applications such as sports flooring. Vegetable oils, lignin and naturally occurring polyphenols have recently emerged as promising multifunctional additives owing to their plasticizing, reinforcing and antioxidant properties [2,3].

Within this framework, the NINSOLA project aims at valorizing by-products (shells, perisperm and oil fractions) derived from the processing of the Piedmont hazelnut through a circular economy approach, transforming them into functional ingredients for the rubber sector. Hazelnut derivatives are particularly attractive because of their content of vegetable oils and bioactive compounds such as polyphenols, which can potentially act as plasticizers and stabilizing agents, respectively, while simultaneously promoting the valorization of agro-industrial residues [4].

In this work, elastomeric compounds were developed by exploiting two innovative strategies (Figure 1): (i) the use of epoxidized hazelnut oil as a bio-based plasticizer, replacing conventional process oils; and (ii) the use of lignin or fillers functionalized with polyphenols (gallic acid) to partially replace both mineral fillers and antioxidant additives. The objective is to assess the feasibility of these substitutions and their effects on the morphology and tensile properties of elastomer compounds intended for sports flooring applications.

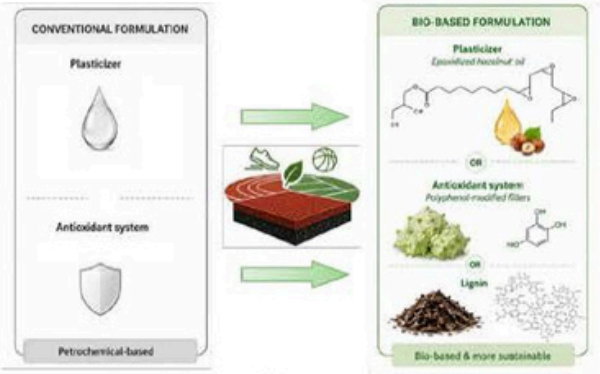


Figure 1. Schematic representation of the bio-based formulation strategy.

Results and discussion

Vulcanized elastomeric compounds, including a reference formulation containing conventional additives, were successfully prepared according to standard melt-mixing and vulcanization procedures. The experimental formulations included: (i) complete replacement of the conventional plasticizing oil with epoxidized hazelnut oil; (ii) complete replacement of the conventional antioxidant with two different commercial lignins; and (iii) complete replacement of both the conventional filler and antioxidant with gallic acid immobilized on different inorganic supports (silica, saponite or kaolin), from either mineral or synthetic origin.

The tensile behavior of the developed compounds was evaluated in terms of elastic modulus (E), tensile strenght at break (σ_B) and elongation at break (ε_B). Overall, most of the bio-based formulations exhibited mechanical properties comparable to those of the reference compound, confirming the feasibility of replacing conventional additives with renewable alternatives. The formulation containing gallic acid immobilized on silica exhibited a markedly higher E (approximately 50% higher than the reference), indicating a stiffer material while maintaining a

comparable ε_B. The kaolin-based formulation showed tensile properties very similar to the reference, with only a slight reduction in ε_B. In contrast, the saponite-based formulation displayed slightly lower E, σ_B and ε_B. The compounds containing commercial lignins exhibited slightly higher E and tensile strength than the reference, whereas the lower ε_B remained within the experimental variability.
Morphological characterization is currently in progress and will provide further insight into the dispersion of the bio-based additives within the rubber matrix. The correlation between morphology and tensile properties will be discussed.

Conclusions

The results demonstrate the feasibility of replacing conventional rubber additives with bio-based alternatives while maintaining tensile properties comparable to those of the reference formulation. In particular, epoxidized hazelnut oil, commercial lignins and gallic acid immobilized on mineral supports represent promising candidates for the development of more sustainable elastomer formulations. These findings contribute to the valorization of hazelnut-derived by-products within the framework of the NINSOLA project and support the development of more sustainable rubber compounds for sports flooring applications. Ongoing morphological characterization will provide further insight into the structure–property relationships governing the mechanical behavior of the developed compounds.

References

[1] J. F. Kennedy, W. H. B. Smith, *J. Renewable Mater.*, vol. 8, 1–23 (2020)
[2] M. Barana, M. Orlandi, et al., *ACS Sustainable Chem. Eng.*, vol. 6, 11843–11852 (2018).
[3] W. Kaewsakul, A. Sahakaro, et al., *Rubber Chem. Technol.*, vol. 92, 590–610 (2019).
[4] D. Licursi, M. Cinelli, et al., *Food Bioscience*, vol. 47, 101637 (2022)

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DEVELOPMENT OF LIGNIN-CONTAINING BIODEGRADABLE POLYMER BLENDS FOR FISHING NET APPLICATIONS

Roberta D'AURIA[1]*, Roberto AVOLIO[1], Rachele CASTALDO[1], Maria Emanuela ERRICO[1], Gennaro GENTILE[1], Immacolata LIOTTA[1], Federico Olivieri[1], Mariacristina COCCA[1].

[1]Institute for Polymers, Composites and Biomaterials National Research Council of Italy, via Campi Flegrei, 34 80078 Pozzuoli (NA), Italy
e-mail: robertadauria@cnr.it

Introduction

The presence of plastic waste in the ocean is increasingly a problem, with lost fishing gear among the sources of persistent pollution in the ecosystem[1]. Lost fishing nets, which are generally called *'ghost nets'*, still trap marine animals and break down into microplastics owing to the effects of the environment[2]. Biodegradable polymers have thus been proposed as substitutes for traditional plastics to minimize the environmental impacts of fishing gear. In this experiment, blends composed of polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT) were chosen as an environmentally friendly matrix for fishing nets[3]. To improve the resistance of the blends to solar radiation, a natural UV absorber such as lignin[4] was incorporated in PBS-PBAT 85:15 blends. This blend was chosen as the reference composition following preliminary experimental activities, as it provided the most suitable balance of properties for the present investigation. The different lignin concentrations used as filler in the blend are reported in Table 1:

Table 1: Lignin concentration in polymeric blends

BLEND	LIGNIN (PHR)
PBS-PBAT 85:15	0
PBS-PBAT 85:15	0.1
PBS-PBAT 85:15	0.5
PBS-PBAT 85:15	1
PBS-PBAT 85:15	2.5

Results and discussion

The developed blends were characterized in terms of rheological behavior to evaluate the effect of lignin on the material these properties. The MFI and viscosity measurements exhibited opposite trends as the lignin content increased.
Films prepared from different formulations reported in Table1, were subjected to both natural and artificial UV light exposure using an Osram Ultra-Vitalux 300 W lamp. The evolution of the samples under UV exposure was monitored through colorimetric analysis at selected exposure times using a CM-23d spectrophotometer (Konica Minolta, Japan). All formulations exhibited a comparable trend under both natural and artificial UV exposure, confirmed by ΔE*ab values that progressively increasing as a function of exposure time. Blends containing lower lignin loadings showed reduced color changes, suggesting a more effective stabilization against UV-induced degradation. In contrast, higher lignin concentrations were associated with slightly higher ΔE*ab values, indicating that increasing the filler content beyond a certain level does not further enhance UV protection. These findings suggest a non-linear relationship between lignin concentration and the photoaging behavior of the PBS-PBAT blends. In addition, the films were morphologically characterized by SEM before and after UV exposure. Representative SEM micrographs,, reported in Fig 1 (A-B), showed a smooth and regular surface of films before UV exposure. Fig1 (C-D) exhibited the polymeric surface after the experiment showing morphology degradation and increased roughness after UV exposure .

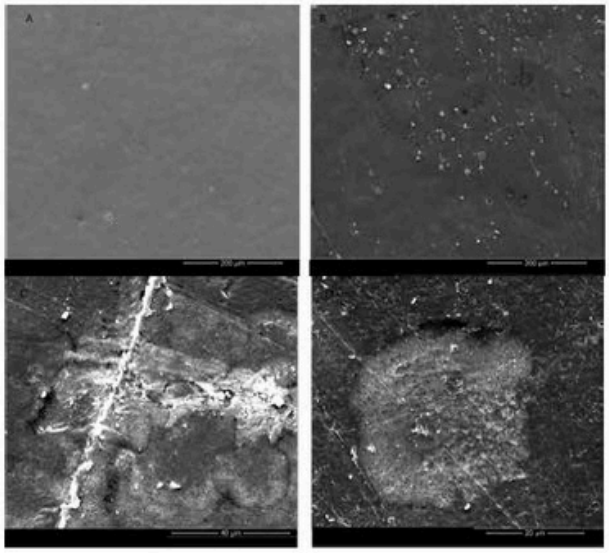


Figure 1. SEM images before (A-B) and after (C-D) UV exposure.

Conclusions

This study investigated PBS-PBAT 85:15 blends containing different lignin loadings to provide a preliminary assessment of their stability under UV irradiation. Colorimetric measurements carried out highlighted that formulations with lower lignin contents exhibited smaller color variations, whereas higher lignin concentrations did not result in further improvements in UV resistance.

References

[1] Jaikumar, I. M., Tomson, M., Meyyazhagan, A., Balamuralikrishnan, B., Baskaran, R., Pappuswamy, M., Kamyab, H., Khalili, E., & Farajnezhad, M. *Green Analytical Chemistry*, *12*, 100202, (2025).

[2] Liotta, I., Avolio, R., Castaldo, R., Gentile, G., Ambrogi, V., Errico, M. E., & Cocca, M. *Process Safety and Environmental Protection*, *182*,1143–1152 (2024).

[3] Muthuraj, R., Misra, M., Amar, bullet, & Mohanty, A. *Journal of Polymers and the Environment*, *22*. (2014).

[4] Zhang, Y., & Naebe, M. *ACS Sustainable Chemistry & Engineering*, *9*(4), 1427–1442. (2021).

Acknowledgments

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PREPARATION AND CHARACTERIZATION OF THERMORESPONSIVE FILMS OBTAINED FROM HYBRID PNIPAM/SILK FIBROIN SYSTEMS

D. Errico [1], T. Posati [2], M. Bertoldo [3], E. Buratti [1].

[1] Dept. of Environmental and Prevention Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy.
[2] Consiglio Nazionale delle Ricerche, Istituto per la Sintesi Organica e la Fotoreattività (CNR-ISOF), via Piero Gobetti 101, Bologna 40129, Italy
[3] Dept. of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy.
e-mail: **davide.errico@unife.it**

Introduction

Poly(N-isopropylacrylamide) (PNIPAM) is a synthetic polymer characterized by hydrophilic/hydrophobic transition of approximately 32 °C, which is close to the human body temperature and matches skin one. Owing to this property, PNIPAM has been extensively investigated for applications in regenerative medicine and controlled delivery systems, both as hydrogels and microgels [1]. In recent years, hybrid materials combining PNIPAM with natural polymers have attracted considerable attention as a strategy to impart bioactivity to thermoresponsive systems. Among these biopolymers, silk fibroin (SF) protein, recovered from silk industry by-products, represents a particularly promising candidate for biomedical applications. In this work, the preparation of hybrid PNIPAM/SF colloidal systems through physical mixing of the two components was investigated, as simple strategy for the fabrication of thermoresponsive films. Gels were finally obtained by thermal activated crosslinking of the protein component and the water-stability and thermoresponsiveness of this materials were studied as a function of the hybrid composition.

Results and discussion

Although previous studies have demonstrated the feasibility of obtaining hybrid colloidal systems by directly feeding proteins during NIPAM precipitation polymerization [2], the addition of SF during the polymerization process did not lead to the formation of stable PNIPAM/SF colloidal systems. This behaviour was attributed to fibroin aggregation induced by the reaction temperature of 70 °C, necessary for the radical polymerization of NIPAM. For this reason a physical mixing approach of SF solution with preformed PNIPAM microgels, characterized by average diameters of 650 and 300 nm, was considered. The resulting blends, prepared at 80/20, 60/40, 40/60 and 20/80 PNIPAM/SF weight ratios, were designated as **MSFX**, where **M** refers to the mixing procedure and **X** indicates the silk fibroin content. Dynamic Light Scattering (DLS) analysis was used to investigate the interaction between colloidal PNIPAM particles and silk fibroin (SF). Measurements were carried out at 20 °C and 40 °C, corresponding to temperatures below and above the LCST of PNIPAM, respectively. For the 650 nm PNIPAM/SF blends, analysis of the correlograms (Figure 1a) showed the presence of two particle populations below the transition temperature only in the MSF80 sample, namely when an high amount of fibroin is present (Figure 2a), suggesting the coexistence of hybrid PNIPAM/SF microgels and neat SF-based particles. In fact the size of the smallest population match the one of neat SF (MSM100) (Table 1).

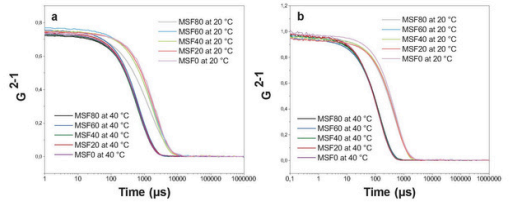


Figure 1: Comparison of correlograms at 20 °C and 40 °C for each 650 nm (a) and 300 nm (b) PNIPAM/SF blends.

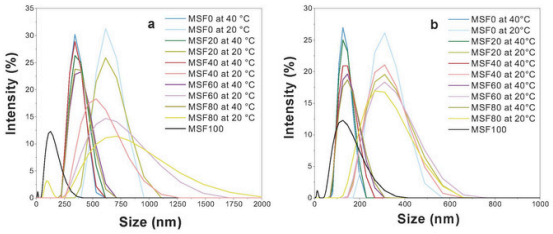


Figure 2: Adaptive correlation at 20 °C and 40 °C for the resulting colloidal particles for each 650 nm (a) and 300 nm (b) PNIPAM/SF blends.

For lower SF contents in the blends, the colloidal particle size at 20 °C decreases from 659 ± 3 nm for neat PNIPAM to 634 ± 9 and 512 ± 13 nm for MSF20 and MSF40, respectively, whereas it increases to 690 ± 20 nm for MSF60. This behaviour suggests the formation of hybrid

particles through fibroin adsorption within the PNIPAM particles up to an SF content of 40%, and both inside and on the particle surface at 60% SF. At 40 °C, the DLS correlograms match that of neat PNIPAM, suggesting SF adsorption onto the microgel surface (Figure 2a). At this temperature, the hard structure of the particles may prevent shrinkage induced by SF adsorption.

Table 1: Average size of colloidal populations (Px) for each PNIPAM/SF blend, both at 20 °C and 40 °C. Hybrid samples were obtained employing 650 nm PNIPAM microgel. Data are presented as ± s.d.

Sample	20 °C		40 °C	
	P1 (nm)	P2 (nm)	P1(nm)	P2 (nm)
MSF0	659 ± 5	-	357 ± 4	-
MSF20	634 ± 9	-	365 ± 5	-
MSF40	512 ± 13	-	346 ± 2	-
MSF60	690 ± 20	-	351 ± 3	-
MSF80	752 ± 12	112 ± 21	382 ± 9	-
MSF100	125 ± 6	13 ± 1	129 ± 18	12 ± 1

In the case of the 300 nm PNIPAM/SF blends, DLS revealed mainly a single particle population at both 20 °C and 40 °C (Figure 1b, 2b). Nevertheless, the relatively small size difference between PNIPAM particles and silk fibroin in solution may limit the resolving power of DLS, preventing the reliable discrimination of closely sized populations. Is therefore difficult to say if all or part of SF is adsorbed on PNIPAM particles.
Regardless of the morphology of the two phases within the dispersed system, stable colloidal dispersions were obtained, from which thin films could be prepared by solution casting at room temperature under a fume hood. All formulations yielded homogeneous, bubble-free films, hereafter referred to MSFX-**f**. FT-IR spectroscopy confirmed the hybrid nature of the materials, revealing the simultaneous presence of characteristic absorption bands of both PNIPAM and silk fibroin, with relative intensities strongly dependent on film composition. Due to their limited stability in aqueous media (Figure 3c), the films were subjected to thermal treatments at 60, 120, and 160 °C.

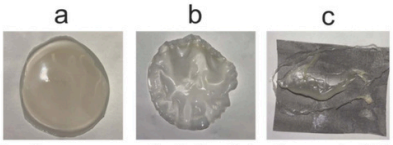


Figure 3: Images of (a) dried and (b) swollen MSF40-f treated at 160 °C. (c) Image of thermally untreated MSF40-f after water-stability test.

Regardless of the treatment temperature, a significant improvement in water stability was observed. This effect can be attributed to the well-known ability of silk fibroin to undergo thermally induced structural rearrangements and crosslinking processes [3], which enhance network cohesion even for treatment at temperatures as low as 60 °C (Figure 3a, 3b). Swelling experiments were subsequently performed on all water-stable samples at 25 and 40 °C. Higher swelling degrees were observed at 25 °C than at 40 °C (Figure 4), in agreement with the hydrophilic-to-hydrophobic transition of PNIPAM across its critical temperature. Furthermore, the swelling degree increased with increasing PNIPAM content, demonstrating that the thermally stabilized hybrid films retained the characteristic thermoresponsive behaviour of PNIPAM (Figure 4).

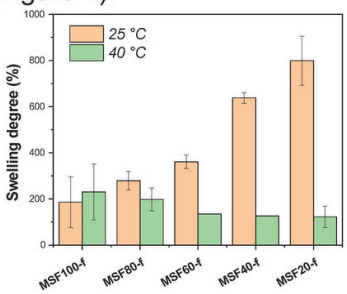


Figure 4: Comparison of swelling degrees in water carried out at 25 °C (orange) and 40 °C (green) for 160°C treated PNIPAM/SF hydrogels (MSF20-f, MSF40-f, MSF60-f, MSF80-f) Samples were obtained employing 650 nm microgel

Conclusions

The present study demonstrated that the physical blending of preformed PNIPAM microgels with silk fibroin is a simple and effective strategy for the fabrication of hybrid thermoresponsive films. This approach enabled the preparation of stable PNIPAM/SF colloidal dispersions suitable for film formation, overcoming the limitations associated with the direct incorporation of silk fibroin during NIPAM polymerization. Thermal treatment was found to be essential for improving the water-stablity of materials, which extends their potential applicability in aqueous environments. Moreover, the combination of a bioactive biopolymer with a thermoresponsive synthetic component may provide a starting point for the future development of PNIPAM/SF biomaterials, suitable for biomedical applications.

References

[1] Guan, Y & Zhang, Y. *Soft Matter,* vol. 7, no. 14, pp. 6375-6384.
[2] E. Buratti, M. Sguizzato, G. Sotgiu, R. Zamboni, and M. Bertoldo, *Gels*, vol. 10, no. 6, p. 411.
[3] A. Sagnella, M. Madaghiele, E. Sannino, M. Miscuglio, V. Bellacicca, A. D'Amora, L. Ambrosio and M. De Vittorio, RSC Adv., Vol. 6, no. 11, pp. 9304-9314, 2016.

DEVELOPMENT OF PBSA BASED BIOCOMPOSITES REINFORCED WITH *CEIBA SPECIOSA* NATURAL FIBRES

V. Fiore[1], L. Botta[1], G. Iacono[1], C. Sciancalepore[2], N. Badalamenti[3], M. Bruno[3]

[1] Dept. of Engineering, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italia
[2] Dept. of Engineering for Industrial Systems and Technologies, Università di Parma, Parco Area delle Scienze 181/A, 43124, Parma, Italia
[3] Dept. of Biological, Chemical and Pharmaceutical Sciences and Technologies, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italia
e-mail: vincenzo.fiore@unipa.it

Introduction

Growing environmental awareness and forthcoming regulations on single-use plastics are driving demand for fully biodegradable and bio-based materials. Poly(butylene succinate-co-adipate) (PBSA) is an aliphatic-aromatic biodegradable copolyester with good processability and compostability, but its relatively low stiffness limits its use in structural or semi-structural applications. Reinforcement with low-cost, locally sourced natural fibres is a sustainable strategy to improve the mechanical performance of biodegradable matrices while valorising underexploited biomass. In this work, the cottony floss that envelops the seeds inside the fruit pods of *Ceiba speciosa* (silk floss tree), widely diffused in Sicily and informally referred to as "false kapok" was investigated as reinforcement for a PBSA matrix, both in flock (long fibre) and particulate (micronized) form. This seed floss has already been explored as a source of cellulose nanofibers for polyvinyl acetate composites [1], confirming its potential as a reinforcing filler. Composite laminates were produced by the film-stacking technique [2]. To optimize the fiber-matrix interfacial adhesion while maintaining an eco-friendly fabrication process, a mild alkaline surface treatment using sodium bicarbonate ($NaHCO_3$) was investigated as a sustainable alternative to traditional harsh chemical modifications [3].

The aim of the work was to develop biodegradable PBSA-based composite laminates reinforced with *Ceiba speciosa* fibres, in flock and micro-particle form, evaluating the effect of fibre form, weight concentration and the $NaHCO_3$ surface treatment through quasi-static tensile tests.

Results and discussion

The seed floss of *Ceiba speciosa* and PBSA pellets were pre-dried in a vacuum oven to remove residual moisture. To improve fibre-matrix adhesion, part of the flock fibre was alkali-treated by immersion in an aqueous solution of sodium bicarbonate ($NaHCO_3$), followed by rinsing and drying. Laminates were manufactured via the film-stacking technique [2]: two PBSA skins, previously obtained by compression moulding, were assembled with an interposed fibre layer and consolidated by compression moulding, using a multi-step load/temperature profile followed by water quenching. In a first experimental campaign, laminates with neat PBSA skins were prepared using either untreated or $NaHCO_3$-treated flock fibre as the core layer, at two weight concentrations (10 and 15 wt%). Specimens were cut with a CO_2 laser cutter to ensure a uniform geometry while avoiding thermal damage to the lignocellulosic fibres. Composites were characterised by quasi-static tensile tests, and scanning electron microscopy (SEM).

Tensile tests showed that the elastic modulus of the biocomposites was markedly higher than that of the neat PBSA matrix for all the flock fibre formulations investigated, for both the untreated and the $NaHCO_3$-treated fibre. At both concentrations, the untreated fibres produced a greater stiffening effect, along with a higher yield stress, than the treated fibres. This stiffening was accompanied, across all reinforced formulations, by a pronounced decrease in the stress at break and a drastic reduction in the strain at break compared to the neat matrix. This trend is consistent with the typically brittle behaviour induced by rigid natural fibre reinforcement in a ductile matrix; the $NaHCO_3$-treated fibre showed a further reduction in residual strain at break compared with the untreated one. Since the alkaline treatment yielded no improvement over the untreated fibers, the latter were selected as the core reinforcement for the second experimental campaign.

In this final part of the work, laminates were prepared using untreated flock fibers in the core layer, combined with composite PBSA skins obtained by melt-blending PBSA with 5 wt% of either untreated or $NaHCO_3$-treated *Ceiba*

speciosa micro-particles. To ensure a consistent reference, neat PBSA and the untreated-fibre-only laminates were re-produced and tested using the same reprocessed (melt-blended) matrix employed for the filled skins. Skins containing only microparticles, without core fibre, showed a moderate increase in modulus compared to the neat matrix, with a very similar effect for untreated and $NaHCO_3$-treated particles. When these microparticle-filled skins were combined with the untreated core fibre, the resulting sandwich laminates achieved the highest elastic modulus among all tested configurations, with the untreated-particle skin yielding a stiffening effect similar to that of the $NaHCO_3$-treated one.

Conclusions

The results show that *Ceiba speciosa* fibre, an underexploited lignocellulosic resource from Sicily, is a viable and effective reinforcement for PBSA-based biodegradable composites, providing a substantial increase in mechanical stiffness. Interestingly, alkaline treatment utilizing sodium bicarbonate ($NaHCO_3$) did not yield a performance improvement for the flock fibre compared to their untreated counterparts. Consequently, untreated fibres were retained as the core reinforcement for the second stage of the investigation. In this subsequent phase, composite PBSA skins filled with either untreated or $NaHCO_3$-treated particles were combined with the untreated flock fibre core. This combined macro/micro-reinforcement strategy successfully yielded the highest stiffness among all investigated configurations.

These findings confirm the high potential of *Ceiba speciosa*, in both its flock and particulate forms, as a sustainable reinforcement. Furthermore, the success of this multi-scale hybridization approach offers a promising design pathway for maximizing the structural performance of fully biodegradable sandwich laminates without relying on intensive chemical pre-treatments.

References

[1] M.R. Leal, T.H.S. Flores-Sahagun, T.S. Franco, G.I.B. Muniz, *Polymer Composites*, 42, 397–411 (2021).

[2] L. Botta, V. Fiore, T. Scalici, A. Valenza, R. Scaffaro, *Materials*, 8, 7770–7779 (2015).

[3] V. Fiore, T. Scalici, F. Nicoletti, G. Vitale, M. Prestipino, A. Valenza, *Composites Part B*, 85, 150–160 (2016).

STABILIZATION OF MAGNETIC NANOPARTICLES IN LIQUID CRYSTALLINE POLYMERS VIA TAILOR-MADE LIGANDS

T. Landovský [1], G. Barrera [2], F. Celegato [2], P. Tiberto [2], D. Martella [3,4], C. Parmeggiani [3,4]
[1] Institute of Physics of the Czech Academy of Sciences, 182 00 Prague 8, Czechia
[2] Department of Advanced Materials Metrology and Life Science, Istituto Nazionale di Ricerca Metrologica (INRiM), 10135 Torino, Italy
[3] Department of Chemistry "Ugo Schiff", University of Florence, 50019 Sesto Fiorentino, Italy
[4] European Laboratory for Non-Linear Spectroscopy (LENS), 50019 Sesto Fiorentino, Italy
e-mail: landovsky@fzu.cz

Introduction

Over the past decades, numerous composites combining liquid crystalline (LC) materials with nanoparticles have been developed. However, achieving adequate mixing of the two components remains far from straightforward. This challenge is especially pronounced for magnetic nanoparticles (MNPs), which exhibit a strong tendency to aggregate. One promising strategy to enhance the stability of MNPs within a LC matrix is to coat their surface with organic ligands that mimic the structure of mesogens used in the system (Fig. 1).[1]

Results and discussion

Initially, we prepared pseudo-spherical magnetite superparamagnetic nanoparticles with a diameter around 11 nm, based on previously published protocol.[2] Subsequently, we synthesized a set of organic ligands with structures inspired by some of the typical reactive mesogens used for the preparation of LC polymers, such as RM105 (Fig. 2a). Phosphonic acid was selected as an anchoring group (responsible for the attachment on the nanoparticle surface, Fig. 2b), due to its ability to form strong covalent bonds with free hydroxyl groups on iron oxide surface and, thus, stable self-assembled monolayers.[3]

In the second step, we coated our MNPs with the ligands. This process was performed in hexanol, using elevated temperature to ensure the formation of covalent bonds.[4] The success of the coating procedure was assessed based on Fourier transform infrared spectra (FTIR) and thermogravimetric analysis (TGA) of selected samples.

Subsequently, we mixed the coated MNPs with 5CB, a typical nematic LC solvent (Fig. 2c). Within the mixing experiments, approx. 1 wt. % of the MNPs was added to 5CB. After the stabilization of mixtures in the nematic phase, aggregated MNPs were collected using an ordinary neodymium laboratory magnet. The key role of the ligand structure was manifested in their different ability to stabilize MNPs in 5CB (in the nematic phase). We observed very different results for MNPs coated with different ligands, some ligands were almost unable to form a stable dispersion, while the most successful ligand, on the contrary, enabled the formation of a long-term stable dispersion without aggregates observable under an optical microscope.

The magnetic properties of the most successful mixture were studied using vibrating sample magnetometry (VSM) across the temperature range of 20–45 °C. The significant increase in magnetic susceptibility of the sample (associated with the LC phase transition between the nematic and isotropic phases) provided further evidence of the low degree of MNP aggregation in the sample.[5] Aggregate formation exhibited a preferred orientation along the measured magnetic field.[5]

Finally, we introduced our coated MNPs into a mixture of 5CB with LC cross-linker RM257 (Fig. 2d). Interestingly, the best ability to stabilize MNPs was shown by the similar ligands as in the previous experiments with pure 5CB. However, in mixtures with RM257, we achieved a stabilization of lower concentrations of MNPs and observed a higher degree of their aggregation. The most successful mixture with RM257 was further photopolymerized into self-standing films with different alignments. Moreover, the magnetic properties of these materials were again studied using VSM.

Conclusions

Within this project, we prepared a series of organic ligands capable of stabilizing superparamagnetic magnetite nanoparticles in mixtures used for the preparation of LC polymers. Notably, some of these ligands showed an extraordinary ability to stabilize MNPs in the nematic LC solvent 5CB. In the future, we plan to use these ligands and the developed coating process to introduce magneto-responsiveness into LC elastomers and networks.

References

[1] M. Hähsler, et al., *Phys Sci Rev*, vol. 7, 1009-1032 (2022)
[2] M. Vassallo, et al., *ACS Omega*, vol. 8, 2143-2154 (2023)
[3] S. P. Pujari, et al., *Angew. Chem. Int. Ed.*, vol. 53, 6322-6356 (2014)
[4] A. Tufani, et al., *Dalton Trans.*, vol. 54, 7906-7922 (2025)
[5] N. Tomašovičová, et al., *Soft Matter*, vol. 12, 5780-5786 (2016)

Acknowledgments
The research was supported by Czech Science Foundation Grant No. 25-18194O.

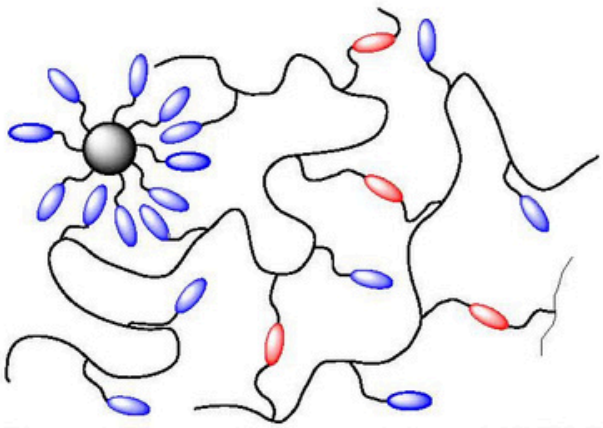


Figure 1. Schematic representation of MNP/LC polymer composite.

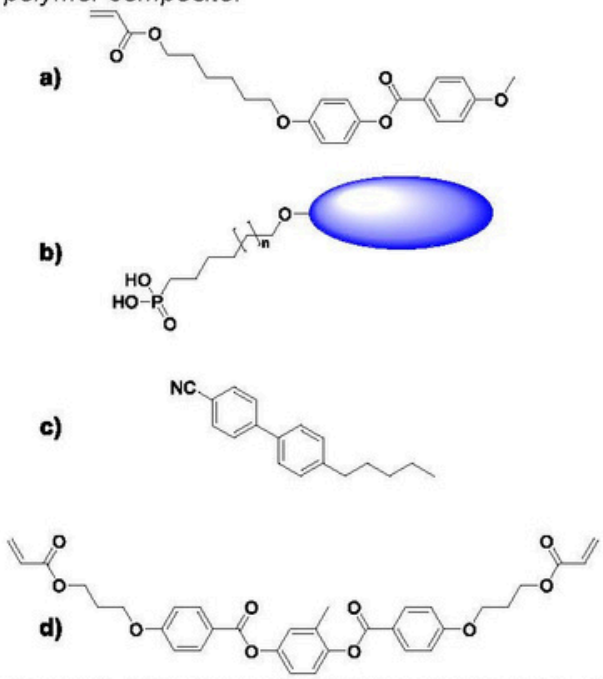


Figure 2. Structures of selected compounds: a) RM105; b) schematic structure of ligands used in this work; c) 5CB; d) RM257.

PHYSICS-INFORMED MACHINE LEARNING FOR PREDICTING OPTICAL TRANSMITTANCE AND HAZE IN TRANSPARENT WOOD

D. Nuvoli[1], A. Bifulco[2], D. Pugliese[3], A. Casciello[2], M. Terzi[4], A. Mariani[1], G. Malucelli[6]

[1] Department of Chemical, Physical, Mathematical, and Natural Sciences, University of Sassari, Via Vienna 2, Sassari 07100, Italy
[2] Department of Chemical, Materials and Production Engineering, University of Naples Federico II, 80125 Naples, Italy
[3] Division of Applied Metrology and Engineering, National Institute of Metrological Research (INRiM), Torino 10135, Italy
[4] Division of Quantum Metrology and Nanotechnologies, National Institute of Metrological Research (INRiM), Torino 10135, Italy
[5] Dept. of Applied Science and Tecnology, Politecnico di Torino, Viale T. Michel 5, 15121, Alessandria, Italy
e-mail: giulio.malucelli@polito.it

Introduction

Transparent wood (TW) has emerged as one of the most promising sustainable materials for advanced optical and energy-related applications. By combining the hierarchical structure of wood with transparent polymers, TW exhibits a unique balance of optical transmittance, light diffusion, low density, mechanical robustness, and thermal insulation. These characteristics make it attractive for smart windows, solar energy harvesting systems, energy-efficient buildings, and optoelectronic devices [1,2].

Despite significant advances in TW fabrication, optimization of optical properties is still largely based on empirical approaches. Optical transmittance and haze depend on a complex combination of variables including sample thickness, refractive index matching, residual lignin content, infiltration quality, and microstructural heterogeneity. As a result, establishing predictive structure–property relationships remains challenging [4].

Machine learning (ML) offers a powerful strategy for identifying hidden correlations within complex datasets and accelerating materials development. However, ML approaches have rarely been applied to transparent wood systems [3]. The present work proposes a physics-informed ML framework aimed at predicting optical transmittance and haze from physically meaningful descriptors, thereby supporting the rational design of transparent wood materials.

Results and discussion

A dataset containing 95 transparent wood samples was assembled from the scientific literature. The dataset covered different wood species, polymer infiltration systems, thicknesses, refractive indices, and optical performances. Particular attention was devoted to the selection of descriptors directly related to light transport phenomena, including thickness, refractive index, transmittance, and haze.

Because literature datasets are often incomplete and heterogeneous, robust preprocessing procedures were implemented. After performing an exploratory statistical analysis of the dataset, missing values were reconstructed through median-based imputation strategies, as the median was found to be more robust to outliers and better suited to the limited number of available observations than mean-based alternatives. Controlled Gaussian data augmentation was subsequently employed to increase statistical robustness without compromising physical consistency.Three supervised learning algorithms were investigated, namely (see Figure 1):

- Multilayer Perceptron (MLP);
- Random Forest (RF);
- Gradient Boosted Trees (GBT).

The predictive performance revealed a clear distinction between the two target properties. Optical transmittance was predicted with relatively high accuracy and stability across different preprocessing strategies. This result is consistent with the underlying physics, since transmittance is mainly controlled by macroscopic variables such as optical path length and refractive index matching.

Conversely, haze prediction proved significantly more challenging. Haze originates from complex multiscale scattering mechanisms and is strongly affected by structural features that were not explicitly included in the dataset, such as porosity, lumen morphology, local density fluctuations, and interface quality. Consequently, larger prediction errors were observed for haze regardless of the selected model.

Among all investigated algorithms, Random Forest consistently exhibited the most robust and reliable performance. Its ability to handle nonlinear relationships, noisy datasets, and limited data availability makes it particularly suitable for transparent wood research, where experimental datasets are often small and heterogeneous. Gradient Boosted Trees achieved competitive results, whereas the Multilayer Perceptron showed greater sensitivity to dataset size and preprocessing conditions. Overall, Random Forest provided the most reliable and consistent performance across the investigated scenarios, whereas Gradient Boosted Trees achieved the highest prediction accuracy in augmented configurations. On the other side, the Multilayer Perceptron with k-NN (k-Nearest Neighbors algorithm) appears significantly affected by the limited amount of available training data, resulting in less stable predictive performance.

The study also highlights the importance of data quality in materials informatics. While data augmentation improved transmittance prediction, its benefits for haze were limited, indicating that future improvements will require richer descriptors capable of directly representing microstructural characteristics.

Figure 1. Some of the machine learning models employed for the prediction of Haze and Optical Transmittance.

Conclusions

A physics-informed machine learning framework was successfully developed for predicting optical transmittance and haze in transparent wood systems. The results demonstrate that physically meaningful descriptors can provide accurate predictions of optical transmittance, while haze prediction remains limited by the absence of explicit microstructural information.

Among the investigated models, Random Forest provided the best overall performance, confirming the suitability of ensemble tree-based methods for small and heterogeneous materials datasets. The proposed approach demonstrates the potential of machine learning to accelerate transparent wood development and establishes a foundation for future data-driven design strategies integrating optical characterization, microstructural analysis, and materials informatics.

References

[1] C. Chen et al., *Nat. Rev. Mater.*, vol. 5 642–666 (2020)

[2] G. Malucelli et al., *Nat. Rev. Mater.* (2026) 10.1038/s41578-026-00901-x

[3] A. Mariani and G. Malucelli, *Next Mater.*, vol. 5 5, 100255 (2024)

[4] D. pugliese and G. Malucelli, Polymers, vol. 17, 3276 (2025)

[5] Li et al., *Chem. Rev.* vol.126, 6776-6803 (2026)

Acknowledgments

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PREPARATION AND CHARACTERIZATION OF UV-LED CURABLE BIO-BASED COATINGS CONTAINING POLYMERIC CARBON DOTS

M. Bartoli[1], E. Piatti[2], G. Malucelli[3]

[1] Istituto Italiano di tecnologia - Center for Sustainable Future Technologies, Via Livorno 60, 10144 Torino, Italy

[2] Dept. of Applied Science and Tecnology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Torino, Italy

[3] Dept. of Applied Science and Tecnology, Politecnico di Torino, Viale T. Michel 5, 15121, Alessandria, Italy

e-mail: giulio.malucelli@polito.it

Introduction

The development of sustainable coatings based on renewable resources is becoming increasingly important due to growing environmental concerns and stricter regulations regarding fossil-derived materials. Among the available alternatives, UV-curable bio-based resins have attracted considerable attention because of their rapid processing, low energy consumption, solvent-free formulations, and tunable chemical architectures [1]. However, the mechanical and thermal performances of many bio-derived resins still require improvement to meet the demands of advanced applications.

Nanofillers offer an effective strategy for enhancing the properties of photocurable systems. In particular, polymeric carbon dots (PCDs) have emerged as versatile nanomaterials owing to their fluorescence emission, low toxicity, tunable surface chemistry, and potential production from sustainable precursors [2,3]. Despite their extensive use in biomedical fields, their application in UV-curable bio-based coatings remains largely unexplored.

In this work, PCDs synthesized from citric acid and 1,4-phenylenediamine were incorporated into an acrylated epoxidized soybean oil (ESBOA) resin and subsequently cured through UV-LED irradiation. The objective was to investigate the influence of PCDs on the optical, thermal, and physicochemical properties of the resulting coatings while maintaining a high bio-based content.

Results and discussion

PCDs were synthesized through an ultrasound-assisted route using citric acid and 1,4-phenylenediamine as precursors. Structural characterization through FTIR, Raman spectroscopy, XPS, and XRD confirmed the formation of nitrogen-containing polymeric carbon structures characterized by aromatic domains interconnected through amide-based linkages.

Optical characterization demonstrated that the synthesized PCDs exhibited intense blue fluorescence emission together with UV-visible absorption bands associated with nitrogen-containing aromatic domains (Figure 1).

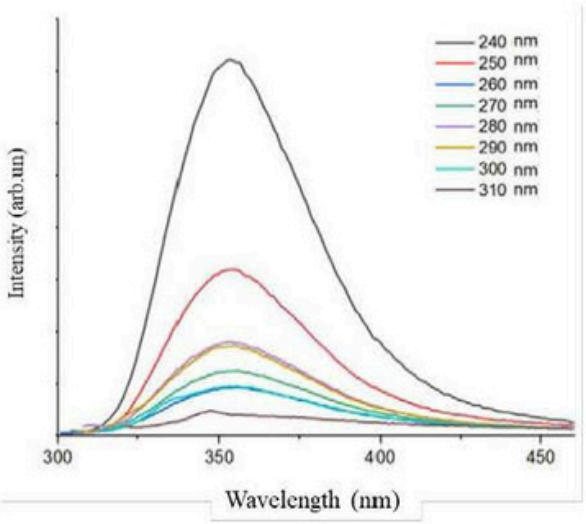


Figure 1. Fluorescence spectra of PCDs in the range between 300 and 470 nm.

Composite coatings were prepared by dispersing different amounts of PCDs (0.5, 1, and 2 wt.%) within the ESBOA resin followed by UV-LED curing at 395 nm. FTIR analyses confirmed the complete conversion of the acrylic double bonds under the adopted irradiation conditions, demonstrating that the presence of the nanofiller did not interfere with the photopolymerization process.

Morphological investigations revealed that low filler loadings generated homogeneous coatings, whereas increasing the PCD loading promoted the formation of nanoscale aggregates that progressively modified the surface topology. Nevertheless, these aggregates did not compromise the curing process or the integrity of the polymer network.

The optical response of the coatings strongly depended on filler concentration. Significant fluorescence emission was observed only for

coatings containing 2 wt.% PCDs, indicating that a threshold concentration is required to achieve detectable luminescent behavior in the cured network. The emission spectra displayed broad bands attributable to the coexistence of differently sized emissive domains and filler–matrix interactions (Figure 2).

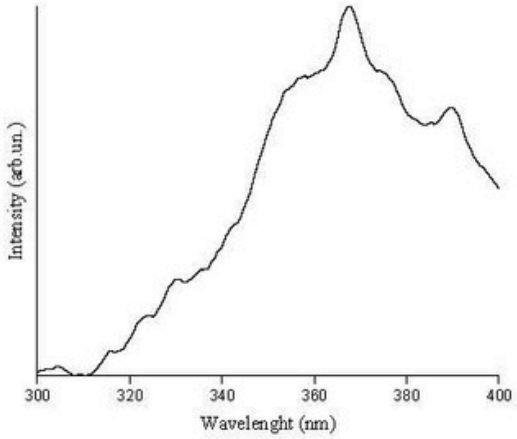


Figure 2. Fluorescence emission of 2 wt.% PCDs-containing film excited at 240 nm.

Differential scanning calorimetry showed that the incorporation of PCDs did not significantly affect the glass transition temperature of the coatings. All systems exhibited Tg values close to 10 °C, indicating that the nanofiller did not alter the crosslinking density or the segmental mobility of the polymer network.

Thermogravimetric analyses revealed a beneficial effect of the nanofiller on thermal stability. Under nitrogen atmosphere, the degradation onset increased from 265 °C for the unfilled coating to 282 °C for the formulation containing 2 wt.% PCDs (Figure 3). Similar improvements were observed under oxidative conditions, where both degradation temperatures and residual char increased with filler loading. These results suggest that the aromatic carbonaceous domains of the PCDs exert a protective effect on the degrading polymer matrix and promote char formation during thermal decomposition.

Conclusions

Polymeric carbon dots synthesized through a sustainable ultrasound-assisted process were successfully incorporated into UV-LED curable coatings based on acrylated epoxidized soybean oil. The obtained composites retained the fluorescence properties of the nanofiller while maintaining complete curing and unchanged crosslinking density.

The incorporation of PCDs enhanced the thermal stability of the coatings and promoted char formation during degradation, while significant fluorescence emission was achieved at the highest filler loading (i.e., 2 wt.%). These findings demonstrate that polymeric carbon dots are promising multifunctional bio-derived nanofillers for the development of sustainable fluorescent coatings suitable for advanced optical and protective applications.

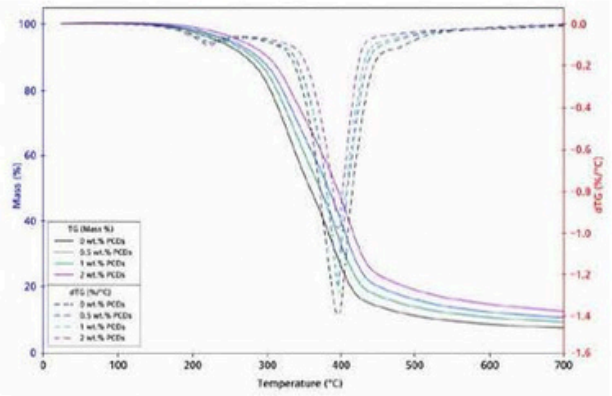


Figure 3. TG and dTG curves of the UV-LED cured coatings (atmosphere: nitrogen).

References

[1] Y. Li et al., *Macromol. Chem. Phys.*, vol. 227, e00319 (2025)

[2] M.G. Giordano et al., *Polymers*, vol. 28, 2772 (2023)

[3] M. Kurian and A. Paul, *Carbon Trends*, vol. 3, 100032 (2021)

Acknowledgments

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SUSTAINABLE TRANSPARENT WOOD BASED ON BIO-BASED ISOBORNYL ACRYLATE/METHACRYLATE MATRICES

A. Cabras[1], D. Nuvoli[1], D. Pugliese[2], M. Terzi[3], A. Mariani[1], G. Malucelli[4]

[1] Department of Chemical, Physical, Mathematical, and Natural Sciences, University of Sassari, Via Vienna 2, Sassari 07100, Italy
[2] Division of Applied Metrology and Engineering, National Institute of Metrological Research (INRiM), Torino 10135, Italy
[3] Division of Quantum Metrology and Nanotechnologies, National Institute of Metrological Research (INRiM), Torino 10135, Italy
[4] Dept. of Applied Science and Tecnology, Politecnico di Torino, Viale T. Michel 5, 15121, Alessandria, Italy
e-mail: giulio.malucelli@polito.it

Introduction

Transparent wood (TW) has recently emerged as one of the most promising bio-based structural and functional materials for sustainable technologies. It is obtained by combining a lignocellulosic scaffold with a transparent polymer matrix, generating a composite capable of retaining the mechanical advantages of wood while exhibiting remarkable optical properties. Compared with conventional transparent materials such as glass and petroleum-derived plastics, transparent wood offers lower environmental impact, reduced density, enhanced toughness, and improved thermal insulation performance. Consequently, TW has attracted considerable attention for applications ranging from energy-efficient buildings and smart windows to solar cells, optical devices, and thermal management systems [1-3].

The fabrication of transparent wood generally involves the removal or modification of lignin, which contains chromophoric groups responsible for light absorption. The resulting porous cellulose-rich template is subsequently impregnated with a polymer possessing a refractive index close to that of cellulose. This refractive index matching minimizes light scattering at internal interfaces and enables high optical transmittance. To date, most TW systems rely on epoxy resins or poly(methyl methacrylate) (PMMA), which provide excellent optical performance but are predominantly derived from fossil resources.

In the present work, transparent wood was fabricated using bio-based isobornyl-derived monomers, namely isobornyl acrylate (IBOA) and isobornyl methacrylate (IBOMA), obtained from renewable terpene feedstocks. These monomers offer a renewable carbon content approaching 75-80%, together with refractive indices compatible with cellulose. The objective of this study was to investigate the suitability of polyIBOA, polyIBOMA, and their copolymers as sustainable matrices for transparent wood, evaluating their optical, thermal, and morphological characteristics.

Results and discussion

TW specimens were prepared starting from 1 mm thick balsa veneers. After delignification through sodium chlorite treatment, the wood templates were infiltrated with IBOA, IBOMA, or mixtures of the two monomers containing different molar fractions. UV-induced polymerization generated the final wood-polymer composites.

The optical performance of transparent wood strongly depends on the refractive index matching between the polymer phase and the cellulose scaffold. Measurements performed on the synthesized polymers revealed refractive indices between 1.492 and 1.498, values sufficiently close to that of cellulose (1.5) to ensure efficient light transmission through the composite.

UV-Vis characterization demonstrated excellent optical properties for all formulations. The transmittance spectra showed a rapid increase above 350-400 nm, followed by a plateau in the visible region. The best optical performance was obtained for the poly(IBOA-co-IBOMA) 50/50 system, which achieved approximately 80% transmittance at 550 nm. Copolymer-based TWs consistently exhibited higher optical transmittance than the corresponding homopolymer systems, suggesting improved refractive index matching and more homogeneous infiltration of the wood microstructure. In addition to transparency, all samples exhibited significant haze values, ranging from approximately 59 to 86% (Figure 1). High haze is a desirable feature for applications such as diffusive glazing and photovoltaic devices because it enhances light scattering while maintaining overall transparency. Pure polyIBOA produced the highest haze values, whereas the copolymer formulations achieved a better balance between transparency and light diffusion. Particularly, the 50/50 copolymer combined the highest optical transmittance with substantially reduced haze, demonstrating the possibility of

tailoring the optical response through copolymer composition.
The effectiveness of UV curing was confirmed by FTIR spectroscopy. The characteristic C=C stretching vibration associated with the monomer double bond disappeared after polymerization, indicating a high degree of conversion and successful network formation within the wood scaffold.

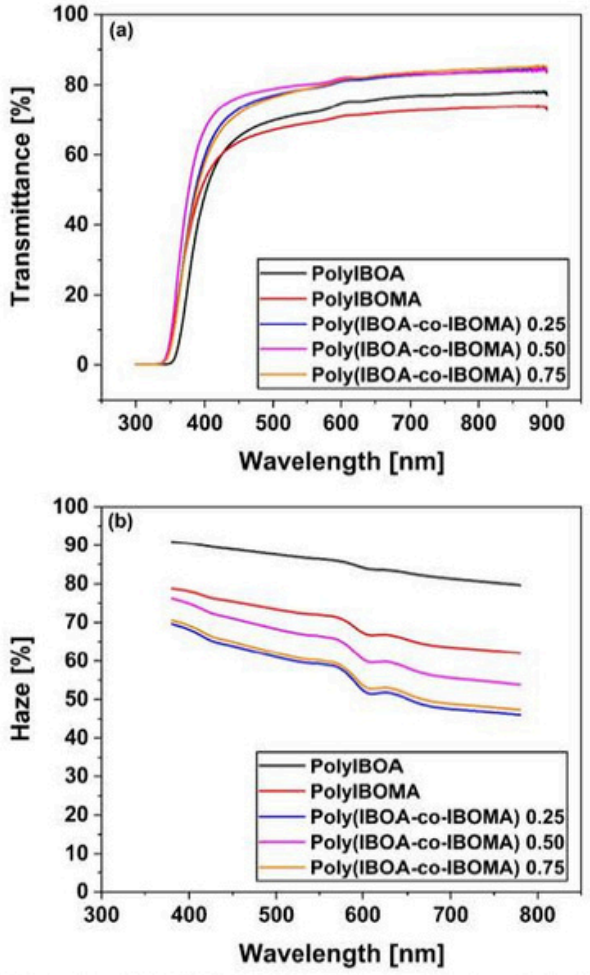


Figure 1. (a) optical transmittance and (b) haze as a function of wavelength for the investigated TW. In copolymers, the molar fraction of IBOA is indicated.

Morphological investigations by scanning electron microscopy revealed homogeneous filling of the wood lumina and intimate interaction between the polymer matrix and the cellulose framework. No significant voids or defects were observed, indicating efficient impregnation of both homopolymers and copolymers while preserving the intrinsic cellular architecture of the wood template.
Thermal conductivity measurements yielded values between 0.15 and 0.18 $W\,m^{-1}\,K^{-1}$ for all investigated formulations. These values are consistent with those reported for advanced transparent wood systems and significantly lower than those of conventional glass. The limited variation among formulations suggests that thermal transport is mainly governed by the composite architecture rather than by the precise chemical composition of the polymer phase. Such low thermal conductivity highlights the potential of these materials for energy-saving building applications and thermally insulating transparent structures. Overall, the results indicate that bio-based isobornyl polymers provide an attractive combination of optical transparency, light diffusion, thermal insulation, and sustainability. The use of renewable terpene-derived monomers represents a significant step toward reducing the environmental footprint of transparent wood while maintaining competitive functional performance.

Conclusions

Transparent wood composites based on bio-derived polyIBOA, polyIBOMA, and their copolymers were successfully fabricated through delignification and UV-assisted polymer infiltration. The developed materials exhibited refractive indices compatible with cellulose, optical transmittance up to 80%, high haze values, homogeneous microstructures, and low thermal conductivity. Among the investigated systems, the poly(IBOA-co-IBOMA) 50/50 formulation provided the best balance between transparency and light diffusion. These findings demonstrate that isobornyl-based polymers constitute promising sustainable alternatives to conventional fossil-derived matrices for transparent wood production, opening new opportunities for environmentally friendly optical and structural materials.

References

[1] C. Chen et al., *Nat. Rev. Mater.*, vol. 5 642–666 (2020)
[2] G. Malucelli et al., *Nat. Rev. Mater.* (2026) 10.1038/s41578-026-00901-x
[3] A. Mariani and G. Malucelli, *Next Mater.*, vol. 5 5, 100255 (2024)

Acknowledgments

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MICROPLASTICS RELEASE FROM PP-BASED BLENDS AND NANOCOMPOSITES

M. Morreale[1], E. Indovino [2], M. Baiamonte [2], V. Titone [2], L. Botta [2,3], F.P. La Mantia [2,3]

[1] Dept. of Engineering and Architecture, Università di Enna "Kore", Cittadella Universitaria, 94100, Enna, Italy
[2] Dept. of Engineering, Università di Palermo, Viale delle Scienze, 90128, Palermo, Italy
[3] National Interuniversity Consortium for Science and Technology of Materials (INSTM) , Via Giusti 9, 50121, Firenze, Italy
e-mail: marco.morreale@unikore.it

Introduction

The release of microplastics and nanoplastics into the environment has recently emerged as a critical consequence of polymer use and subsequent degradation, raising major concerns for both ecosystem integrity and health. Microplastics are generally defined as particles smaller than 5 mm, whereas nanoplastics fall within the sub micrometric domain (<1 µm). These may originate as "primary" microplastics (intentionally incorporated into formulations, e.g., coatings, cosmetics), or as "secondary" microplastics generated through the physicochemical degradation and mechanical fragmentation of larger plastic items. This pathway is strongly influenced by external factors, epsecially photo oxidation and mechanical stress, which progressively decrease the molecular weight and promote embrittlement [1].
In this context, the degradation behaviour of multiphase polymer systems needs further attention. Polymer blends and polymer nanocomposites, in fact, show complex degradation pathways, due to interfacial interactions, phase specific behaviours to degradation, and possible filler induced modifications of oxidation kinetics. In blends, microplastics (and, potentially, nanoplastics) may originate from the dispersed domains, already in the micrometric size range, as well as from the matrix; in nanocomposites, particle release may come from the filler itself and from the degraded matrix. Despite their relevance, these aspects are not widely investigated in the Literature, especially for polyolefin based systems. This study, therefore, examined two polypropylene (PP)/polyethyleneterephtalate (PET) blends, with and without a compatibilizer, and a PP nanocomposite containing an organically modified nanoclay.

Results and discussion

The blends based on PP and PET had 75/25 (wt/wt) composition, without and with (5 wt%) a styrene-ethylene-butadiene-styrene (SEBS) copolymer functionalized with maleic anhydride (MA) compatibilizer, and were prepared by melt mixing; likewise, the preparation of the PP based nanocomposites, filled with 5 wt% organically modified nanoclay. Samples for tensile characterization, photo-oxidation and microplastics generation were prepared by compression molding. The systems were subjected to mechanical fragmentation using a high-speed cutting mill, and photo-oxidation using a UV Accelerated Weathering Tester, in order to evaluate the impact of both mechanisms of microplastics generation and release. Size distribution of the released particles was investigated, and the underlying mechanisms were deepened via FTIR-ATR and TGA analysis. The blends exhibited a higher propensity to generate microplastics, especially following photo oxidation, whereas compatibilization significantly reduced this susceptibility by improving interfacial interactions. On the other hand, in the nanocomposite, the presence of nanoclay decreased microplastics formation in both unweathered and photo oxidized samples, suggesting a stabilizing effect. The FTIR spectra further proved that the nanoclay presence helps in reducing the formation of photo-oxidation products in the carbonyl region.

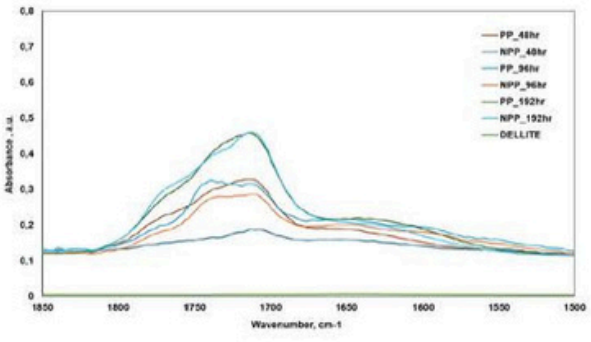


Figure 1. FTIR spectra of photooxidized PP, nanocomposite and nanoclay samples.

TGA measurements (residual ash content) performed on the PP and nanocomposite samples confirmed that there never was any significant nanoclay release after fragmentation.

Conclusions

Uncompatibilized and compatibilized PP/PET blends, as well as PP/clay nanocomposites, were subjected to photo-oxidation and mechanical fragmentation.
The photo-oxidized blend samples showed higher tendency to generate microplastics, while the compatibilized blends showed a reduced tendency to releasing.
On the other hand, this beneficial effect from compatibilization is reduced in the case of photo-oxidized systems, and this was explained by higher occurrence of reactions at the interface.
In the case of the nanocomposites, nanoclay presence proved to lower the microplastics generation and release in all cases, and this was attributed to the slowdown of the photooxidation process.

References

[1] M. Morreale, F.P. La Mantia, *Polymers*, vol. 16, 1525 (2024)

SUSTAINABLE ROUTES TO LEAD-FREE FLEXIBLE PIEZOELECTRIC POLYMER-CERAMIC FILMS FOR ENERGY HARVESTING

P. Stagnaro[1], M. Vignolo[1], R. Manfredi[1], M. Fortunato[2], R. Utzeri[1], L.P. Curecheriu[3], A.I. Cosutchi[4], M.T. Buscaglia[2]

[1] SCITEC-CNR, Via De Marini 6, 16149, Genova, Italy
[2] ICMATE-CNR, Via De Marini 6, 16149 Genova, Italy
[3] Faculty of Physics, Alexandru Ioan Cuza University, 11 Blv. Carol I, 700506, Iasi, Romania
[4] "Petru Poni" Institute of Macromolecular Chemistry, 41a Grigore Ghica Voda Alley, 700487 Iasi, Romania
e-mail: paola.stagnaro@cnr.it

Introduction

Polymer-ceramic composites have gained significant attention for energy harvesting and storage applications as they combine the flexibility and high breakdown strength (BDS) of polymers with the functional properties of embedded functional inorganic particles [1]. These materials are well-suited for flexible power-generating devices integrated into miniaturized wireless applications, including wearable and implantable tools, as well as remote monitoring and control sensors [2].

Among polymer matrices, poly(vinylidene fluoride) (PVDF) is particularly attractive due to its intrinsic ferroelectric and piezoelectric behaviour, together with excellent flexibility, processability, and chemical stability. On the ceramic side, barium titanate ($BaTiO_3$, BT) is a promising lead-free alternative to PZT, combining high dielectric and piezoelectric performance with improved environmental sustainability.

Here PVDF-BT composites containing 30 vol.% BT microparticles were fabricated using four different processing routes: a one-step method based on hot pressing (HP), and three double-step procedures, namely, melt blending (MB), solvent casting (SC) and microwave irradiation and mixing (MW), all followed by a final hot pressing step [3]. Neat PVDF films were also prepared using the same processing techniques and characterized as reference materials.

In this study, the main aim was to evaluate how the fabrication method, in particular the innovative MW-based approach [4], affects the structural, morphological, thermal, mechanical, dielectric, and piezoelectric properties of the resulting polymer-ceramic composites.

Results and discussion

The different fabrication routes strongly affected the microstructure and properties of the flexible PVDF-BT composites achieved (Fig. 1a). SEM and SEM-EDX analyses revealed that direct HP as well as SC methods produced large BT aggregates/agglomerates, whereas MB resulted in a more homogeneous filler distribution within the PVDF matrix. Composites prepared by microwave-assisted heating and mixing (MW) also exhibited a highly uniform microstructure (Fig. 1b), with well-dispersed BT particles and only a few small clusters showing limited necking between neighbouring filler particles. Overall, MB and MW processing led to the most homogeneous BT dispersion among the investigated fabrication routes.

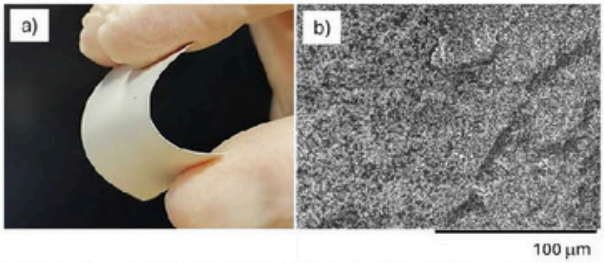


Figure 1. Manual bending showing flexibility of a PVDF-BT composite film (a) and SEM micrograph of the composite prepared by the MW-assisted method showing homogeneous dispersion of BT particles within the polymer matrix (b).

Thermogravimetric analysis confirmed that all composites maintained good thermal stability, with MB and MW samples exhibiting slightly higher degradation temperatures, likely due to improved filler dispersion and local processing-induced structural modifications.

The relative fractions of non-polar α-phase and electroactive β- and γ-phase of PVDF were determined by ATR-FTIR. Introducing the BT filler, the relative fraction of β-phase found in the polymer matrix (around 30%, except for the neat PVDF sample from SC which exhibited equal amounts of β- and γ-phase) is substantially maintained in the HP and MB composites, whereas it results practically absent in PVDF-BT SC (with preponderant γ-phase). The PVDF-BT

MW sample revealed regions composed of α- and β-phases and others with only α- and γ-crystals. Investigations on these aspects are in due course. DSC analysis showed slightly higher crystallinity for the PVDF-BT composites with respect to neat PVDF, in particular for the composites prepared by the MB and MW methods. Overall the mean crystallinity degree is around 50%.

Uni-axial tensile tests showed that the incorporation of 30 vol.% BT significantly increased stiffness (E_t values in the range 2000-3300 MPa) while drastically reducing the elongation at break by one order in magnitude. The MB composites displayed the best mechanical performance, whereas MW samples showed intermediate properties consistent with correspoding microstructure.

Rheological analysis further confirmed the superior homogeneity achieved through MB and MW processing compared to the other fabrication methods, consistently with the SEM and SEM-EDX observations.

Dielectric characterization demonstrated a substantial increase in permittivity for all composites compared with neat PVDF. HP, SC, and MW samples exhibited the highest dielectric constants, while MB showed lower permittivity due to its more uniform filler dispersion. Dielectric losses remained low for most samples, except for SC composites, due to residual solvent.

After electrical poling, all composites exhibited enhanced piezoelectric activity, with d_{33} values increasing significantly compared to the unpoled samples. Under optimized poling conditions, the d_{33} coefficient increased markedly, reaching values consistent with those reported for similar PVDF-$BaTiO_3$ systems. The highest piezoelectric response was obtained for the HP composites after prolonged poling, while MW samples also showed comparable performance despite their more homogeneous microstructure. Overall, the results indicate that filler dispersion and microstructural organization play a key role in determining dielectric and piezoelectric behaviour. Among the investigated techniques (Fig. 2), microwave-assisted processing emerged as a promising, scalable, solvent-free, and energy-efficient approach capable of producing composites with balanced mechanical, dielectric, and piezoelectric properties.

Conclusions

PVDF-$BaTiO_3$ composite films were successfully fabricated using different scalable processing routes, including hot pressing, solvent casting, melt blending, and microwave-assisted heating and mixing. The incorporation of BT particles enhanced the dielectric and piezoelectric response of the hosting PVDF matrix, while the fabrication method strongly influenced filler dispersion and overall material performance. The most homogeneous microstructures were obtained by MB and MW processing, leading to a synergistic combination of mechanical, dielectric, and electromechanical properties. A clear correlation was observed between microstructural homogeneity, dielectric behaviour, and piezoelectric response. Microwave irradiation and mixing emerged as a promising alternative, combining solvent-free processing with reduced time and energy consumption, while delivering competitive morphological, thermal, dielectric, mechanical and piezoelectric properties. Among the investigated approaches, MW stands out as a sustainable and efficient route for producing flexible lead-free piezoelectric composites with performance comparable or even better with respect to conventional fabrication methods. The achieved lead-free PVDF-$BaTiO_3$ composite materials represent promising candidates for next-generation flexible piezoelectric energy-harvesting devices and sustainable self-powered systems.



Figure 2. Scheme illustrating the various preparation methods employed for the fabrication of piezoelectric flexible composites.

References

[1] L. Padurariu, E. Brunengo et al., *ACS Appl. Mater. Interfaces*, *15*, 13535−13544 (2023)

[2] F. Craciun, F. Cordero et al., *Compos. -B: Eng.*, *263*, 110835 (2023)

[3] R. Manfredi, M. Fortunato et al., *Compos. - A: Appl. Sci. Manuf.*, *209*, 110023 (2026)

[4] M. Vignolo, P. Stagnaro, R. Manfredi, M.T. Buscaglia, M. Fortunato, Production of a piezoelectric composite material by mixing powders and microwave-assisted heating. PCT/IT2025/000039 (2025)

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POSTERS

Processabilitá e stampa 3D di materiali polimerici

PROCESSING AS A DESIGN TOOL FOR TAILORING MICROSTRUCTURE AND PROPERTIES IN COMPLEX POLYMER SYSTEMS

R. Arrigo[1], A. Frache[1]

[1] Dept. of Applied Science and Technology, Politecnico di Torino, Viale Teresa Michel 5, 15121, Alessandria, Italia

e-mail: rossella.arrigo@polito.it

Introduction

In polymer-based complex systems, final properties are rarely governed by chemical composition alone. Processing defines the thermo-mechanical history experienced by the material, controlling flow-induced deformation, phase morphology, filler dispersion, interfacial area, phase continuity and, in additive manufacturing, also the mesoscopic architecture of the final object. Therefore, processing can be regarded as an active design variable to engineer the microstructure and tailor the resulting properties. This concept is especially relevant for multiphase blends and polymer nanocomposites, where even subtle morphological changes may strongly affect ductility, processability, printability or flame-retardant behavior.

Here, three case studies are presented to demonstrate how processing/microstructure/properties relationships can be deliberately exploited in different polymer-based systems. The selected examples include biopolymer blends processed under elongational-flow-dominated conditions, immiscible polymer/nanoclay blends prepared through different mixing sequences, and nanocomposite filaments designed for Fused Filament Fabrication. Overall, these systems provide complementary evidence that the rational selection and optimization of processing routes can control microstructure across different length scales, from dispersed domains and filler localization to printed architectures, ultimately enabling the design of complex polymer systems with targeted mechanical, functional and fire-retardant properties.

Results and discussion

The first case study concerns PLA/PHBH 70/30 biopolymer blends processed by compression molding, cast extrusion and film blowing. The compression-molded sample displayed the typical droplet-matrix morphology of an immiscible blend and a brittle tensile response. Conversely, cast extrusion and, even more effectively, film blowing imposed an elongational flow able to deform and orient the PHBH phase, progressively refining the morphology until the two phases became almost indistinguishable in the blown film. This physical compatibilization increased the interfacial area and improved stress transfer, leading to a brittle-to-ductile transition: the elongation at break increased from about 10% for the isotropic sample to 43% and 74% for cast-extruded and blown films, respectively [1].

The second case study focuses on HDPE/PA6/Cloisite 20A blends. Keeping constant the overall composition (HDPE/PA6 80/20 with 5 wt.% nanoclay), different mixing sequences were used: direct clay addition during extrusion; introduction of the nanofillers in PA6, and subsequent melt-compounding with HDPE; introduction of the nanofillers in HDPE, and subsequent melt-compounding with PA6. This strategy modified clay localization and the structuring of the melt. In particular, systems in which the nanoclay was preferentially located in the continuous polyethylene phase showed a stronger low-frequency rheological response, consistent with the formation of a more effective filler network. The different microstructures translated into different combustion behaviors. Nanoclay-containing blends showed reduced peak heat release rate compared with the unfilled blends; among the studied formulations, direct addition and HDPE-based masterbatch were generally the most effective solutions, whereas the PA6-based masterbatch was less advantageous. For low-viscosity PA6 systems, the HDPE-based masterbatch formulation reached the lowest pkHRR (871 kW/m^2), although the higher smoke release must be considered when selecting the best formulation for a given application.

The third case study involves polypropylene nanocomposites containing 5 wt.% organo-modified nanoclay, developed as flame-retardant

filaments for fused filament fabrication (FFF). The addition of nanoclays amplified the non-Newtonian behavior of the PP copolymer, increasing the low-frequency viscosity and yield stress while preserving flowability at high shear rates, thereby improving the PP printability. After optimizing filament extrusion and printing conditions, defect-free FFF specimens were obtained. Notably, the 3D-printed samples showed better flame-retardant behavior than the corresponding compression-molded samples: cone calorimetry revealed slower combustion and lower HRR peak, while horizontal UL-94 tests were passed by the 3D-printed samples with a +/-45 degrees infill pattern but not by the compression-molded specimens. This improvement was ascribed to shear-induced nanoclay dispersion during nozzle flow and to the layer-by-layer architecture, which provided a more homogeneous clay concentration at the irradiated surface and promoted a compact protective char [2].

Conclusions

The three case studies demonstrate that processing can be used as a rational tool to engineer microstructure and properties in polymer-based complex systems. Elongational flow can act as a physical compatibilization route for immiscible biopolymer blends, mixing sequence can direct nanoclay localization in multiphase flame-retardant blends, and FFF can create architectures that outperform conventionally molded nanocomposites in fire tests. Overall, the results highlight a common design strategy: processing selection and optimization enable microstructure control, and microstructure control enables targeted mechanical, functional and flame-retardant properties.

References

[1] R. Arrigo, F. Ianniello, C. Gnoffo, G. Trapani, A. Frache, *Materials Letters*, vol. 406, 139940 (2026)
[2] E. Lorenzi, R. Arrigo, A. Frache, *Polymers*, vol. 16, 858 (2024)

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POSTERS

Chimica e fisica dei polimeri

FLUORINE-FREE PROTON EXCHANGE MEMBRANES: SYNTHESIS AND CHARACTERIZATION OF SULFONATED PPO-PBI NETWORKS FOR PEMWES

BANDINI[1], CARLOTTI[1], GIOVANELLI[1], GUAZZELLI[1], PUCCI[1]

[1]Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy

e-mail: a.bandini8@studenti.unipi.it

Introduction

The transition to a sustainable energy economy relies heavily on green hydrogen produced via proton exchange membrane water electrolyzers (PEMWE) and utilized in PEM fuel cells. However, the commercialization of these technologies is hindered by the high cost and environmental concerns of state-of-the-art perfluorosulfonic acid (PFSA) membranes, like Nafion, which face strict PFAS regulations. To overcome these limitations, research must focus on developing robust, fluorine-free alternatives. Poly(p-phenylene oxide) (PPO) and polybenzimidazole (PBI) have emerged as highly promising hydrocarbon candidates. This study focuses on the design of novel polymer electrolytes that leverage functionalized PPO and PBI networks to combine high thermo-mechanical stability with excellent proton conductivity, providing a sustainable, cost-effective replacement for PFSA ionomers in next-generation hydrogen devices.

Results and discussion

The synthesis of fluorine-free proton exchange membranes was successfully achieved by functionalizing poly(p-phenylene oxide) (PPO) with bromo-terminated side chains, reaching a high initial functionalization degree of 92%. A critical optimization step was performed to improve the chemical stability of the polymer by reducing the vulnerable carbonyl groups. While standard ionic reduction yielded limited conversions (21-34%) , utilizing $NaBH_4$ and $AlCl_3$ in THF successfully achieved the complete reduction of carbonyls into fully aliphatic side chains

Subsequently, 35% of the available bromide groups underwent nucleophilic substitution to introduce proton-conducting sulfonic sites. To enhance dimensional stability, the resulting PPO-SO3H was crosslinked with a polybenzimidazole (PBI) matrix via solvent casting. The successful formation of the covalent network was confirmed by ATR-FTIR spectroscopy, which revealed the appearance of the characteristic imidazole ring band at 780 cm^{-1} and by gel content test demonstrating a high crosslinking degree of 85.0 ± 0.6%.

Thermal analyses proved that the PBI crosslinking significantly enhanced the material's stability, raising the glass transition temperature (T_g) to 274 °C and the primary degradation onset (T_{onset1}) above 200 °C, confirming the membrane's suitability for standard operating conditions. Furthermore, the robust crosslinked architecture effectively restricted swelling: the PPO-SO_3H-PBI membranes exhibited a water uptake of ~20%, notably lower than the 30% typically observed for the Nafion 117 benchmark. Crucially, the optimized PPO-SO_3H-PBI membranes achieved a remarkable Ion Exchange Capacity (IEC) of 1.44 mmol/g. This value falls perfectly between the theoretical limits for purely sulfonic conduction (0.83 mmol/g) and fully combined conduction (2.38 mmol/g). This intermediate IEC strongly suggests a highly efficient synergistic proton exchange mechanism, where both the sulfonic groups and the basic nitrogen sites of the PBI matrix actively participate in proton transport. By significantly outperforming the conductive capacity of the Nafion N117 benchmark (0.93 mmol/g), this crosslinked system validates its outstanding potential as a high-performance, cost-effective alternative for next-generation PEM applications.

Conclusions

Fluorine-free PPO-SO_3H-PBI membranes were successfully optimized. They show excellent thermo-mechanical stability, low water uptake (~20%), and a high IEC of 1.44 mmol/g, outperforming Nafion 117, making them suitable materials for PEMWEs and fuel cell application. Future work will be focused on tuning functionalization and sulfonation degrees to maximize PEM performance in order to achieve highly promising materials for next-generation, high-performance, fluorine-free PEMs.

TOWARDS CIRCULAR FLAME-RETARDED POLYPROPYLENE: FIRE PERFORMANCE AFTER RECYCLING AND AGING

A. Frache[1], R. Arrigo[1]

[1] Dept. of Applied Science and Technology, Politecnico di Torino, Viale Teresa Michel 5, 15121, Alessandria, Italia

e-mail: alberto.frache@polito.it

Introduction

The transition towards a circular economy for plastics requires not only efficient recycling routes, but also the preservation of functional properties after service life and reprocessing.
This issue is particularly critical for flame-retarded (FR) polymers, since fire safety must be retained even when the material undergoes thermo-mechanical degradation during mechanical recycling or oxidative damage during use.
Polypropylene (PP), one of the most widely used polyolefins, is intrinsically flammable and is therefore often modified with FR additives for applications in which ignition, flame spread and heat release must be controlled.
However, FR-containing plastics are still difficult to include in circular material flows: additives may remain active, degrade, redistribute or interact with the polymer matrix during recycling, thus affecting processability, mechanical performance and combustion behaviour.
In this work, the circularity of FR-PP was investigated through two complementary approaches.
In the first one, FR systems were introduced into reprocessed PP, in order to assess whether recycled matrices can be upgraded for fire-safe applications. Three halogen-free systems were considered: two intumescent formulations, based either on piperazine pyrophosphat/melamine polyphosphate (PAPP/MPP) or ammonium polyphosphate/pentaerythritol (APP/PER), and magnesium hydroxide (MH).
In the second approach, PP already containing a PAPP/MPP intumescent system was subjected to repeated reprocessing cycles, thus simulating the mechanical recycling of FR products at their end of life.
Finally, an ongoing study extends this framework by considering thermo-oxidative and photo-oxidative aging before reprocessing, with the aim of evaluating fire performance under more realistic service-life and recycling conditions.

Results and discussion

In the first approach, reprocessed PP (rPP) was obtained by repeated extrusion cycles and subsequently compounded with FR additives. Reprocessing reduced the PP melt viscosity, as expected from chain scission phenomena, strongly influencing the dispersion of the IFR. In the case of PAPP/MPP, SEM analysis showed a finer particle distribution in rPP, with a lower average Feret diameter than in the virgin matrix. This improved dispersion promoted the formation of a more compact and graphitized char during combustion. As a result, the PAPP/MPP system was effective in both virgin and recycled PP: both materials achieved UL-94 V-0 classification and comparable LOI values, while cone calorimeter tests showed a strong reduction in heat release rate (HRR). Notably, the recycled PP-based system displayed a higher time to ignition, a pronounced delay of the second HRR peak, lower MARHE and a lower effective heat of combustion, indicating that fire performance was not only retained, but even improved because of a more efficient condensed-phase barrier. The same approach was extended to APP/PER and MH systems in reprocessed PP. The APP/PER formulation confirmed the key role of matrix viscosity and particle dispersion on intumescent behaviour. Compared with the corresponding virgin PP-based system, the recycled matrix led to smaller additive-rich domains and to a longer HRR plateau, indicating a more stable protective char. Although small-scale flammability was more affected by dripping phenomena in the low-viscosity recycled matrix, cone calorimetry confirmed that APP/PER retained its ability to reduce heat release and fire growth. Conversely, MH showed a flame-retardant action essentially independent of the matrix degradation level. In both virgin and recycled PP, the high MH loading produced an approximately 80% reduction in peak HRR and a marked decrease in smoke production, due to endothermic decomposition, release of water vapour and formation of a MgO-rich protective residue. Overall, these results

demonstrate that reprocessed PP can be effectively upgraded with different FR strategies, although the efficiency of intumescent systems is more sensitive to the rheological and morphological features of the recycled matrix than that of inorganic MH [1].

In the second approach, the recyclability of an already flame-retarded PP was evaluated by subjecting a PP/PAPP-MPP formulation to up to five consecutive reprocessing cycles. The material maintained stable processability throughout the cycles, with no need to adjust extrusion conditions. Rheological and morphological analyses revealed only moderate changes: after the first cycles, the IFR dispersion remained comparable to that of the virgin FR-PP, whereas longer reprocessing promoted partial re-agglomeration of FR particles. Nevertheless, these morphological variations did not compromise the fire response. All reprocessed samples maintained UL-94 V-0 classification and LOI values close to those of the non-reprocessed FR-PP. Cone calorimeter curves remained almost unchanged after recycling, with comparable heat release rate, total heat release, mass loss rate, smoke production and MARHE values. The intumescent char-forming ability was preserved, as also confirmed by char morphology and Raman analysis, which indicated a progressive increase in graphitization at higher reprocessing cycles. Mechanical properties were also largely retained: tensile, flexural and impact strength remained nearly constant, while ductility decreased only at the highest number of cycles. These findings indicate that the studied PP/PAPP-MPP system can undergo mechanical recycling without losing its fire-safety function [2].

Finally, an ongoing aging study addresses the additional question of whether FR-PP materials retain their performance when recycling is preceded by service-life degradation. Thermo-oxidative and photo-oxidative aging are expected to modify both PP molecular architecture and additive/matrix interactions, potentially affecting dispersion, dripping, char formation and heat-release dynamics. Preliminary results suggest that combining aging and reprocessing is essential for a realistic assessment of FR-PP circularity, since the material entering a recycling stream may differ significantly from a simply reprocessed laboratory formulation.

Conclusions

The combined results show that flame-retarded PP can be integrated into circular material flows through two complementary routes. Reprocessed PP can be upgraded with halogen-free FRs, with fire performance comparable to, and in some cases better than, that of virgin PP-based systems as a consequence of improved char formation. At the same time, PP already containing an intumescent PAPP/MPP system can be reprocessed several times while retaining processability, mechanical properties and fire safety. The inclusion of thermo- and photo-oxidative aging before recycling will further clarify the long-term reliability of these materials, supporting the design of recycling-compatible FR formulations for circular fire-safe PP applications.

References

[1] G. Bernagozzi, R. Arrigo, Y. Xu, M. Xu, A. Frache. *ACS Applied Polymer Materials*, Accepted for publication, (2026)

[2] G. Bernagozzi, R. Arrigo, Y. Xu, M. Xu, M. Bartoli, A. Frache. *Polymers*, vol. 18, 845 (2026)

DESIGN OF CARBAZOLE-FUNCTIONALIZED POLY(TRIPHENYLAMINE)S FOR VISIBLE-DRIVEN WATER REMEDIATION

Muhammad Furqan Farooq[1], Martina Recupero[1], Olga Sacco[1], Vincenzo Venditto[1], Vincenzo Vaiano[2] and Stefania Pragliola[1]

[1] Department of Chemistry and Biology "A. Zambelli"and INSTM Research Unit, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano (Salerno), Italy

[2] Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano (Salerno), Italy
e-mail: spragliola@unisa.it

Introduction

Polytriphenylamines (PTPAs) have attracted considerable interest as conjugated polymers with semiconducting properties due to their efficient hole-transport capacity, which, combined with their high thermal stability and good processability, makes them suitable for optoelectronic applications.[1] The incorporation of chromophoric units into the PTPA backbone represents an effective strategy for tailoring the material photophysical properties, extending its light absorption into the visible region, and promoting the separation of photogenerated charge carriers. These characteristics also make these materials promising as metal-free organic photocatalysts, active even under visible-light irradiation for the degradation of organic pollutants in aqueous media, offering a sustainable approach to water treatment.[2]

Herein, we report the synthesis of two para-substituted triphenylamine monomers incorporating carbazole-based chromophoric units, namely 9H-carbazole and 3,6-dimethyl-9H-carbazole, and their corresponding polymers. Moreover, the photocatalytic activity of the polymers was evaluated through the degradation of model organic pollutants in aqueous solution under visible-light irradiation.

Results and discussion

The synthesis of the monomers 4-((9H-carbazol-9-yl)methyl)-N,N-diphenylaniline (M1) and 4-((3,6-dimethyl-9H-carbazol-9-yl)methyl)-N,N-diphenylaniline (M2) was performed following literature-reported procedures with slight modifications.[3,4] The corresponding synthetic route is illustrated in Figure 1. The respective polymers (PM1 and PM2) were synthesized via oxidative polymerization in solution, using iron(III) chloride as the oxidizing agent. Polymerization reactions were carried out under an inert nitrogen atmosphere at room temperature (Figure 2). The polymerization results are summarized in Table 1.

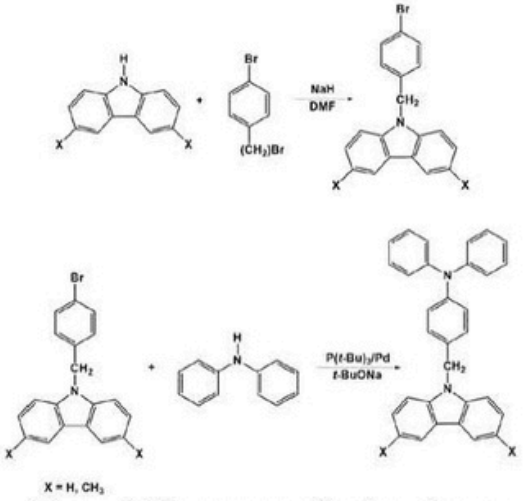


Figure 1. Monomer synthesis scheme

The polymers PM1 and PM2 exhibit chloroform solubility of 23% and 37%, respectively. This behavior suggests partial cross-linking during the polymer synthesis, likely arising from the reactivity of the carbazole aromatic carbon atoms. The higher solubility of PM2 can probably be attributed to the lower tendency of monomer M2 to undergo cross-linking, owing to the presence of two methyl groups at the 3- and 6- positions of the carbazole unit.

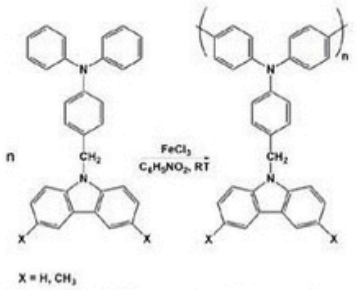


Figure 2. Polymerization scheme

Table 1: Polymerization results

Entry	Yield (%)	$F_{CHCl3sol}$ (%)	M_w (Da)	Đ	T_d (°C)
PM1	60	23	5900	2.5	420
PM2	57	37	5700	2.3	420

The microstructures of the soluble fractions of polymers PM1 and PM2 were identified by ^1H and ^{13}C NMR spectroscopy. The NMR spectra revealed that in both polymers, PM1 and PM2, consecutive monomer units along the polymer chains are connected solely via 4',4''-linkages. The polymer samples exhibit average molecular weights in the range of 5,000 - 6,000 Da, with dispersity values between 2.0 and 2.5. Despite the relatively low molecular weights, all samples were able to form stable films.

Both differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyses confirm the amorphous nature of the polymers. The DSC thermograms of all samples exhibit only a glass transition, and the corresponding XRD patterns display a broad amorphous halo.

The optical properties of both polymers were studied using UV-Vis absorption, UV-Vis diffuse reflectance and photoluminescence spectroscopy, with emission measurements performed under excitation at 300 nm. In both cases, the spectra display the characteristic features of carbazole-containing polymers.

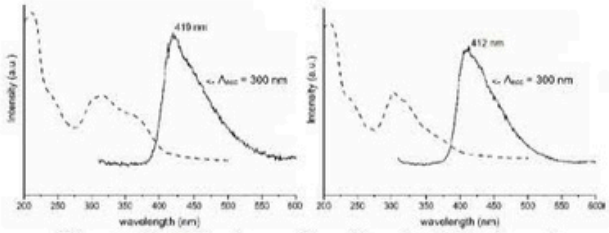


Figure 3. UV absorption(dashed line) and emission (solid line) spectra of PM1 (left) and PM2 (right) film samples.

For PM1, the optical band gap was estimated to be 2.90 eV by the Kubelka–Munk method (Figure 4). This value is consistent with those typically reported for conjugated organic semiconducting materials and is compatible with photoinduced charge generation under near-UV/visible-light irradiation. Preliminary photocatalytic tests using methylene blue as a model organic pollutant demonstrated the promising photoactivity of PM1 toward water decontamination (Figure 5). Under visible-light irradiation, the characteristic absorption band of methylene blue almost completely disappeared after 3 h, indicating efficient removal of the dye from the aqueous solution. Further studies are currently underway to comprehensively investigate the photocatalytic performance of both PM1 and PM2.

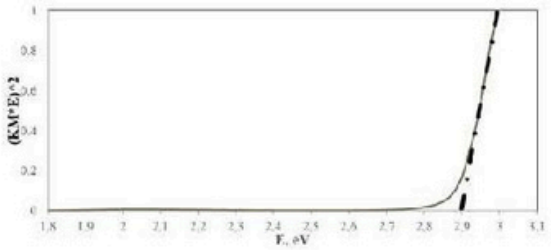


Figure 4. Tauc plot of PM1 derived from the Kubelka–Munk function for optical band gap determination.

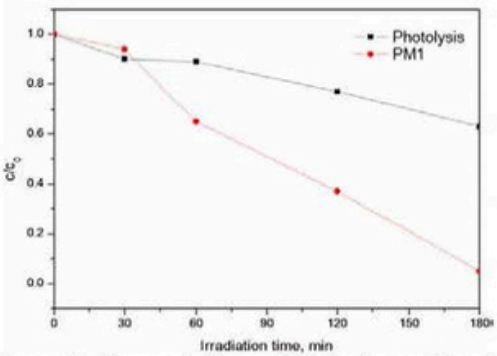


Figure 5. Degradation of Methylene Blue by PM1; [PM1] = 1g/L; [Methylene Blue] = 5 ppm.

Conclusions

In conclusion, carbazole-functionalized polytriphenylamines were successfully synthesized and characterized, showing tunable solubility while preserving the characteristic optical properties of carbazole-based polymers. Preliminary photocatalytic experiments demonstrated that PM1 is a promising metal-free photocatalyst for the degradation of organic pollutants in water, thus encouraging further investigation of this class of conjugated materials for sustainable photocatalytic applications.

References

[1] H. J. Yen, G. S. Liou, *Progress in Polymer Science*, vol. 89, 250-287 (2019)

[2] C. Dai, B. Liu, *Energy Environ. Sci.*, vol. 13 (1), 24-52 (2020)

[3] C. Takahashi, S. Moriya, N. Fugono, H. C. Lee, H. Sato, *Synthetic Metals*, vol. 129, 123-128 (2002)

[4] Z. Yin, M. Gu, H. Ma, X. Jiang, J. Zhi, Y. Wang, H. Yang, W. Zhu, Z. An, *Angew. Chem. Int. Ed.*, vol. 60, 2058-2063 (2021)

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