

Jóvenes Investigadores en Polímeros 2025

Bilbao, 14 - 17 Julio 2025



*Inspira, investiga, innova : polímeros
que transforman el futuro*

Ongi etorria

Estimadas personas participantes,

En nombre del Comité Organizador, es un placer invitaros a participar en el **XII Congreso de Jóvenes Investigadores en Polímeros JIP2025 Bilbao**, que tendrá lugar en **Bilbao del 14 al 17 de Julio de 2025**. Bajo el lema "**Inspira, investiga, innova: polímeros que transforman el futuro**", este encuentro busca ser un espacio abierto al intercambio de ideas, la inspiración mutua y el impulso de nuevas perspectivas en el ámbito de la ciencia de polímeros.

El congreso representa una excelente oportunidad para conocer los avances más recientes en investigación, compartir experiencias y establecer redes de colaboración entre quienes comienzan su carrera científica en este campo. También contaremos con la participación de personas investigadoras consolidadas que contribuirán con conferencias plenarias.

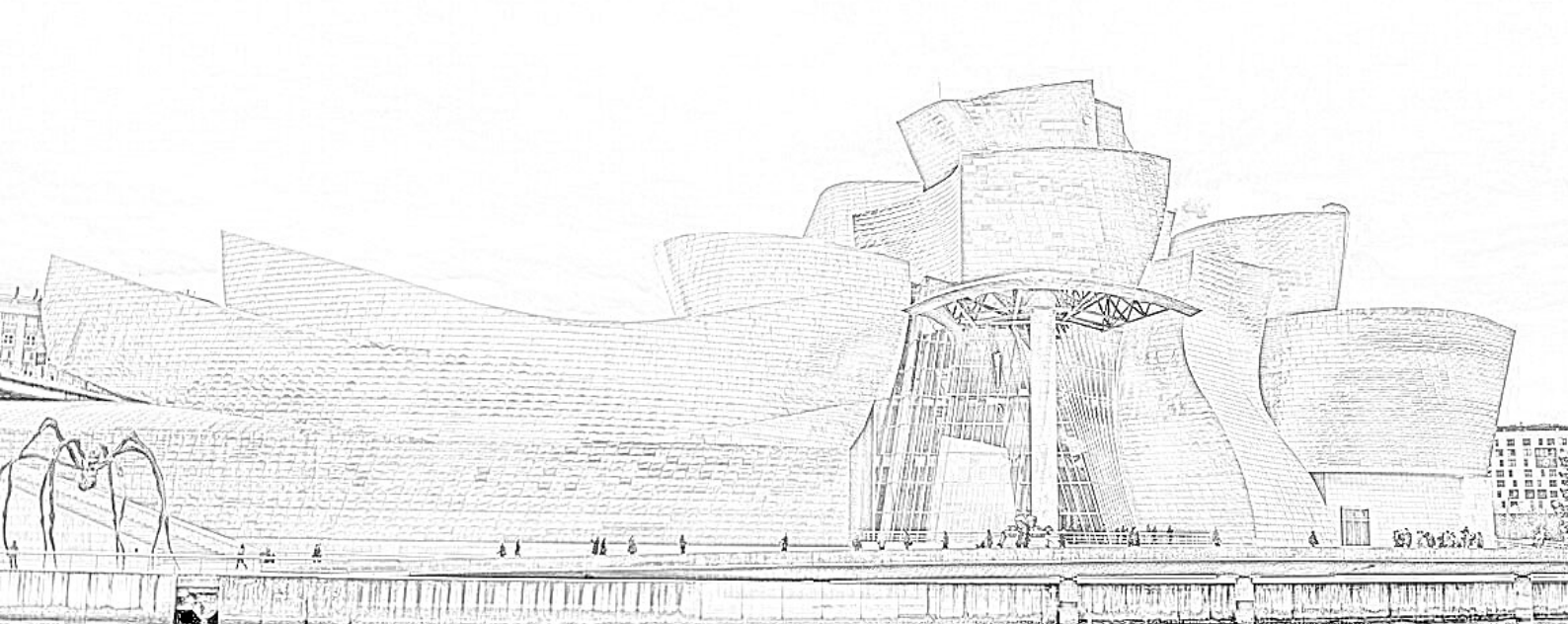
Bilbao, ciudad dinámica y reconocida por su apuesta por la innovación y la cultura, será el escenario ideal para este evento. Las actividades se desarrollarán en un entorno pensado para fomentar el diálogo, el aprendizaje y la conexión entre quienes formamos parte de esta comunidad científica.

El programa social está diseñado para complementar la experiencia académica, ofreciendo momentos de encuentro en un ambiente relajado y propicio para fortalecer vínculos, al tiempo que se disfruta de la riqueza cultural y gastronómica de la ciudad.

Desde el Comité Organizador, agradecemos al **Grupo Especializado de Polímeros (GEP)** su apoyo y confianza en este proyecto. Estamos trabajando con entusiasmo para que este congreso sea una experiencia enriquecedora para todas las personas participantes.

Quedamos a vuestra disposición para cualquier consulta o información adicional.

¡Nos vemos en Bilbao!

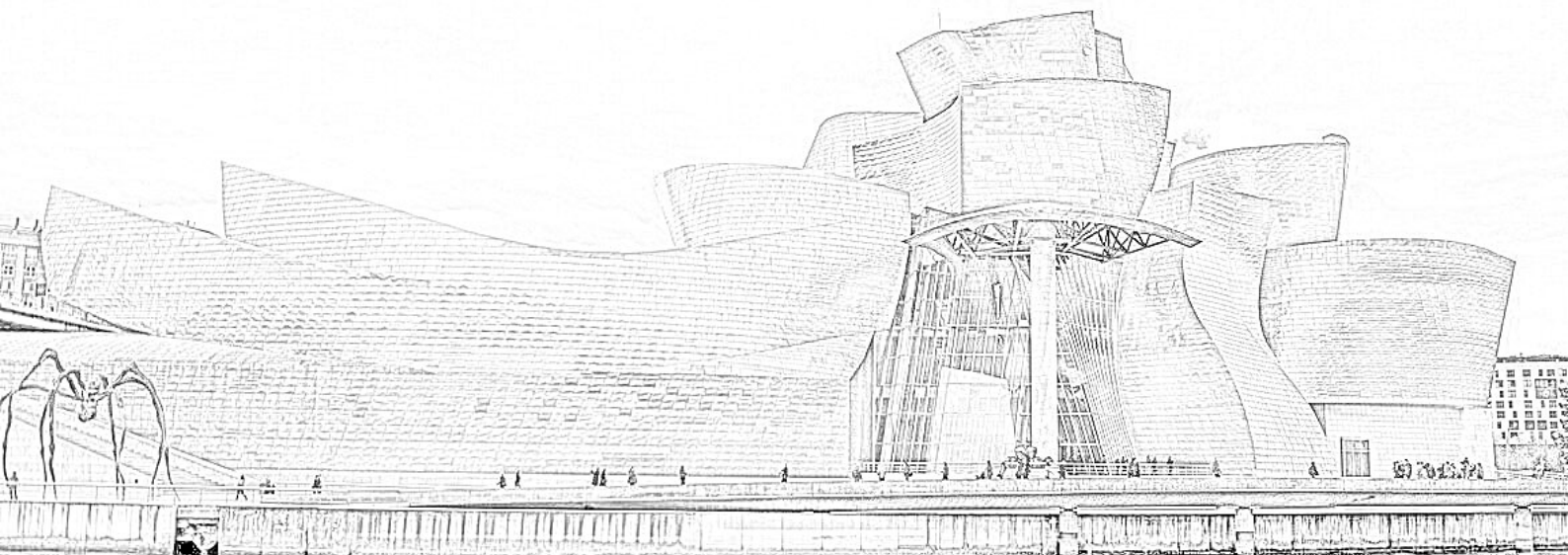


Comité organizador

- Estíbaliz Hernáez (UPV/EHU)
- Maria Isabel Moreno (UPV/EHU)
- Ana Catarina Lopes (UPV/EHU)
- Julia Sánchez (UPV/EHU)

Comité científico

- José Luis Vilas (UPV/EHU)
- Carmen Mijangos (ICTP-CSIC)
- David Mecerreyes (POLYMAT-UPV/EHU)
- Leyre Pérez (UPV/EHU)
- Jaime Martín (Universidad de A Coruña)
- Leire Ruiz Rubio (UPV/EHU)



Organiza



imacromat

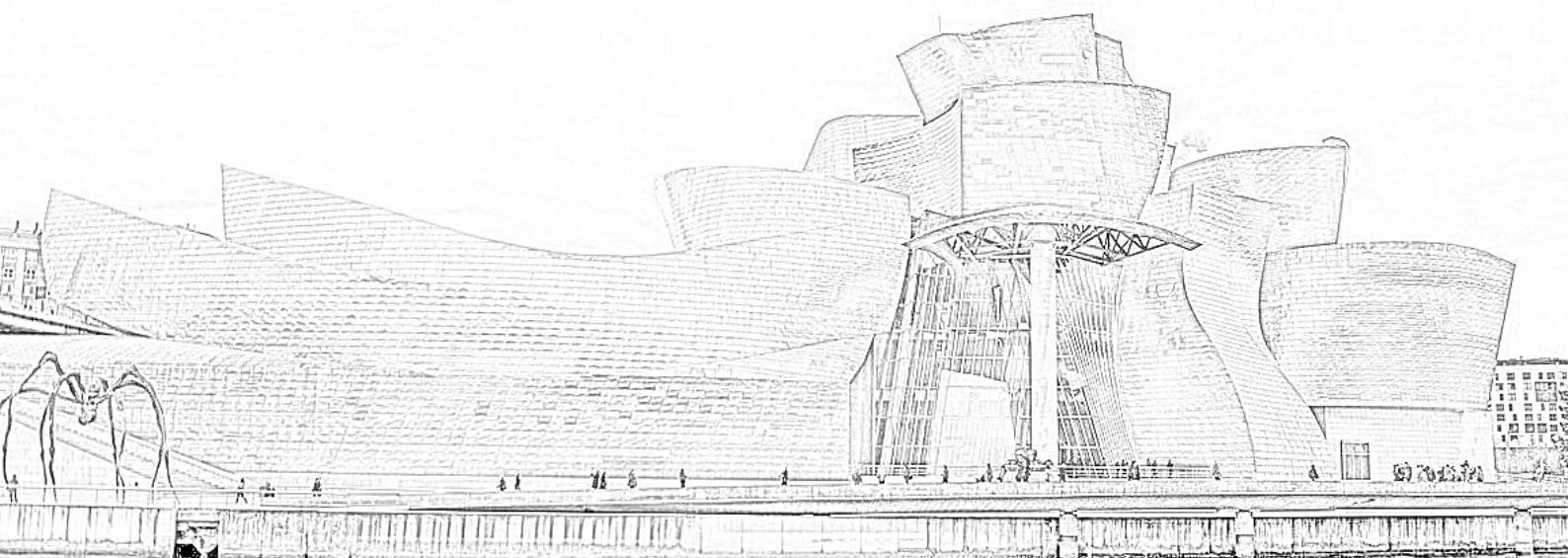
INNOVATIVE
MACROMOLECULAR
MATERIALS

eman ta zabal zazu



Universidad
del País Vasco

Euskal Herriko
Unibertsitatea



Sponsors

tecnal:a

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

T **Tekniker**

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

BOMATERIALS
BASQUE CENTER FOR MATERIALS, APPLICATIONS & NANOSTRUCTURES ehu group

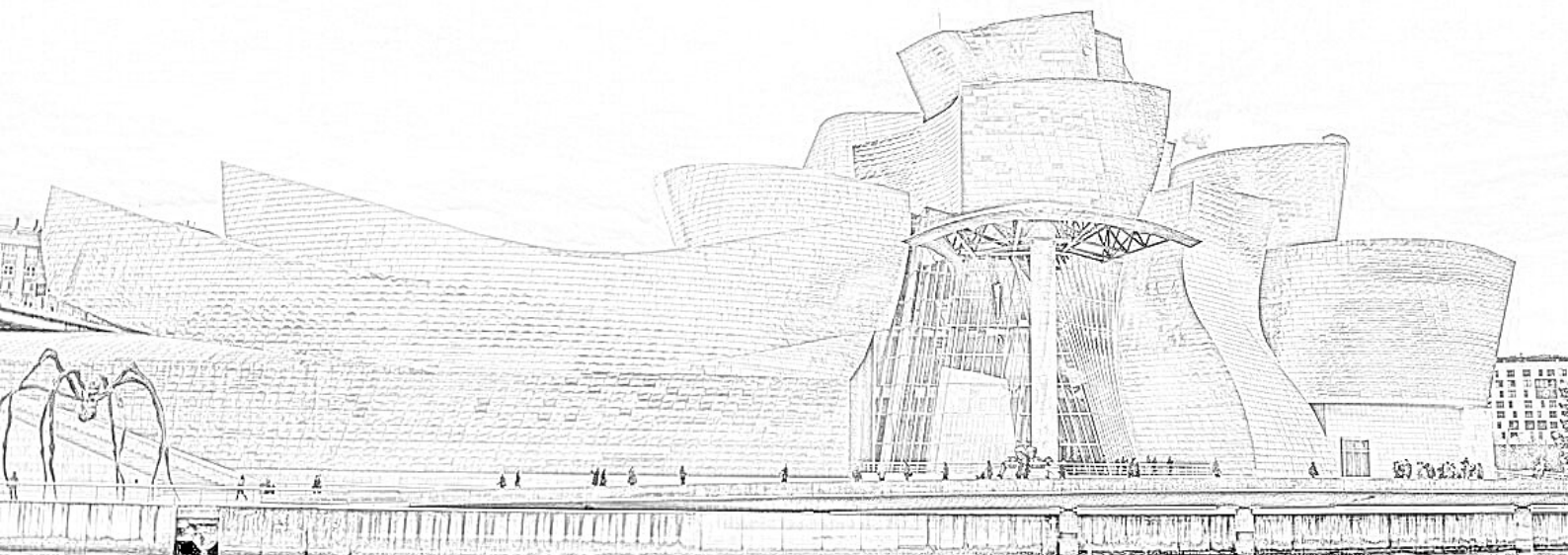
Leartiker

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

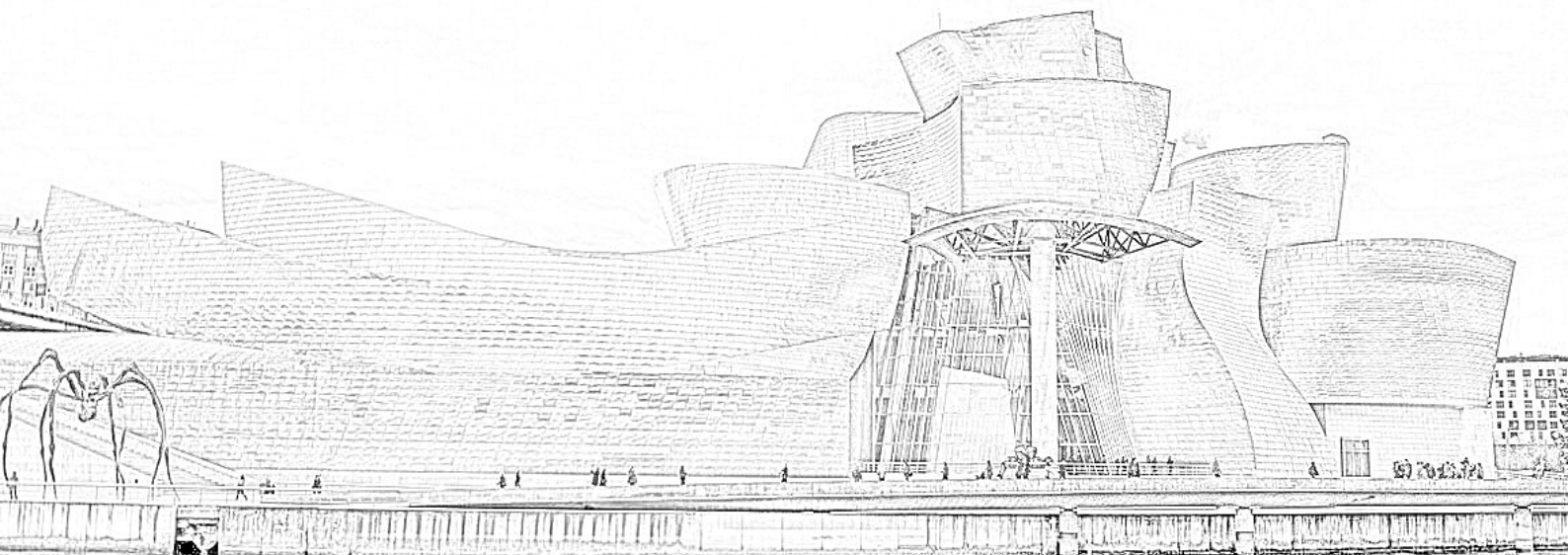
Bilbao  **Bizkaia**
foru aldundia
diputación foral



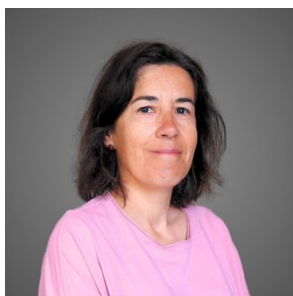
EUSKO JAURLARITZA
GOBIERNO VASCO



Inspira



Alexandra Muñoz Bonilla (ICTP-CSIC)



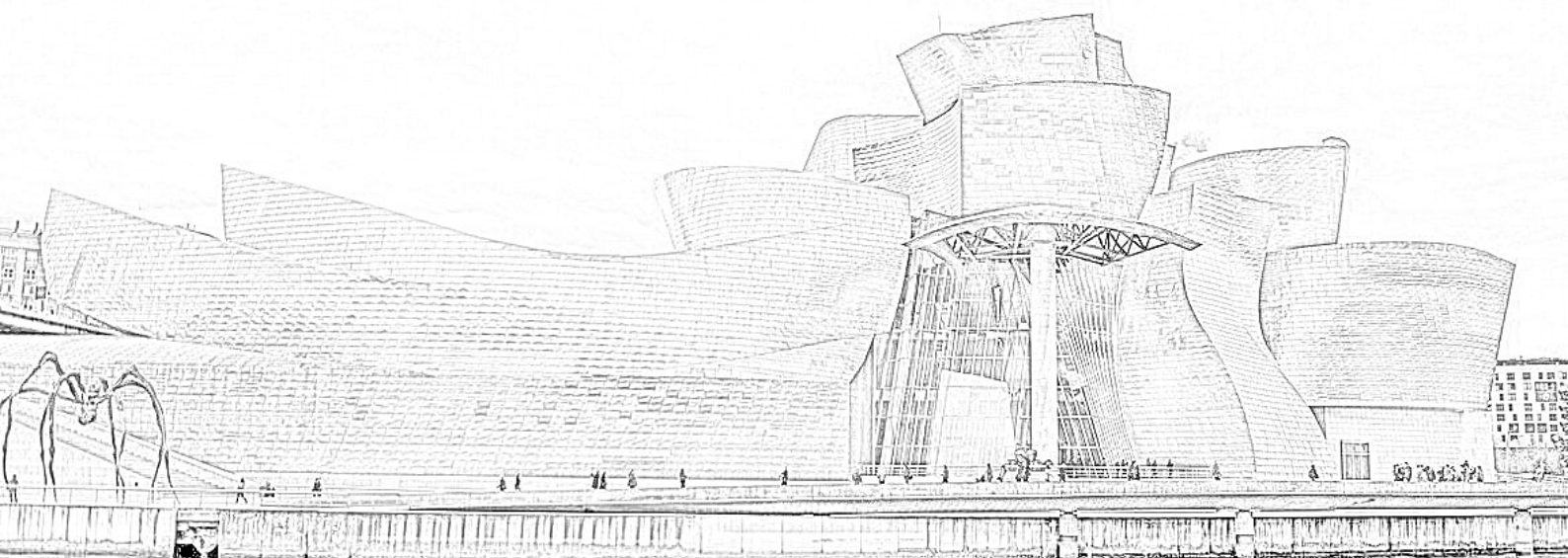
Investigadora Científica y Directora del Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC). Ha realizado estancias de investigación en prestigiosos centros internacionales y cuenta con más de 20 años de experiencia en Química de Polímeros y Ciencia de Materiales. Su investigación se centra en la síntesis de precisión de polímeros funcionales con especial énfasis en el desarrollo de polímeros bioactivos y biorresponsivos, glicopolímeros para reconocimiento biomolecular, polímeros antimicrobianos y materiales biohíbridos.

La síntesis de polímeros de precisión incluye la combinación de técnicas de polimerización controlada, metodologías ortogonales de química click, enfoques sintéticos eficientes y respetuosos con el medio ambiente y el uso de la química biomimética. Actualmente, sus principales líneas de investigación son el desarrollo de materiales antimicrobianos con alta actividad frente a un amplio espectro de microorganismos y sistemas poliméricos biodegradables y de base biológica. Es autora de 3 patentes y más de 140 artículos publicados, h-index: 34, 9 capítulos de libros y editora de dos libros. Ha liderado/participado en 43 proyectos de financiación competitiva y 9 contratos de investigación con la industria.

Mario Culebras Rubio (UV)



Obtuvo su doctorado en Química por la Universidad de Valencia en 2017. A lo largo de su carrera investigadora, ha liderado y contribuido a numerosos proyectos financiados a nivel nacional, europeo e industrial. Su experiencia incluye roles de liderazgo en cinco iniciativas nacionales de investigación (actuando como Investigador Principal en dos de ellas) y tres proyectos regionales financiados por la GVA (liderando uno como IP). También ha estado muy activo en iniciativas internacionales, participando en tres proyectos europeos (como Investigador Principal en uno), un proyecto nacional irlandés y cuatro colaboraciones financiadas por empresas. La investigación del Dr. Culebras ha impulsado significativamente el avance de materiales termoeléctricos orgánicos y la



valorización de la lignina, logrando mejoras en la eficiencia termoeléctrica de hasta 1000 veces respecto al estado del arte. Estos avances han dado lugar a publicaciones de alto impacto y a la obtención de patentes. Es autor de más de 90 artículos de investigación, que en conjunto han recibido más de 4.000 citas. Además, ha realizado estancias de investigación en instituciones de prestigio como la Universidad de Texas A&M, el Instituto Max Planck y la Universidad de Limerick, apoyado por becas competitivas.

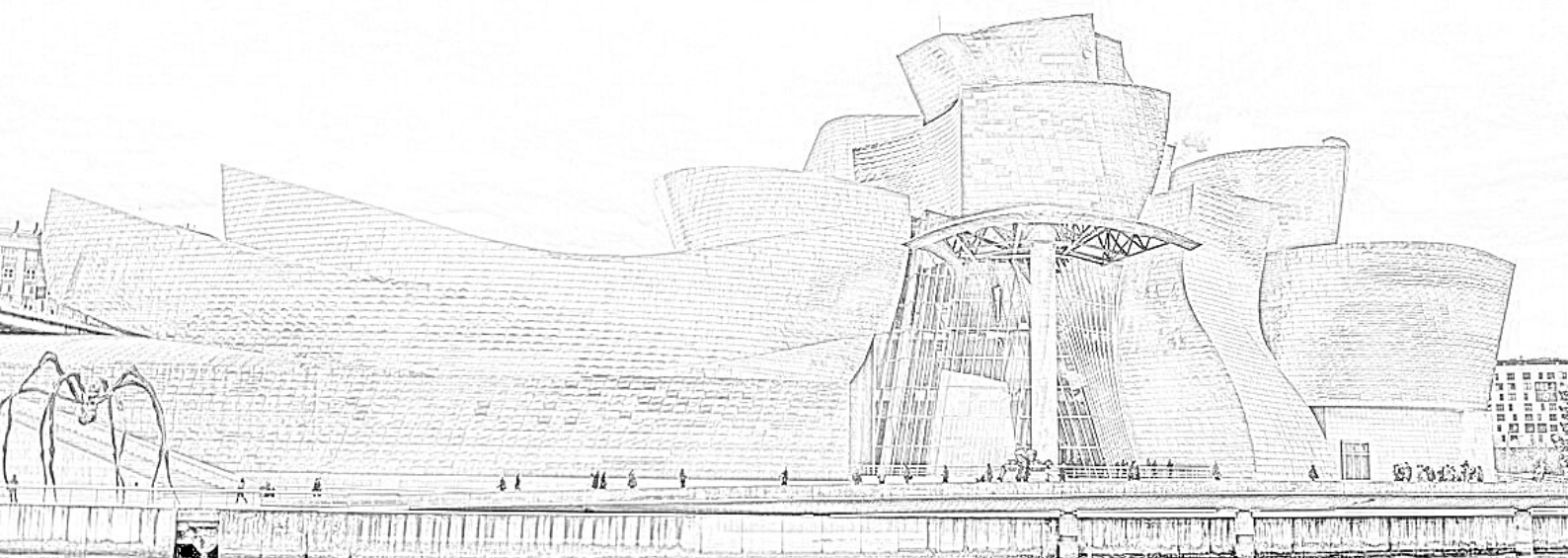
Reconocido con premios como el Premio Investigador Joven SUSCHEM-2020 y la Beca IRC GOI (2020), el Dr. Culebras ha asegurado múltiples patentes que respaldan proyectos financiados tanto a nivel nacional como europeo. Desde 2017, ha supervisado a cuatro doctores graduados, 20 estudiantes de trabajos de fin de grado y 18 estudiantes de máster, contando actualmente con ocho doctorandos. Muchos de sus tutelados han sido galardonados con premios prestigiosos. Además de sus contribuciones académicas, el Dr. Culebras ha trabajado como Consultor Tecnológico para empresas como Johnson & Johnson, trasladando los resultados de su investigación a aplicaciones industriales. Participa activamente en redes profesionales, colaborando como revisor de revistas científicas de alto nivel y como evaluador de propuestas de investigación para agencias de financiación en Europa y América Latina.

Marta Martínez (CIAL)



Científica titular en el Instituto de Investigación en Ciencias de la Alimentación (CIAL), un Instituto mixto del CSIC y la Universidad Autónoma de Madrid. En 2023 recibió el Premio Nacional de Investigación para Jóvenes en el área de ciencias y tecnologías de los recursos naturales.

Llevó a cabo su tesis doctoral en el Instituto de Agroquímica y Tecnología de Alimentos (IATA), especializándose en el desarrollo de materiales bio-basados con aplicación como envases alimentarios. Desarrolló su carrera postdoctoral en Australia, en ANSTO y la Universidad de Queensland, especializándose en el estudio de la estructura de paredes celulares vegetales utilizando técnicas avanzadas de “scattering” y difracción de neutrones y rayos-X, en combinación con técnicas de microscopía, espectroscopía y reología. Además, durante su carrera ha realizado estancias en centros



internacionales como KTH, Fraunhofer Institut, USDA, Chalmers University, RISE y la Universidad de Illinois.

En la actualidad, sus intereses científicos se enmarcan en el estudio estructural de distintas fuentes de biomasa, incluyendo residuos y fuentes de origen acuático, y su correlación con propiedades tecno-funcionales, para desarrollar estrategias encaminadas a una utilización más eficiente de los recursos naturales en alimentación.

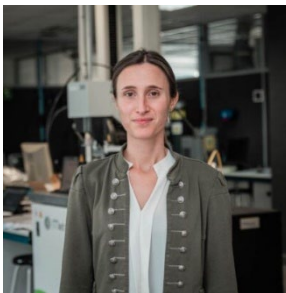
Haritz Sardon (UPV/EHU)



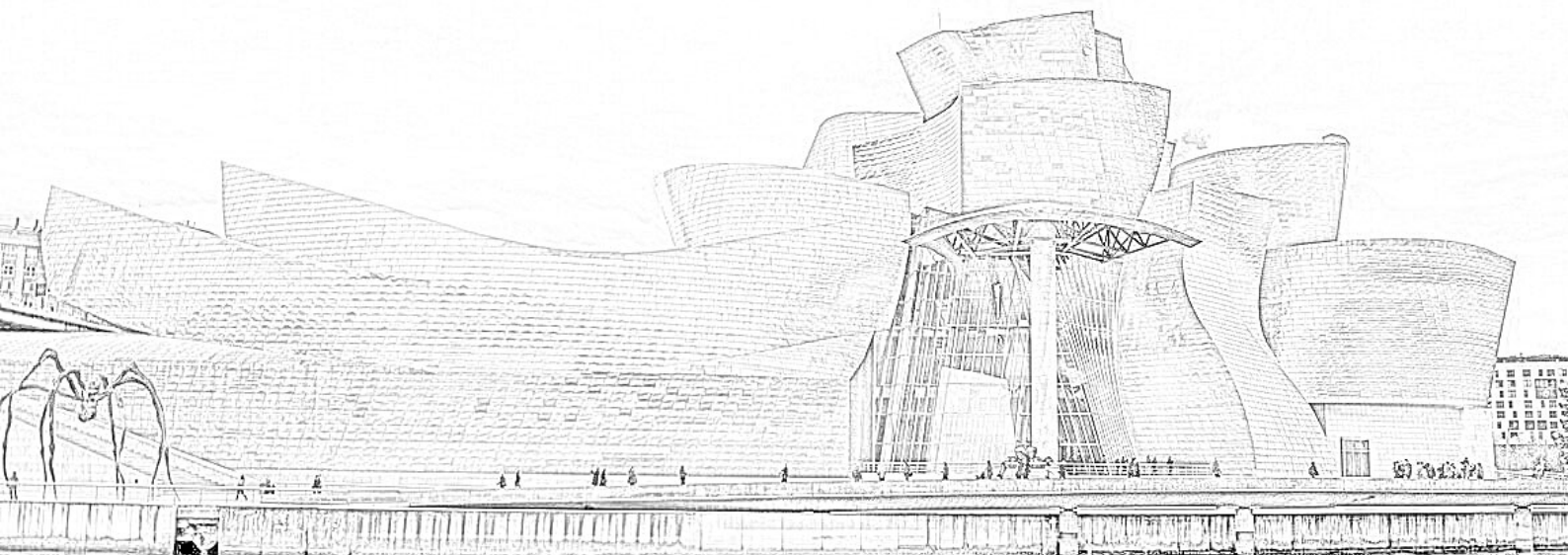
Profesor Titular en la Universidad del País Vasco (UPV/EHU) desde 2024 y lidera el grupo de Catálisis y Polímeros Sostenibles en POLYMAT. Obtuvo su Grado, Máster y Doctorado en la UPV/EHU, realizando parte de su tesis en el LCPO de Lyon. Tras una breve etapa en Histocell, realizó un postdoctorado en IBM, California, bajo la supervisión del Dr. Hedrick, centrado en organocatálisis para la polimerización. Regresó a POLYMAT con un contrato Juan de la Cierva y en 2016 fue nombrado Ikerbasque Fellow, incorporándose como profesor ayudante en la UPV/EHU en 2018.

El Dr. Sardon ha publicado más de 150 artículos científicos—120 en revistas Q1 y 70 como autor de correspondencia—con cerca de 10.000 citas y un índice h de 56 (enero de 2025). Su trabajo ha sido publicado en revistas de alto impacto como *Science*, *Nature*, *JACS* y *Angew Chem*. Ha recibido varios premios, entre ellos los de Excelencia de la RSC (2024), de la RSEQ y ACS (2021), el Premio GEP al Joven Investigador y la Beca Leonardo de la Fundación BBVA (2020). Ha impartido más de 60 conferencias invitadas y actualmente dirige a 15 doctorandos, habiendo supervisado 10 tesis hasta la fecha.

Aizeti Burgoa (Leartiker)



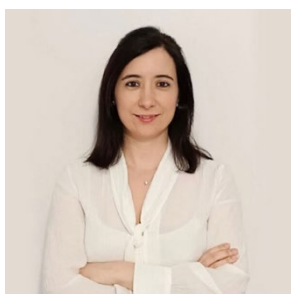
Investigadora en la especialización de Transporte Sostenible en Leartiker. Doctora en Ciencia y Tecnología de Materiales por la Universidad del País Vasco UPV/EHU en 2020. Anteriormente, realizó los grados de Física e Ingeniería Electrónica y el máster en Nuevos



Materiales en la Universidad del País Vasco. Durante los últimos años su labor investigadora se ha centrado en la caracterización, modelado y simulación de materiales y componentes elastoméricos, principalmente para el sector de la automoción.

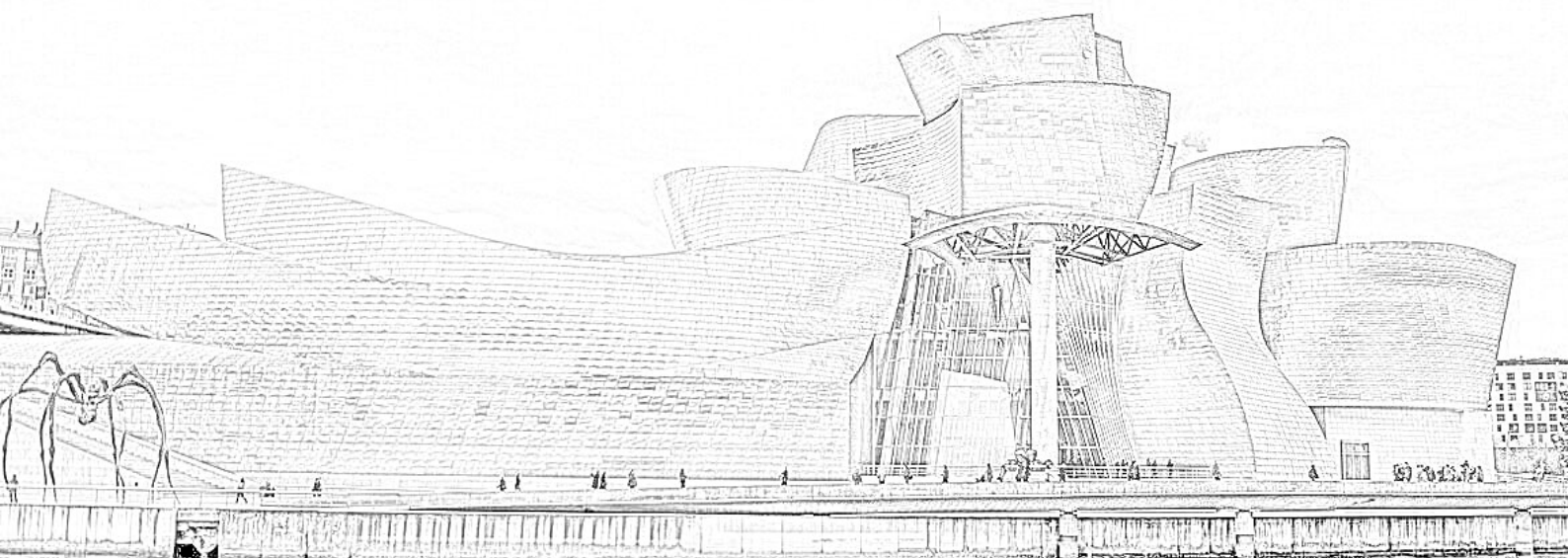
Actualmente en LEARTIKER, dirige y colabora en diversos proyectos de investigación y desarrollo a nivel nacional y europeo, además de participar en la creación de propuestas de proyectos. Asimismo, ha publicado diversos artículos científicos en revistas internacionales de referencia, y ha participado en congresos y jornadas tanto nacionales como internacionales.

Miryam Criado-González (ICTP-CSIC)

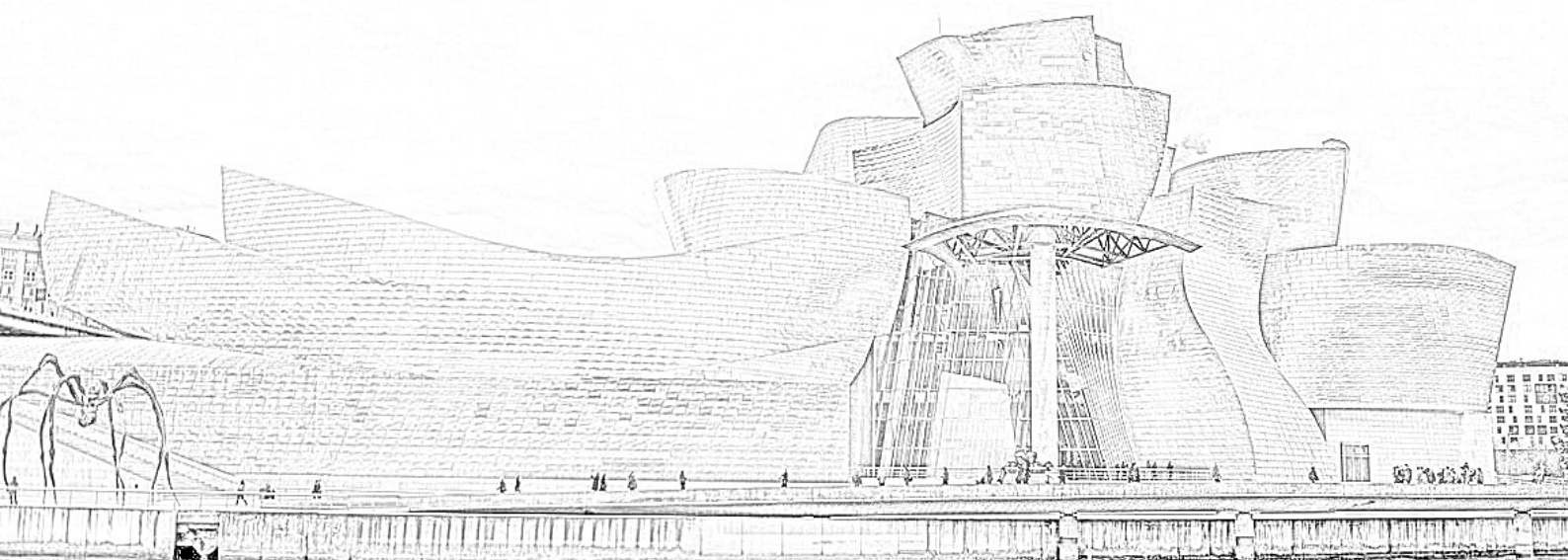


Obtuvo su Grado y Máster en Ingeniería Química por la Universidad de Salamanca, así como un Máster en Ciencia de Polímeros por el CSIC y la Universidad Internacional Menéndez Pelayo. Recibió una beca FPU para realizar su doctorado en el Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC, Madrid), obteniendo su título de doctora en 2017. Posteriormente, trabajó como investigadora postdoctoral en el Institut Charles Sadron (ICS-CNRS) y en el INSERM, además de

desempeñarse como profesora asistente en la Universidad de Estrasburgo (Francia). En 2021 se incorporó a POLYMAT-UPV/EHU (San Sebastián), convirtiéndose en investigadora independiente en 2022 gracias al proyecto Emakiker, y en 2023 fue nombrada coordinadora del área de investigación de Polímeros para Bioelectrónica. En 2024, fue galardonada con un contrato Ramón y Cajal y comenzó a trabajar como investigadora independiente en el ICTP-CSIC. Su investigación se centra en materiales inteligentes basados en polímeros y polipéptidos para aplicaciones biomédicas, incluyendo la síntesis de polímeros funcionales de origen biológico, estudios de autoensamblaje, desarrollo de geles inteligentes sostenibles y procesos de impresión 3D/4D con fines biomédicos. Es co-autora de más de 54 artículos en revistas de revisión por pares y una patente. Ha recibido múltiples reconocimientos: el Premio de Joven Investigadora de la E-MRS en 2021, el reconocimiento como Revisora Destacada de la revista *Nature Communications Materials* en 2025 y el *EPF Future Faculty and Researchers Award* en 2025.



Investiga



Contenido

L1-1 Development of biodegradable polylactic acid SLIMs via modified non- solvent induced phase inversion method	1
L1-2 Electro-Responsive Thermoplastics Obtained Applying Electro-Thermal Re-orientation and Charged Gas Activation to Dielectric Thermoplastics	2
L1-3 Thermal Stimulated Polarization: Conductivity-Enhancement Engineering for Thermoplastics Tailoring	3
L1-4 Multifunctional Polymer-Inorganic Nanoparticle Hybrid Tandems as Selective Metal Sensors	4
L 2-1 Fabrication and characterization of polymer optical fibers for solar concentrator application	5
L 2-2 Semisolid Polymer Gel Electrolytes for Aluminum Batteries	6
L 2-3 Enhanced Energy Harvesting Performance of Biodegradable Polylactic Acid/3D Anodic Aluminum Oxide Composite Triboelectric Nanogenerators	7
L 2-4 A Novel Polymeric non-aqueous Pickering Emulsion System for Thermal Energy Storage Applications	8
L 2-5 Supramolecular polysaccharide-based hydrogels for green energy storage	9
L 2-6 Efficient Supercapacitive CO₂ Capture Enabled by a Neutral, Water-Based Polymer Electrolyte	10
L 3-1 Blending of Polymers of Intrinsic Microporosity (PIMs) with Nanomaterials for use as CO₂ separation membranes	11
L 3-2 Innovative Polymers of Intrinsic Microporosity (PIMs) based on diazabenzotriptycene units for use as CO₂-ultrapermeable membranes	12
L 3-3 Ultrafast Crystallization Kinetics of Semiconductive Polymers by Fast Scanning Calorimetry	13
L 3-4 Poly(ether-imide-ester)s Incorporating Sulfur-Containing Amino Acids: A First Step Toward More Sustainable High-Dielectric Polymer Materials	14
L 3-5 New nucleophilic monomers for energy applications	15
L 3-6 Desarrollo de Mezclas de Polímeros Biodegradables para contribuir a una Agricultura Sostenible	16
L 3-7 Understanding organic photovoltaics-relevant blend structures in relation to the acceptor's chemical structure	17
L 3-8 Bio-based PEBA[®]X Hollow Fiber Membranes	18
L 4-1 Ionic Cross-linked Thiophene-based Copolymers for Application in Bioelectronics	19
L 4-2 Mixed Ionic Electronic Conducting Polymers Based on PEDOT:PSS and Protic Ionic Liquids	20
L 4-3 Mass transport study for microneedle biosensors	21
L 4-4 4D Printable Electroactive and Biodegradable PEDOT:κ-Carrageenan inks for (bio)electronics	22
L 4-5 Freeze-Thaw PVA Hydrogels with Crystallizable Alkyl Chains: Structure, Adhesion, and Thermal Response	23

L 4-6 Bio-Based PU Coatings Reinforced with Nanoparticles: Active Protection in Harsh Marine Environments	24
M 1-1 Development of Antimicrobial and Antioxidant PLA Fibers for Food Packaging Applications	25
M 1-2 Synthesis and degradation of Eugenol-derived Polyamides: Advancing Towards a Circular Economy.	26
M 1-3 Sustainable Bioplastics from Potato Peel Waste: A Circular Economy Approach Using Deep Eutectic Solvents.	27
M 1-4 PHAs en el Mediterráneo: un estudio integral desde su biodegradación hasta su biosíntesis	28
M 1-5 Development of a multilayer packaging system based on microbial polyesters and agri-food waste bioactives.	29
M 1-6 Biodegradable and Bio-Based Foams: Influence of Processing Techniques on Swelling Behavior in Various Aqueous Media	30
M 2-1 Recycled polyols as partial substitutes in elastomeric PU formulations: characterisation and evaluation of their performance	31
M 2-2 Vitrímeros poli(epoxi-amina) con propiedades personalizables para la preparación de CFRCs	32
M 2-3 Valorization of Lignocellulosic Forestry Derivatives into Functional Acrylic Polymers as Surfactants for Emulsion Polymerization	33
M 2-4 Incorporación de neumáticos al final de su vida útil en elastómeros termoplásticos y caracterización de los productos finales	34
M 2-5 Synthesis of polyurethanes from polyols derived from bacterially-sourced polyesters.	35
M 2-6 Reshape of EoL Polyester Glass Fibre Composites	36
M 3-1 Valorization of Lignin into Magnetic Biopolymer Nanoparticles for Catalytic Applications ...	37
M 3-2 Crystallization behavior of Poly(3-hydroxybutyrate) systems with ATBC plasticizer and mesoporous silica, neat or ATBC modified	38
M 3-3 Enhancing processability and properties of PLA/PBSA blends for packaging applications ...	39
M 3-4 Sustainable and Self-Healable Rubbers: A New Perspective in Materials Science	40
M 3-5 Designing Sustainable TPEs: From Bio-Based Inputs to Functional Performance	41
M 3-6 Pectin-Based Hydrogels for the Removal of Pharmaceutical Pollutants	42
M 4-1 Electrospinning of Cashew Gum/Polyvinyl Alcohol Blends. From Nanofibers to Flexible Thin Films with High Oxygen Barrier for Sustainable Food Packaging	43
M 4-2 Valorization of Marine Resources for the Development of Green Plastics: Sustainable Extraction and Formulation of Active and Edible Packaging	44
M 4-3 Biopolymer-Based Microgel Systems for Encapsulation of Nutrients and Microorganisms in Soil Remediation	45
M 4-4 Valorization of Polymeric and Agroforestry Residues and By-products (Biomass) for the Development of Materials Used in Sports Surfaces	46
M 4-5 Lignin Microcapsules for Controlled Release of Plant Protection Products	47
X 1-1 Controlling latex particle coagulation	48

X 1-2 Self-nucleation promotes the formation of the most stable crystal polymorph in triple polymorphic polythioethers	49
X 1-3 Biopoliésteres hiperramificados funcionalizados como aditivos sostenibles en formulaciones de PHA	50
X 1-4 Amphiphilic cyclic branched polyglycerols: synthesis and evaluation as drug carriers.....	51
X 1-5 Tribological performance of bio-based acrylic resin coatings on mild steel and their lubricated response.....	52
X 1-6 Polymerization of Ethylene Dioxythiophene (EDOT) with Customized Electrical Properties through an Atmospheric-Pressure Plasma-Jet	53
X 2-1 Quantitative characterization of reinforced rubber-silica elastomers by the combination of time-domain NMR and tensile test	54
X 2-2 Thermodynamic parameters of P3HT based on Flory´s relation	55
X 2-3 Methodologies for Safe-and-Sustainable-by-Design production of polyurethane foams	56
X 2-4 Solid-State Processing of P3HT: Effect of Temperature and Pressure on Polymer Film Formation	57
X 2-5 Discovering a new family of boron photocatalyst and photoinitiators	58
X 3-1 Development of Eco-Friendly Semisolid Lubricants: Impact of Silica/Clay, Biopolymer and Base Oil	59
X 3-2 Structure-property design in dynamic hydrogels for additive manufacturing	60
X 3-3 Diseño de Tintas Biomateriales Basadas en Hidrogeles Granulares Reticulados Químicamente para Impresión 3D	61
X 3-4 3D printing ternary blends of poly (butylene succinate), polylactide and poly (butylene adipate-co-terephthalate)	62
X 3-5 Carbon Nanotube Coatings Enabling the Conversion of Polyacrylonitrile Fibers into Carbon Fibers via Microwave Carbonization	63
X 3-6 Optimización del proceso de infusión VARI para laminados de fibra de carbono con resina termoplástica	64
X 4-1 Morphological Control of PBSA/PLA Microfibrillar Composites for packaging applications ..	65
X 4-2 Lignin, SCG and Ox-SCG influence on FDM printability and electrical conductivity of PLA/MWCNT composites for electronic devices	66
X 4-3 Lignin's Thermal Fingerprint: Guiding Sustainable 3D Printing through TGA-FTIR of Isolated and Acylated Variants.....	67
X 4-4 Improving the Anti-Corrosion Efficiency and Electrical Functionalization of Sustainable Bio-Epoxy Coatings from Epoxidized Soybean Oil and Tannic Acid with Carbonaceous Nanofillers.	68
X 4-5 Sustainable Biopolymer-Based Coatings for Corrosion and Fouling Protection in Offshore Structures.....	69
J 1-1 Sustainable polymers derived from itaconic acid for biomedical applications	70
J 1-2 Development and characterization of modified chitosan scaffolds for tissue engineering applications.....	71

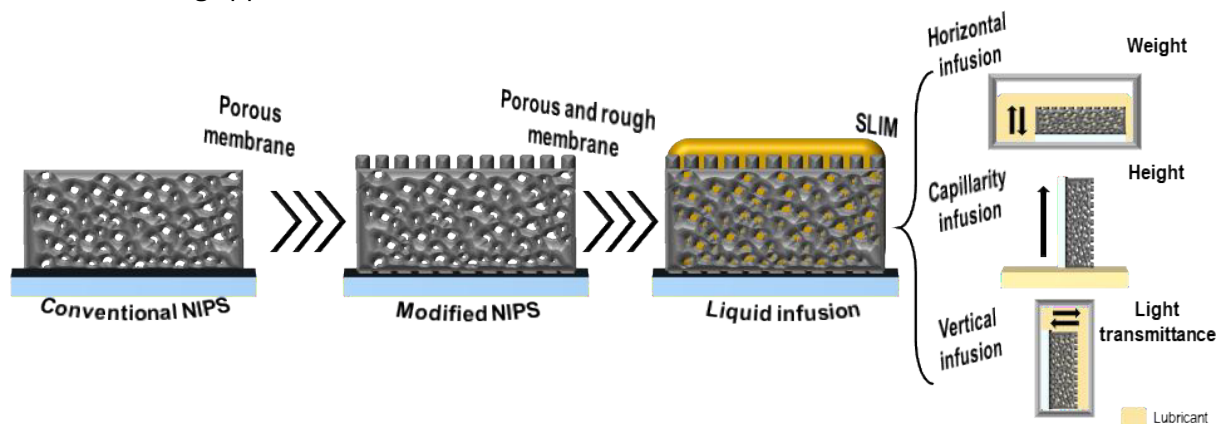
J 1-3 Encapsulación y liberación de proteínas a partir de hidrogeles covalentes dinámicos basados en iminoboronatos	72
J 1-4 Studying the viscoelastic properties of the human tear film: microrheology of complex polymer solutions.....	73
J 1-5 Polyelectrolytes for Fluorescence-Based Detection of Serum Protein Composition Changes in Liquid Biopsy Cancer Diagnostics.....	74
J 1-6 3D-Printable Gelatin-based Hydrogels with tunable mechanical and degradation behaviour for Tissue Engineering.....	75
J 2-1 Analysing the potential of laser femtosecond technology for the mass production of Cyclic Olefin Copolymer microfluidic devices for biomedical applications	76
J 2-2 Natural polysaccharide based hydrogels for cardiac tissue repair	77
J 2-3 Biofunctional PLLA <i>via</i> Amoxicillin Immobilization through Amino-yne Click Chemistry.....	78
J 2-4 3D Printing of Responsive Polymeric Bioinks for Bacterial Detection	79
J 2-5 Design of polysaccharide-based copolymers with potential biomedical applications.....	80

L1-1 Development of biodegradable polylactic acid SLIMs via modified non-solvent induced phase inversion method

C. Rodríguez Gómez^{1*}, M. Hernández-Rivas¹, A. Martínez-Gómez¹, P. Tiemblo¹, N. García¹.

¹Institute of Polymer Science and Technology, ICTP-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

Slippery Liquid-Infused Porous Surfaces (SLIPS) emerged in 2011 inspired by the structure of the digestive tube of the carnivorous plant *Nepenthes*. Unlike superhydrophobic surfaces, based on the lotus leaf, where there is a three-phase contact between solid, vapor, and liquid, SLIPS create a continuous liquid-liquid interface by impregnating rough and porous structures with a lubricant [1]. However, two-dimensional SLIPS surfaces face the drawback of lubricant loss over time, which reduces their long-term stability. To mitigate this issue, three-dimensional (3D) systems have been developed, retaining the lubricant within the internal structure as a reservoir. In this context, membrane technology has explored the functionalization of porous membranes with liquids trapped within their structure, called Slippery Liquid-Infused Membranes (SLIMs) [2]. This study aims to develop polylactic acid (PLA) SLIMs using green solvents. Firstly, phase inversion methods (NIPS) were employed to obtain the materials, followed by the thermal stability and crystallization analysis using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Then, structural stability was seen using scanning electron microscopy (SEM). After that, the materials were infused with several lubricants: some of them naturally produced, while others synthetic. The infusion kinetics were studied through capillarity, ultraviolet-visible light transmission, and the gravimetric method, obtaining the diffusion coefficients for each of the liquids in the material measuring different properties (weight, height or light transmittance). Wettability, transparency and lubricant depletion of the infused membranes were investigated by contact angle measurements and profilometer images. Finally, small-scale tests were conducted for anti-icing applications.



Keywords: Porosity, roughness, SLIMs, lubricants, capillarity.

Acknowledgments

The authors would like to thank to the Spanish Ministry of Science, Innovation and Universities for funding Project PoEMA (PID2022-143310OB-I00) and to EU H2020 R&I programme under G.A N° 958174 (M-ERA.Net-3 Call2021) for funding SuSaNa project

References

- [1] J. Li, E. Ueda, D. Paulssen, and P. A. Levkin, "Slippery Lubricant-Infused Surfaces: Properties and Emerging Applications," *Adv Funct Mater*, vol. 29, no. 4, Jan. 2019.
- [2] H. Bazyar, P. Lv, J. A. Wood, S. Porada, D. Lohse, and R. G. H. Lammertink, "Liquid-liquid displacement in slippery liquid-infused membranes (SLIMs)," *Soft Matter*, vol. 14, no. 10, pp. 1780–1788, 2018.

L1-2 Electro-Responsive Thermoplastics Obtained Applying Electro-Thermal Re-orientation and Charged Gas Activation to Dielectric Thermoplastics

M. Gul¹, A. Fontana-Escartín^{1,2}, M. Arnau^{1,2}, J. Sans^{1,2}, S. Lanzalaco^{1,2}, E. Armelin^{1,2}, E. Chiesa³, I. Genta³, M. M. Pérez-Madrigal^{1,2} and C. Alemán^{1,2*}

¹IMEM-BRT Group, Departament d'Enginyeria Química, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain

²Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, 08930 Barcelona, Spain

³Department of Drug Sciences, University of Pavia, V.le Taramelli, 12, 27100 Pavia (PV), Italy

The transition from insulator to electro-responsive materials has been achieved for certain inorganic [1]. and polymeric substances [2] using external stimuli or chemical modifications. Here, we introduce a novel approach to transform insulating 3D-printed polymers into electro-responsive materials through two sequential processes: electro-thermal (ET) re-orientation and charged gas activation (CA), as displayed on **Figure 1**.

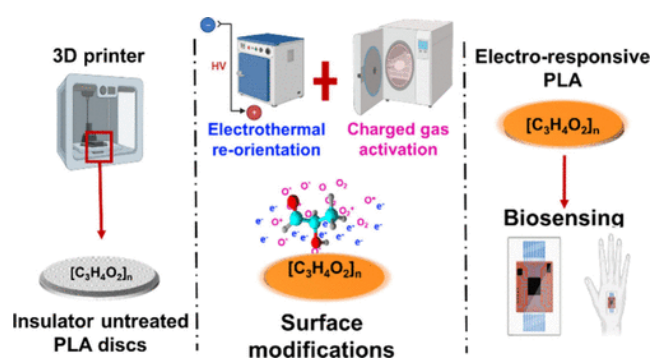


Figure 1. Procedures used to prepare Electro-responsive PLA discs.

This method, initially developed for poly(lactic acid) (PLA), enhances crystallinity via ET and modifies surface properties through CA, as confirmed by Raman spectroscopy, X-ray analyses, and microscopy. Cyclic voltammetry revealed that treated PLA becomes electro-responsive and electrocatalytic, enabling its use as a sensor for dopamine detection. The approach has also been extended to polypropylene (PP) and polyethylene terephthalate glycol (PETG), demonstrating broader applicability for thermoplastics.

Keywords: Electroresponsive polymers; Plasma treatment; Thermoelectric treatment; Thermoplastic polymers; Electrochemical sensors; 3D printing

Acknowledgments

This work received funding from the European Union under the Marie Skłodowska-Curie grant agreement No. 101072645. IMEM-BRT group is thanked to the Agència de Gestió d'Ajuts Universitaris i de Recerca (2021 SGR 00387) for financial support. The Barcelona Research Center in Multiscale Science and Engineering is supported by CEX2023-001300-M.

References

- [1] M Sans, J.; Arnau, M.; Estrany, F.; Turon, P.; Alemán, C. Regulating the Superficial Vacancies and OH⁻ Orientations on Polarized Hydroxyapatite Electrocatalysts. *Adv. Mater. Interfaces* 2021, 8, 2100163.
- [2] Fontana-Escartín, A.; Lanzalaco, S.; Bertran, O.; Alemán, C. Electrochemical Multi-Sensors Obtained by Applying an Electric Discharge Treatment to 3D-Printed Poly(lactic acid). *Appl. Surf. Sci.* 2022, 597, 153623.

L1-3 Thermal Stimulated Polarization: Conductivity-Enhancement Engineering for Thermoplastics Tailoring

J. Sans^{1,2*}, M. Arnau^{1,2}, A. Fontana-Escartín^{1,2}, and C. Alemán^{1,2*}

¹IMEM-BRT Group, Departament d'Enginyeria Química, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain

²Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, C/Eduard Maristany, 10-14, 08019 Barcelona, Spain

Tailoring polymeric materials electrical properties has become the cornerstone for next-generation smart systems development. In this work, the Thermal Stimulated Polarization (TSP) treatment, a process involving the application of a constant electric field at elevated temperatures to induce permanent dipole alignment and lattice refinement, is extended to synthetic polymers. Although TSP has previously been applied to ceramics and inorganic oxides,[1,2] herein we report its first application to polymeric systems. The treatment offers a novel pathway for permanently enhancing thermoplastics conductivity without employing chemical modification routes, being a greener and environmental-friendly alternative approach.

For that, polyethylene terephthalate glycol (PETG) and polylactic acid (PLA) were subjected to TSP treatment near their respective glass transition temperatures, resulting in significant improvement regarding their electrochemical performance. Cyclic voltammetry measurements indicated an increase in current density of up to 4000% compared to untreated controls, while Raman spectroscopy revealed subtle distinct structural reorganizations consistent with the formation of stable polarized superstructures. The results presented demonstrate that TSP is an effective and scalable approach for customizing electrical properties in synthetic polymers, providing new opportunities for the design of smart materials for applications in flexible electronics, sensing platforms, biomedical devices, and energy storage systems.

Keywords: Polarization, Advanced Materials, Electroresponsive polymers, Thermoplastic polymers, Conductivity, Electrical Properties.

Acknowledgments

This work is supported by the predoctoral program AGAUR-FI ajuts (2023 FI-100056) Joan Oró, which is backed by the Secretariat of Universities and Research of the Department of Research and Universities of the Generalitat of Catalonia, as well as the European Social Plus Fund. Authors acknowledge the Agència de Gestió d'Ajuts Universitaris i de Recerca (2021 SGR 003879). This work is part of Maria de Maeztu Units of Excellence Programme CEX2023-001300-M / funded by MCIN/AEI / 10.13039/501100011033 and Agencia Estatal De Investigación for supporting the project SeC-PLA, PDC2023-145834-I00. Support for the research of C.Alemán was also received through the prize "ICREA Academia" for excellence in research funded by the Generalitat de Catalunya.

References

- [1] Sans, J.; Arnau, M.; Turon, P.; Alemán, C. Permanently Polarized Hydroxyapatite, an Outstanding Catalytic Material for Carbon and Nitrogen Fixation. *Materials Horizons*, **2022**, 9, 1566–1576.
- [2] Arnau, M.; Teixidó, I.; Sans, J.; Turon, P.; Alemán, C. Thermoelectrically Polarized Amorphous Silica Promotes Sustainable Carbon Dioxide Conversion into Valuable Chemical Products. *Sustainable Energy & Fuels*, **2024**, 8, 5937–5949.

L1-4 Multifunctional Polymer-Inorganic Nanoparticle Hybrid Tandems as Selective Metal Sensors

T. Plaza-Santos*, I. Quijada and O. García

Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), Madrid, España.

Multifunctional polymers are materials that combine multiple properties within a single structure, offering significant improvements in properties such as mechanical strength, electrical conductivity, biocompatibility, and responsiveness to external stimuli (such as temperature, light, or pH).[1,2] In particular, multi-catechol polymers have gained significant attention for their unique adhesive properties and ability to interact strongly with both organic and inorganic surfaces. In the fields of Nanotechnology and Composite Materials, catechols are used to functionalize nanoparticles, improving their dispersion and adhesion within polymer matrices, or enhancing the mechanical and adhesive properties of composites.[3] Environmentally, they are utilized for the adsorption, decomposition, and removal of heavy metals, organic compounds, and other contaminants from water owing to their high affinity and adsorption capacity.[4] Dopamine methacrylamide (DMA)-derived polymers combine the adhesive properties of dopamine due to its catechol group with the versatility of methacrylate, allowing the development of smart materials that change their properties in response to external stimuli. Furthermore, they have been used for stabilizing metallic nanoparticles (such as gold, silver, and platinum), preventing their aggregation and improving their dispersion in aqueous and organic media. The presence of catechol groups can control the growth and nucleation of nanoparticles, allowing the synthesis of particles with specific sizes and shapes. [5]

This work focuses on the synthesis and characterization of new multifunctional smart nanostructured copolymers containing catechol groups via light-initiated RAFT polymerization. Furthermore, we have used Polymerization-Induced Self-Assembly (PISA) technique to fabricate polymer nano-objects. These versatile nanopolymers serve then as templates for the functionalization and stabilization of luminescent Ag and Cu nanoclusters. The luminescent properties of nanohybrids synthesized using block copolymeric nano-objects obtained via PISA exhibit significant differences compared to those synthesized with statistical copolymers with the same functionality. Finally, we have explored their potential for sensing applications for the detection of heavy metal ions in aqueous media. This detection is facilitated by fluorescence quenching (switch-off) or the opposite effect (switch-on) when NCs are in the presence of specific metal ions.

Keywords: multifunctional polymers, smart polymeric nano-objects, nanohybrid system, metal ion sensors.

References:

- [1] Fattah-alhosseini, A.; Chaharmahali, R.; Alizad, S.; Kaseem, M.; Dikici, B. A review of smart polymeric materials: Recent developments and prospects for medicine applications. *Hybrid Adv.* **2024**, *5*, 100178.
- [2] Lang, F.; Pang, J.; Bu, X.-H. Stimuli-responsive coordination polymers toward next-generation smart materials and devices. *eScience* **2024**, *4* (3), 100231.
- [3] Ball, V. Polydopamine nanomaterials: Recent advances in synthesis methods and applications. *Front. Bioeng. Biotechnol.* **2018**, *6*, 109.
- [4] Al-Hazmi, H. E.; Łuczak, J.; Habibzadeh, S.; Hasanin, M. S.; et al. Polysaccharide nanocomposites in wastewater treatment: A review. *Chemosphere* **2024**, *347*, 140578.
- [5] Zhang, Q.; Nurumbetov, G.; Simula, A.; Zhu, C.; Li, M.; Wilson, P.; et al. Synthesis of well-defined catechol polymers for surface functionalization of magnetic nanoparticles. *Polym. Chem.* **2016**, *7* (45), 7002–7010.

L 2-1 Fabrication and characterization of polymer optical fibers for solar concentrator application

M. Guadaño-Sánchez¹, N. Guarrotxena¹, M. A. Illarramendi², J. Zubia³

¹*Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (ICTP-CSIC), Juan de la Cierva 3, 28006., Madrid, España*

²*Física Aplicada I, Escuela Ingeniería Bilbao, Universidad del País Vasco, Plaza Ingeniero Torres Quevedo 1, 48013., Bilbao, España*

³*Ingeniería de Comunicaciones, Escuela Ingeniería Bilbao, Universidad del País Vasco, Plaza Ingeniero Torres Quevedo 1, 48013., Bilbao, España*

The increase global energy demand, the scarcity of fossil fuels and the need to reduce the global warming and emission make necessary to find renewable energy resources. Luminescent solar concentrators (LCS)-based polymer optical fibers (POFs) appear to be a suitable alternative, since sunlight can be efficiently concentrated in small areas and re-emitted at the end of fibers wherein photovoltaic cells are strategically placed.[1] POFs are flexible and can be easily integrated into various structures, making them versatile for different applications. POFs were self-fabricated following two-step process of preform synthesizing and fiber drawing, using methacrylate-based polymers and copolymers as dispersing host material for the luminescent perylene-derivatives dyes (violet, yellow, orange, and red) or fluorescent nanoparticles.[2]

Along this talk, I will discuss the two different approaches to obtain polymeric preforms: extrusion and bulk free-radical polymerization (from now on named casting). To determine the best method to synthesize preforms, a comparative analysis of the optical properties, as LSCs, of dye-doped POFs will be performed. The studied parameters will be absorption and emission, power intensity, attenuation, photostability and thermal stability. From all this it is possible to conclude that casting fibers offer the highest optical values, and the best results, in terms of type of dye, correspond to the fibers doped with lumogen red. The data also reveals that the casting fibers can be used as temperature sensor to monitor the surrounding medium temperature. Finally, to increase the sunlight-collecting capacity of the casting POFs, a new core – cladding fiber structure and different types of fluorescent nanoparticles as novel dopants will be considered.

Keywords: polymer preform, polymer optical fibers, dyes, extrusion, casting.

Acknowledgments

Authors acknowledge MCIN/AEI/10.13039/501100011033 and the European Union “NextGenerationEU”/PRTR» grant TED2021-129959B-C22.

References

[1] Clark, J., Lanzani, G. Organic Photonics for Communications. *Nat. Photonics*, **2010**, 4, 438.

[2] Arrue, J., Jiménez, F., Ayesta, I, Illarramendi, M.A., Zubia, J. Polymer-Optical-Fiber Lasers and Amplifiers Doped with Inorganic Dyes. *Polymers* **2011**,3, 1162.

L 2-2 Semisolid Polymer Gel Electrolytes for Aluminum Batteries

Á.Campo¹, A. Kunverji², K. Ryder², G. Ellis¹, N. García¹, P. Tiemblo¹

¹ *Institute of Polymer Science and Technology, ICTP-CSIC, Juan de la Cierva 3, Madrid, Spain*

² *Centre for Sustainable Materials Processing, School of Chemistry, University of Leicester, Leicester, , UK*

The demand for advanced energy storage systems is experiencing a huge growth driven by the increasing use of portable electronics, electric vehicles, and renewable energy technologies. Moreover, the next generation of batteries requires significant changes, as the current state-of-the-art lithium-ion batteries (LIBs) are to become a bottleneck due to the low abundance of lithium. Consequently, there is a need for new batteries based on accessible raw materials like sodium, aluminum, zinc, and others.

Aluminum-based batteries are promising due to aluminum's abundance, low cost, and high theoretical energy density. However, developing suitable electrolytes remains a key challenge, demanding the elimination of toxic or corrosive liquid leaks, metal dendrite growth, and subsequent short-circuits. While the adoption of all-solid electrolytes can overcome safety issues, their ionic conductivity is significantly lower than that of liquid electrolytes.

Polymer gel electrolytes offer a promising solution, maintaining high ionic conductivity while improving mechanical stability and safety. However, chloroaluminate systems introduce additional challenges. Almost a decade ago it was shown that the $Al_2Cl_7^-$ anion reacts with Lewis bases, such as common solvents or polymers employed in the battery fields, generating $AlCl_4^-$, which is electrochemically inactive [1].

This work explores the effect of UHMW poly(ethylene oxide) (PEO) concentration on the electrochemical properties and rheology of gel electrolytes prepared with EMIC- $AlCl_3$ (1:1.5) ionic liquid and PEO at varying concentrations (2–10 wt.%). The preparation method is fast, simple and sustainable (does not require auxiliary solvents) [2]. The effect on electroactive species and gel rheology was studied using Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and nuclear magnetic resonance (NMR).

Keywords: polymer gel electrolytes; ionic speciation; polyethylene oxide; aluminium battery

Acknowledgments

The authors would like to thanks to financial support from CSIC Project PIE 202360E035.

References

- [1] X.G. Sun, Y. Fang, X. Jiang, K. Yoshii, T. Tsuda, S. Dai. Polymer gel electrolytes for application in aluminum deposition and rechargeable aluminum ion batteries. *Chem. Commun.* 2016, 52(2), 292-295.
- [2] Á. Miguel, N. García, V. Gregorio, A. López-Cudero, P. Tiemblo. Tough polymer gel electrolytes for aluminum secondary batteries based on urea: $AlCl_3$, prepared by a new solvent-free and scalable procedure. *Polymers*, 2020, 12(6).

L 2-3 Enhanced Energy Harvesting Performance of Biodegradable Polylactic Acid/3D Anodic Aluminum Oxide Composite Triboelectric Nanogenerators

Carlos G. Cobos¹, Mariana Ramos², Ana Carolina Silva¹, Cátia Rodrigues², João Ventura², André Pereira², Marisol Martín-González¹

¹ Instituto de Micro y Nanotecnología IMN-CNM CSIC, Tres Cantos, Spain

² IFIMUP and Faculty of Sciences of the University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

Modern electronics, which are essential for human health, safety, and communication, provide a wide array of opportunities to evolve our society into an intelligent world. However, with the rapid growth of the Internet of Things (IoT), the energy supply for electronics and sensors has become a critical challenge [1]. Triboelectric nanogenerators (TENGs) have been developed as a key technology for mechanical energy harvesting, but further improvements in their triboelectric properties are still necessary to meet the demands of practical and functional devices. [2].

Three-dimensional anodized aluminum oxide (3D-AAO) features hexagonal column-shaped cells with cylindrical central holes of varying diameters and transversal channels. Due to this structure, it can be used as a template for nanostructuring processes. This nanostructuring method offers several advantages over lithography-based techniques, such as cost-effectiveness, broad accessibility, and the ability to fabricate with nanoscale precision from the top down. [3,4].

Polylactic acid (PLA), one of the most promising biopolymers due to its non-toxicity, and excellent mechanical properties, has found industrial and medical applications thanks to its wide range of properties, from amorphous to crystalline states. [5].

This study investigates the potential of TENGs for efficient mechanical energy harvesting through contact-separation triboelectrification and electrostatic induction. Nanoengineered PLA films with controlled nanostructuring, enabled by the use of 3D-AAO, are utilized in a simple, fast, controllable, and cost-effective process. The influence of 3D nanocavities within PLA films on triboelectric power generation is examined, revealing a correlation with the triboelectric charge density and the polymer's relative permittivity.

Keywords: Triboelectric nanogenerators (TENG), Polylactic acid (PLA), Three-dimensional anodized aluminum oxide (3D-AAO).

Acknowledgments

Financial support by the ERC Advanced Grant POWERbyU (ERC-2021-ADG-101052603) are acknowledged.

References

- [1] J. Tian, X. Chen, Z.L. Wang, Environmental energy harvesting based on triboelectric nanogenerators, *Nanotechnology* 31 (2020).
- [2] Y. Liu, X. Wang, Y. Yan, Z. Rao, H. Chen, T. Guo, A novel post-processed surface modified double-network polymer layer for a triboelectric nanogenerator, *J Mater Chem A Mater* 8 (2020) 6328–6336.
- [3] J. Martín, C. V. Manzano, O. Caballero-Calero, M. Martín-González, High-aspect-ratio and highly ordered 15-nm porous alumina templates, *ACS Appl Mater Interfaces* 5 (2013) 72–79.
- [4] J. Martín, C. V. Manzano, M. Martín-González, In-depth study of self-ordered porous alumina in the 140-400 nm pore diameter range, *Microporous and Mesoporous Materials* 151 (2012) 311–316.
- [5] R. Nandhini, B. Sivaprakash, N. Rajamohan, D.V.N. Vo, Lignin and polylactic acid for the production of bioplastics and valuable chemicals, *Environ Chem Lett* 21 (2023) 403–427.

L 2-4 A Novel Polymeric non-aqueous Pickering Emulsion System for Thermal Energy Storage Applications

S. Sanabria, C. Delgado-Sánchez, F.J. Navarro

Pro2TecS-Chemical Process and Product Technology Research Center, Department of Chemical Engineering, Physical Chemistry and Material Sciences ETSI, Universidad de Huelva Campus El Carmen 21071 Huelva (Spain)

Global concerns about environmental sustainability, rising energy demands, and the need to reduce greenhouse gas emissions have driven the development of cleaner energy technologies. However, the intermittent nature of renewable energy sources such as solar and wind presents challenges in ensuring a stable and reliable energy supply. Thermal energy storage (TES) systems, which store excess thermal energy for later use, have emerged as a key technology to address these challenges and enhance energy efficiency and grid stability in applications such as solar thermal plants, district heating, and industrial waste heat recovery. [1]

Among TES technologies, phase change materials (PCMs) are particularly promising due to their ability to store and release significant amounts of energy through phase transitions. Nevertheless, their practical implementation is often hindered by limitations related to processability, stability, and compatibility with heat transfer systems. To overcome these challenges, phase change material emulsions (PCMEs) have been proposed. These systems consist of PCM droplets dispersed within an immiscible heat transfer fluid and are stabilized by emulsifying agents to prevent coalescence and phase separation. However, selecting a suitable heat transfer fluid remains a challenge, as it must possess specific properties such as chemical and thermal stability, immiscibility with the PCM, and high thermal conductivity. Polymers have been widely used as heat transfer fluids, as many exhibit the required properties[2].

Pickering emulsions—stabilized by solid particles instead of surfactants—offer enhanced thermal and long-term stability. This method may reduce degradation during thermal cycling and eliminate issues such as emulsifier oxidation [3]. This study investigates a novel oil-in-oil Pickering emulsion for TES, employing paraffin as the dispersed phase and polyethylene glycol (PEG) as the continuous phase. Hydrophobic silica nanoparticles serve as stabilizing agents, forming an interfacial barrier around the paraffin droplets to enhance structural stability. The thermal and rheological properties of these emulsions are evaluated to assess their potential for energy storage. Key parameters such as phase change enthalpies, crystallization behavior, and flow characteristics are analyzed. The results underscore the potential of Pickering-stabilized PCM emulsions as efficient and scalable solutions for practical thermal energy storage applications.

Keywords: Thermal energy storing, Phase change materials, Pickering emulsions.

References/Referencias

- [1] Zalba, B.; Marín, J. M.; Cabeza, L. F.; Mehling, H. Review on Thermal Energy Storage with Phase Change: Materials, Heat Transfer Analysis and Applications. *Applied Thermal Engineering* **2003**, *23* (3), 251–283. [https://doi.org/10.1016/S1359-4311\(02\)00192-8](https://doi.org/10.1016/S1359-4311(02)00192-8).
- [2] Cabaleiro, D.; Agresti, F.; Fedele, L.; Barison, S.; Hermida-Merino, C.; Losada-Barreiro, S.; Bobbo, S.; Piñeiro, M. M. Review on Phase Change Material Emulsions for Advanced Thermal Management: Design, Characterization and Thermal Performance. *Renewable and Sustainable Energy Reviews* **2022**, *159*, 112238. <https://doi.org/10.1016/j.rser.2022.112238>.
- [3] Albert, C.; Beladjine, M.; Tsapis, N.; Fattal, E.; Agnely, F.; Huang, N. Pickering Emulsions: Preparation Processes, Key Parameters Governing Their Properties and Potential for Pharmaceutical Applications. *Journal of Controlled Release* **2019**, *309*, 302–332. <https://doi.org/10.1016/j.jconrel.2019.07.003>.

L 2-5 Supramolecular polysaccharide-based hydrogels for green energy storage

Sergio J. Peñas-Núñez^{1*}, Koray Cavusoglu², Sima Lashkari¹, Virginia Ruiz², David Mecerreyes¹, Irune Villaluenga¹, Edgar Ventosa², Miryam Criado-Gonzalez^{1,3}

¹POLYMAT, University of the Basque Country UPV/EHU, San Sebastian (Spain)

²Universidad de Burgos, Facultad de Ciencias, Dpto. Química Analítica, Burgos (Spain)

³Institute of Polymer Science and Technology CSIC, Madrid (Spain)

Recent advances in polymer science have led to the development of natural polymer-based electrodes for batteries, which are a fundamental technology to enable the transition towards more sustainable energy systems based on renewable sources.[1] The environmental impact of the usage of conventional batteries has been a major concern for a long time, and the development of sustainable batteries has been an important challenge for researchers.[2] Moreover, power sources that are free from shape constraints and can conform to various shapes are highly desired to facilitate the integration of the energy storage system into the device, which has also been an important limitation for emerging technologies applications.[3] Therefore, the development of flexible or shape factor-free batteries are of high importance to achieve this. In this work natural polymer-based hydrogels are investigated as injectable matrixes to host carbonaceous electrically conductive materials leading to shape-defined semi-solid electrodes with the potential to reduce the environmental impact of the batteries of the future.[4] In addition, the suitability of these injectable semi-solid electrolytes for 3D-printing applications have also been studied, which offer several advantages over conventional solid electrolytes, being able to be integrated directly into the device. Alginate-based hydrogels have turned out to meet all these properties as they can be applied as injectable and sustainable electrolytes for batteries, and present good ionic and electronic conductivities. This novel material is developed to be part of the battery's electrodes and electrolyte, and can be an alternative to conventional systems for the transition to more sustainable energy devices.[5]

Keywords: Electrochemical energy storage, biobased polymer hydrogels, semi-solid electrode.

Acknowledgments

The authors thank the Emakiker Grant of POLYMAT and funding from the Spanish State Research Agency (TED2021-131651B-C21 and TED2021-131651B-C22).

References

- [1] Ye, Y. et al. Cellulose-Based Ionic Conductor: An Emerging Material toward Sustainable Devices. *Chemical Reviews* 2023, 123, 15, 9204–9264.
- [2] Sánchez-Díez, E. et al. Redox flow batteries: Status and perspective towards sustainable stationary energy storage. *Journal of Power Source* 2021, 481, 228804.
- [3] Peñas-Núñez, S. J. et. al. Recent Advances and Developments in Injectable Conductive Polymer Gels for Bioelectronics. *ACS Applied Bio Materials* 2024, 7, 12, 7944–7964.
- [4] Borlaf, M. et. al. Semi-solid electrodes based on injectable hydrogel electrolytes for shape-conformable batteries. *Energy Advances* 2023, 2, 1872-1881.
- [5] Peñas-Núñez, S. J. et. al. Natural polymer-based hydrogels as injectable semi-solid electrolytes for sustainable batteries. In preparation.

L 2-6 Efficient Supercapacitive CO₂ Capture Enabled by a Neutral, Water-Based Polymer Electrolyte

Daniel García-Giménez, Marta Santos-Rodríguez, Antoniou Maria-Anna, Mohammad Sanan-Ali, Miguel A. López-Manchado and Javier Carretero-González*

Institute of Polymer Science and Technology, ICTP, CSIC, Madrid, Spain

Supercapacitive swing adsorption (SSA) using aqueous electrolytes offers more economical and a safer approach for carbon dioxide (CO₂) capture compared to traditional systems [1,2]. Yet, their limited electrochemical window remains a challenge for achieving low-cost, high-efficiency operation. In this study, we present a new electrolyte based on polyethylene glycol combined with a NaCl aqueous solution, enabling efficient CO₂ capture in an asymmetric supercapacitor setup. At 40 °C, neutral pH, 30 mA/g current density, and 2.5 V, the system captures 69 mmol of CO₂ per kilogram of electrode material. Studying the negative voltage to -2.5 V, the adsorption capacity increases dramatically to 356 mmol/kg, indicating a symmetric-like behavior where capture and release are independent of the charging direction. This is interpreted by the expulsion of bicarbonate ions initially adsorbed in the electrode pores and their slow diffusion towards the counter electrode. Additionally, the use of polymer-based electrolytes notably increases the stored energy, achieving up to four times higher gravimetric energy compared to similar devices operating around 1 V with microporous carbon electrodes. The system also reveals excellent durability and corrosion resistance under long-term cycling at high voltages. These findings highlight a promising pathway for scalable, high-performance electrochemical CO₂ capture technologies

Keywords: Supercapacitor, CO₂ adsorption, Energy storage

Acknowledgments. Project: PID2020-119658RB-I00

References

- [1] Kokoszka B, Jarrah NK, Liu C, Moore DT, Landskron K. Supercapacitive swing adsorption of carbon dioxide. *Angew Chem Int Ed Engl.* **2014 Apr** 1;53(14):3698-701.
- [2] Grace Mapstone, Tim M. Kamsma, Zhen Xu, Penelope K. Jones, Alpha A. Lee, Israel Temprano, James Lee, Michael F. L. De Volder, Alexander C. Forse Understanding the Mechanism of Electrochemical CO₂ Capture by Supercapacitive Swing Adsorption, *ACS Nano* **2025**, 19, 4, 4242–4250, 2024.

L 3-1 Blending of Polymers of Intrinsic Microporosity (PIMs) with Nanomaterials for use as CO₂ separation membranes

Javier Laguna-Humayor¹, Alessio Fuoco² and Bibiana Comesaña-Gándara¹

¹IU CINQUIMA, Universidad de Valladolid, Valladolid, Spain

²Institute on Membrane Technology, CNR-ITM, Rende, CS, Italy

In today's carbon-constrained world, membrane gas separation is a competitive alternative to conventional energy-intensive separation processes such as cryogenic distillation and pressure swing adsorption. Polymers of Intrinsic Microporosity (PIMs) have shown a promising permeability-selectivity balance, making them potential candidates for use as gas separation membranes.[1] Their rigid and contorted structures prevent efficient packing of the polymer chains, providing an intrinsic microporous structure with high fractional free volume (FFV) and high surface areas, so that they behave like molecular sieves. However, PIM-based membranes lack long-term operational stability due to their physical aging, which reduces FFV and is manifested by a decrease in gas permeability over time. In recent years, membrane research is being actively committed to enhance gas separation performance and manage physical aging issues, with emphasis on the emerging approach of blending with nanomaterials to give mixed matrix membranes (MMMs).[2]

In this work we report the synthesis of a hyper-crosslinked Porous Organic Polymer (POP) via Friedel-Craft reaction using 1,3,5-triphenylbenzene (TPB) as starting material. The obtained polymer network showed a high BET surface area (2496 m²/g) and was used at different loading percentages as filler in the preparation of the archetypal PIM-1-based MMMs. Due to the purely organic nature of the POP-based fillers, the filler-polymer matrix interfacial compatibility is enhanced. In addition, the dispersed POPs particles act as scaffolds “freezing” the physical aging and extending the durability of membranes. Regarding the gas transport properties, all the fabricated MMMs show improved CO₂/CH₄ gas mixture separation performance comparing the neat PIM-1 membrane.

Keywords: Mixed Matrix Membranes (MMMs), CO₂ Gas Separation.

Acknowledgments

The research leading to these results has received support by Grants TED2021-131170A-I00 and CNS2022-135430 funded by MCIN/AEI/10.13039/501100011033 and by European Union NextGenerationEU/PRTR. In addition, this work was also supported by Grant PID2023-148145OA-I00 funded by MCIN/AEI/10.13039/501100011033 and FEDER/UE.

References

- [1] Budd, P.M; McKeown, N.B. Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. *Chemical Communications* **2004**, 4, 230-231.
- [2] Lu, X. et al. Mixed matrix membranes for gas separations: A review. *Chemical Engineering Journal* **2024**, 494, 152912.

L 3-2 Innovative Polymers of Intrinsic Microporosity (PIMs) based on diazabenzotriptycene units for use as CO₂-ultrapermeable membranes

N. Carrera-Carranza, J. Laguna-Humayor, B. Comesaña-Gándara

IU CINQUIMA, Universidad de Valladolid, Valladolid, Spain

Global warming issue, resulting from rising CO₂ levels, is a severe environmental challenge and, accordingly, it is urgent to develop an environmental-friendly and cost-efficient CO₂ treatment technology. For large-scale applications, highly CO₂-permeable membrane materials are crucial to the technological and economic competitiveness of membrane technology over concurrent technologies. In recent years, Polymers of Intrinsic Microporosity (PIMs)-based membrane materials have demonstrated great potential for most important industrial gas separations due to their stiff-contorted backbone that induces strongly interconnected fractional free volume and exceptional gas separation performance, with high permeability and significant size-sieving behavior.¹ In particular, for CO₂ separation, a series of ultrapermeable PIMs was recently reported, of 2D ribbon-like chain conformation and based on benzotriptycene structural units, which behaves like typical PIMs but much more permeable due to enhanced intrinsic microporosity arising from its 2D-chain structure. The outstanding data from these ultrapermeable PIMs allowed the redefinition of the CO₂-involved benchmark Robeson upper bounds in 2019.²

Current research focuses on enhancing membrane CO₂ separation performance by incorporating diazabenzotriptycene units as building blocks – instead of benzotriptycenes moieties – as their high CO₂ affinity due to the presence of nitrogen in the structure will increase the CO₂ solubility. We introduce a novel series of shape-persistent ladder polymers with a 2D ribbon-like chain conformation based on 1,4-diazabenzotriptycene (DABTrip-PIMs), which have been used to fabricate defect-free membranes. Gas separation performance of high-microporosity membranes was evaluated, showing CO₂-ultrapermeability and remarkable selectivity, and demonstrating PIMs-based membranes as potential candidates for low-cost and energy-effective carbon capture and natural/biogas upgrading.

Keywords: Polymers of Intrinsic Microporosity (PIMs), CO₂ separation, diazabenzotriptycene units, defect-free membranes.

Acknowledgments

The research leading to these results has received support by Grants TED2021-131170A-I00 and CNS2022-135430 funded by MCIN/AEI/10.13039/501100011033 and by European Union NextGenerationEU/PRTR. In addition, this work was also supported by Grant PID2023-148145OA-I00 funded by MCIN/AEI/10.13039/501100011033 and FEDER/UE.

References

- [1] Budd, P.M., McKeown, N.B. & Fritsch, D. Polymers of Intrinsic Microporosity (PIMs): High Free Volume Polymers for Membrane Applications. *Macromol Symp* **2006**, 245-246, 403-405.
- [2] Comesaña-Gándara, B. et al. Redefining the Robeson upper bounds for CO₂/CH₄ and CO₂/N₂ separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity. *Energy Environ Sci* **2019**, 12, 2733–2740.

L 3-3 Ultrafast Crystallization Kinetics of Semiconductive Polymers by Fast Scanning Calorimetry

Josep Tent-Pérez¹, Francisco Blanco Vázquez¹, Matteo Sanviti¹, Jaime Martín^{1*}

¹Universidad da Coruña, Campus Industrial de Ferrol, CITENI, Esteiro, 15471 Ferrol, Spain

Motivated by the promise of large-area and low-cost production of devices such as organic photovoltaic (OPV) cells, the field of polymer electronics has experienced a “revolution” in the last 2 decades. It is now well recognized that the performance of devices is critically linked to the solid-state microstructure of advanced semiconducting polymers, which is generated during solidification of the material via a crystallization-like process [1,2]. Consequently, it is of paramount importance to understand how the crystallization process occurs in this special class of polymers. However, due to a number of experimental difficulties (e.g. the whole crystallization process occurs in the 10^{-1} s time scale at >300 °C), the crystallization kinetics of advanced semiconducting polymers have been poorly investigated.

In this presentation I will show the first experimental methodology (based on Fast Scanning Calorimetry) that allows investigating the crystallization of semiconducting polymers in one step. Using PTQ10 as a model system of a crystallizable donor polymer with high performance in organic solar cells [3], I will argue that the modelling of the crystallization kinetics of PTQ10 needs to consider a fast Avrami-like nucleation step, followed by a rapid autocatalytic growth, as described in the Malkin model [4], [5]. Four different isothermal crystallization temperatures were investigated (ranging from 340 to 343 °C) with fitting coefficients R^2 over 0.99.

It is anticipated that the comprehension of the crystallization kinetics of semiconducting polymers will enable the design of rational processing pathways for these materials, impacting the entire field of organic electronics, from organic photovoltaics to bioelectronics to wearable electronics.

Keywords/Palabras clave: conjugated polymers, crystallization, kinetics, fast scanning calorimetry

Acknowledgments

The author gratefully acknowledges funding from the Spanish Ministry of Science, Innovation and Universities through the FPI (Formación de Personal Investigador) fellowship, associated with the project PID2021-126242NB-100.

References/Referencias

- [1] R. Noriega *et al.*, ‘A general relationship between disorder, aggregation and charge transport in conjugated polymers’, *Nat Mater*, vol. 12, no. 11, pp. 1038–1044, Nov. **2013**.
- [2] X. Shen, V. V. Duzhko, and T. P. Russell, ‘A study on the correlation between structure and hole transport in semi-crystalline regioregular P3hT’, *Adv Energy Mater*, vol. 3, no. 2, pp. 263–270, Feb. **2013**.
- [3] C. Sun *et al.*, ‘A low cost and high performance polymer donor material for polymer solar cells’, *Nat Commun*, vol. 9, no. 1, Dec. **2018**.
- [4] M. Avrami, ‘Kinetics of phase change. I: General theory’, *J Chem Phys*, vol. 7, no. 12, pp. 1103–1112, **1939**.
- [5] A. Y. Malkin, V. P. Beghishev, and I. A. Keapin, ‘Macrokinetics of polymer crystallization’, **1983**.

L 3-4 Poly(ether-imide-ester)s Incorporating Sulfur-Containing Amino Acids: A First Step Toward More Sustainable High-Dielectric Polymer Materials

Sebastian Bonardd¹, Maksim Bratukhin^{2,3}, Federico Guerrero¹, Sara Zanchi⁴, Florian Le Goupil⁴, David Díaz Díaz^{2,3}, José A. Pomposo^{1,5,6}, Jon Maiz^{1,5}

¹Centro de Física de Materiales (CFM-MPC), CSIC-UPV/EHU, Donostia-San Sebastián, Spain.

²Departamento de Química Orgánica, Universidad de La Laguna, La Laguna, Spain.

³Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna, La Laguna, Spain.

⁴Univ. Bordeaux, CNRS, Pessac, France.

⁵IKERBASQUE – Basque Foundation for Science, Bilbao, Spain.

⁶Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología, Universidad del País Vasco-Euskal Herriko Unibertsitatea (UPV/EHU), Donostia-San Sebastián, Spain.

The development of high-dielectric polymer materials is critical for advancing energy storage and conversion technologies.^[1] In this study, we report the synthesis and characterization of novel poly(ether-imide-ester) (PEIE) polymers incorporating sulfur-based amino acid residues as dipolar units. Specifically, we designed and synthesized two PEIEs containing methionine (PEIE-Met) and its oxidized form, methionine sulfone (PEIE-Met(O₂)), to investigate the impact of pendant thioether and sulfone groups on the dielectric properties. The synthesized polymers were thoroughly characterized via spectroscopic (FTIR, NMR), thermal (TGA, DSC), and dielectric (BDS) techniques. The results confirm the successful incorporation of methionine-based moieties into the polymer backbone, leading to the formation of materials showing high thermal stability, as evidenced by onset degradation temperatures above 300 °C, glass transition temperatures (T_g) in the 162–182 °C range, and excellent dielectric performance. Notably, at room temperature, PEIE-Met(O₂) exhibited a higher dielectric constant ($\epsilon_r' = 7.1$ at 1 Hz) than did PEIE-Met ($\epsilon_r' = 5.7$ at 1 Hz), which was attributed to the increased dipole moment of the sulfone groups. Both polymers maintained low dielectric loss values ($\tan(\delta) < 0.01$) at room temperature, making them promising candidates for capacitor applications.^[2] Notably, the materials developed in this work exhibited discharge efficiency values above 85 % at 100 °C under electric fields of 100 and 200 MV/m, confirming their suitability as dielectric layers for energy storage applications. This study highlights the potential of bioderived amino acid residues as functional building blocks for high-dielectric polymer design. Our findings open new avenues for the development of sustainable, high-performance dielectric materials tailored for next-generation electronic and energy storage applications.

Keywords: Polymer Dielectrics, Energy Storage, Dipolar Glass Polymers, Amino Acids

Acknowledgments

The authors thank the projects 2023-CIEN-000069-01 and IT-1566-22 funded by the Basque Government, the project PID2021-123438NB-I00 funded by Spanish Ministry of Science and Innovation and the project PID2022-142118OB-I00/MCIN/AEI/10.13039/501100011033/UE funded by Spanish Ministry of Science and Innovation and the Fundación Ramón Areces.

References

- [1] Feng, Q. K., Zhong, S. L., Pei, J. Y., Zhao, Y., Zhang, D. L., Liu, D. F., Zhang Y. X. & Dang, Z. M. Recent progress and future prospects on all-organic polymer dielectrics for energy storage capacitors. *Chemical Reviews*, **2021**, 122(3), 3820-3878.
- [2] Baer, E. & Zhu, L. 50th anniversary perspective: dielectric phenomena in polymers and multilayered dielectric films. *Macromolecules*, **2017**, 50.6, 2239-2256

L 3-5 New nucleophilic monomers for energy applications

O. R. Presa¹, J. Mañanes-Mateos², M. Santos-Rodríguez¹, J. M. Martínez-Ilarduya², C. Bartolomé², C. Álvarez¹, A. E. Lozano^{1,2,3}

¹Department of Applied Macromolecular Chemistry, Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain;

²IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47071 Valladolid,

³Surfaces and Porous Materials (SMAP, UA-UVA_CSIC), Associated Research Unit to CSIC, University of Valladolid, Paseo Belén 7, E-47011 Valladolid, Spain.

The polyhydroxy alkylation reaction is a synthetic procedure that yields a wide variety of polymeric materials, many of which have potential applications in energy-related fields [1]. This synthetic methodology is derived from the superelectrophilic theory of Olah and Klumpp [2], and in the last decade of the 20th century, was applied in synthesizing polymers possessing desirable properties [3].

These polymers exhibited high thermal and chemical resistance, particularly when the monomers were well-chosen. However, the materials' fraction free volume (FFV) has not been adequately studied. Therefore, we have obtained a series of electrophilic rigid monomers, that, in some cases, possess a contortion point capable of imparting intrinsic microporosity, which should increase the FFV of polymers.

Subsequently, we made polymers by reacting these electrophilic monomers with activated ketones as isatin and N-methylisatin, or mixtures of both, to tune the FFV of the resulting materials. Monomers and polymers were characterized by common techniques (NMR and FTIR spectroscopy), and their mechanical properties and thermal stabilities were studied. Finally, derivatization of isatin-based materials was carried out to incorporate sulfonic groups, increasing their hydrophilic character to improve the ionic transport properties in aqueous medium.

Keywords: polyhydroxy alkylation reaction, Fractional free volume, thermal stability, mechanical properties, hydrophilic character.

Acknowledgments

This work was supported by the Spanish research agency, projects PID2023-149594OB-C22 (financed by MCIU/AEI /10.13039/501100011033 / FEDER, UE), and PID2023-148145OA-I00 (MCIU/AEI/10.13039/501100011033 ERDF/UE) (financed by MCIU/AEI /10.13039/501100011033 / FEDER, UE)

References

- [1] Olah, G. A.; Klumpp, D. A. Study of Superelectrophiles. In *Superelectrophiles and Their Chemistry*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, **2008**; pp 17–80. <https://doi.org/10.1002/9780470185124.ch2>.
- [2]Hernández-Cruz, O.; Zolotukhin, M. G.; Fomine, S.; Alexandrova, L.; Aguilar-Lugo, C.; Ruiz-Treviño, F. A.; Ramos-Ortíz, G.; Maldonado, J. L.; Cadenas-Pliego, G. High- T g Functional Aromatic Polymers. *Macromolecules* **2015**, *48* (4), 1026–1037. <https://doi.org/10.1021/ma502288d>.
- [3] González-Díaz, M. O.; Cetina-Mancilla, E.; Sulub-Sulub, R.; Montes-Luna, A.; Olvera, L. I.; Zolotukhin, M. G.; Cárdenas, J.; Aguilar-Vega, M. Novel Fluorinated Aromatic Polymers with Ether-Bond-Free Aryl Backbones for Pure and Mixed Gas Separation. *J. Memb. Sci.* **2020**, *606*, 118114. <https://doi.org/10.1016/j.memsci.2020.118114>.

L 3-6 Desarrollo de Mezclas de Polímeros Biodegradables para contribuir a una Agricultura Sostenible

Teresa Corrales¹, Celsa Alonso¹, Víctor Hevilla¹, Fernando Catalina¹, Jesús L.Pablos²

¹Grupo de Fotoquímica, Instituto de Ciencia y Tecnología de Polímeros (CSIC) Madrid, España

²Dpto Química en Ciencias Farmacéuticas, Facultad de Farmacia, UCM, Madrid, España

Los polímeros son materiales fundamentales para múltiples sectores industriales y han tenido un papel clave en el avance de la agricultura. Un ejemplo destacado es el polietileno de baja densidad (PE-LD), ampliamente empleado en la fabricación de filmes de acolchado agrícola. No obstante, su resistencia a la degradación genera preocupaciones ambientales, ya que contribuye a la acumulación de residuos plásticos. Al final del periodo de cultivo estos residuos han de ser recogidos para posteriormente ser reciclados, proceso muy complejo debido a los fragmentos de tamaño micrométrico producto su degradación, y a la suciedad de la tierra impregnada sobre el plástico. Todo ello conlleva a la acumulación de microplásticos en el medioambiente [1]. Esta problemática ha impulsado la búsqueda de alternativas biodegradables, cuya adopción es esencial para reducir el impacto ambiental del PE-LD. El polímero que más atención ha recibido es el poli(butileno adipato-co-tereftalato) (PBAT), un poliéster biodegradable con propiedades mecánicas y procesado similares al PE. El principal inconveniente en el empleo de PBAT reside en su alta sensibilidad a la radiación UV.

Por este motivo, en el presente Trabajo se han desarrollado mezclas de diferentes composiciones basadas en PBAT y polietilencarbonato (PEC), un polímero biodegradable que posee gran interés ecológico. Para el desarrollo de estas mezclas se empleó extrusión y moldeo por compresión. El alcance de este trabajo comprende el estudio de la compatibilidad de ambos polímeros, el estudio de sus propiedades térmicas, mecánicas y superficiales y la evaluación de su estabilidad frente a la radiación UV y de su comportamiento en condiciones de compostaje. Los resultados obtenidos muestran como las mezclas de PBAT/PEC presentan, por un lado, propiedades mecánicas similares al PBAT y, por otro lado, mayor fotoestabilidad, la cual se estudió por análisis de quimioluminiscencia, Fig1a. Además, se observa mejor compostabilidad en las mezclas con el contenido en PEC, con respecto al PBAT puro, Fig1b.

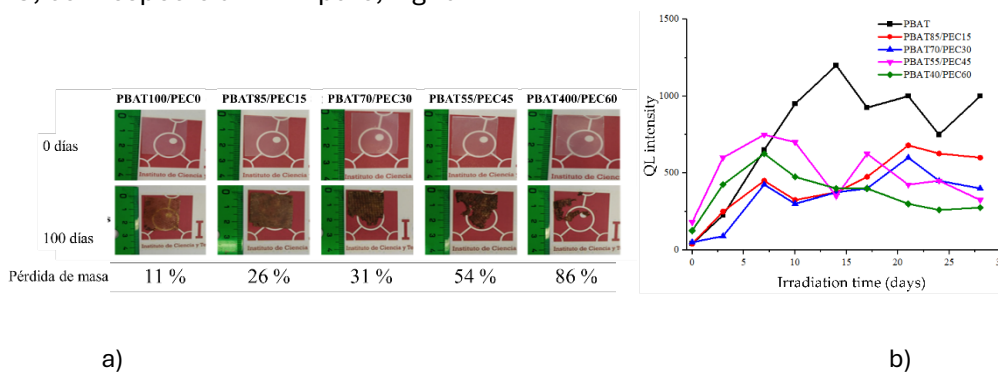


Figura 1. Resultados del estudio por a) quimioluminiscencia y b) compostaje.

Palabras clave: agricultura, biodegradabilidad, fotoestabilidad

Agradecimientos: Los autores agradecen al proyecto PID2021-124926NB-I00

Referencias:

[1] Abrusci,C.; Pablos,J.L.; Marín,I.; Espí,E.; Corrales,T.; Catalina,F. Comparative effect of metal stearates as pro-oxidant additives on bacterial biodegradation of thermal- and photo-degraded low density polyethylene mulching films.

International Biodeterioration **2013**, 83, 25-32.

L 3-7 Understanding organic photovoltaics-relevant blend structures in relation to the acceptor's chemical structure

A. Peinador Veiga¹, J. Lemos-Chapela¹, X. Rodriguez-Martinez^{1*}, J. Martín^{1*}

¹Universidad da Coruña, CITENI, Campus de Esteiro, Ferrol, Spain.

The field of organic photovoltaics (OPV) has experienced a significant development in recent years with record power conversion efficiencies (PCEs) surpassing 20%. That is especially due to the chemical flexibility and tuneability of non-fullerene-acceptors (NFAs) as fundamental component in archetypal donor:acceptor blends used as photoactive layer. However, such a structural, chemical design freedom comes with the drawback of not having a clear material development roadmap.¹ On the other hand, it should be possible to link specific structural parameters of the donor:acceptor blend morphology to the solar cell PCE and stability.^{2,3} Therefore, clear connections between how the chemical structure and composition alters the overall donor:acceptor morphology can guide new design pathways to higher PCEs.

For this purpose we have carried out grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements in a wide variety of donor polymer:NFA blends. The chosen polymer was D18 as it is one of the most promising for OPV, and it was blended with a selection of 9 different acceptors - including 5 Y-family NFAs which yield PCEs in excess of 18%.

Density Functional Theory (DFT) calculations were performed on all donor polymer and NFA molecular structures involved in order to optimize their 3D geometries and extract accurate molecular descriptors. Then, these descriptors were correlated to a number of the structural parameters obtained through a careful quantitative analysis of the aforementioned GIWAXS diffractograms.

Among the analyzed parameters we highlight the fraction of *face-on oriented crystallites* in polymer:NFA samples: there exists a correlation between the fraction of crystalline material with preferred orientation in the out of plane direction and literature-reported PCEs of the corresponding donor:acceptor blends. Based on the molecular descriptors of the most promising NFAs blended with D18, we provide guidelines for the deliberate design of small molecular acceptors toward better-performing organic solar cells.

Keywords: semiconducting polymers, polymer photovoltaics, material design, GIWAXS, DFT

Acknowledgments

GIWAXS experiments were performed at NCD-SWEET beamline at ALBA Synchrotron with the collaboration of ALBA staff. Authors acknowledge funding from the ERC CoG project PARACRYST (Grant ID: 101086805).

References

- [1] Yi, J.; Zhang, G.; Yu, H.; Yan, H. Advantages, Challenges and Molecular Design of Different Material Types Used in Organic Solar Cells. *Nat. Rev. Mater.* **2024**, *9* (1), 46–62.
- [2] Fan, B.; Gao, W.; Wu, X.; Xia, X.; Wu, Y.; Lin, F. R.; Fan, Q.; Lu, X.; Li, W. J.; Ma, W.; Jen, A. K.-Y. Importance of Structural Hinderance in Performance–Stability Equilibrium of Organic Photovoltaics. *Nat. Commun.* **2022**, *13* (1),
- [3] Mazzolini, E.; Qiao, Z.; Muller, J.; Furlan, F.; Sanviti, M.; Nodari, D.; Rimmel, M.; Collauto, A.; Deibel, C.; Heeney, M.; Martin, J.; Eisner, F.; Nelson, J.; Gasparini, N.; Panidi, J. Discerning Blend Microstructure and Charge Recombination for Stable Biorenewable-Based Organic Photovoltaics. *Adv. Energy Mater.* *n/a* (n/a), 2405635.

L 3-8 Bio-based PEBAX® Hollow Fiber Membranes

M. Etxeberria-Benavides¹, S. M. Otaño¹, J. J. Flat², Q. Pineau², M. Sleczkowski³, H.W. Spakman³, K. V. Bernaerts³, O. David¹

¹TECNALIA, Basque Research and Technology Alliance (BRTA), Donostia, San Sebastian, 20009, Spain

²CERDATO ARKEMA, Serquigny, F-27470, France

³Sustainable Polymer Synthesis Group, Aachen Maastricht Institute for Biobased Materials (AMIBM), Faculty of Science and Engineering, Maastricht University

Currently, polymeric materials are dominant in the market for gas separation applications. For example, ARKEMA's polyamide-*b*-polyether (PEBAX®) segmented block copolymers have shown good selectivity of CO₂ over other light gases [1]. Because of the linear and aliphatic structure of state of the PEBAs, membranes are processed as flat sheet, by coating of a polymeric solution into a porous support [2]. The resulting composite structure has the disadvantage that the polymer cannot be recycled. In addition, the flat geometry leads to a low packing density of the membrane into a separation module. To overcome these drawbacks, we have investigated the synthesis of new, PEBAX® with a modified chemical structure, tuned to offer processability into a hollow fiber membrane (HF). In addition, aiming to offer reduced environmental footprint we have focused our efforts in using monomers derived from renewable feedstocks.

Experimental/methodology. Polymer synthesis was done by polycondensation in two steps. First the polyamide (PA) was synthesized from dimer fatty acid (Pripol® 1009) and 1,10 diaminododecane, second the PA was copolymerized with polyethylene oxide (PE). The manufacture of hollow fiber membranes involved air step evaporation followed by non-solvent-induced phase separation done by co-extrusion of one or two polymer solutions with an inner fluid through an air gap into a coagulation bath [3].

Results and discussion.

Best hollow fiber membrane morphology and separation properties were achieved when different PA to PE weight ratios were used for the same co-polymer. The co-polymer with a higher PA weight % was co-extruded around the same co-polymer with a higher PE weight %, both around the inner fluid. The selective layer was formed at the interior surface and a high porosity was contained within the wall and at the outer surface [4]. The dual layer hollow fiber morphology is shown in Figure 1.

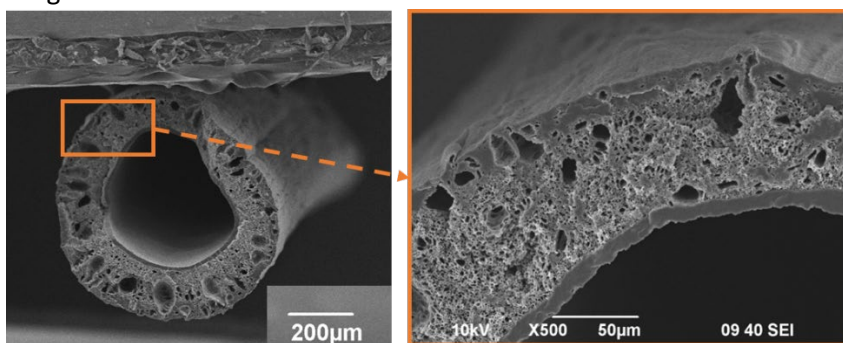


Figure 1. Cross sectional morphology of dual layer hollow fiber membranes developed in this work.

Keywords: gas separation, hollow fiber membrane, polyamide-*b*-polyether (PEBAX®).

Acknowledgments

This work has received funding from the European Union's Horizon Europe Research and Innovation program under Grant Agreement No. 101091812 (CUMERI project) and under Grant Agreement No. 887075 (BIOCOMEM project).

References

- [1] Nematollahi, M. H.; Carvalho, P. J.; Coutinho, J. A. P.; Abedini, R.; Energy & Fuels, **2022**, 36, 12367–12428.
- [2] Martínez-Izquierdo, L.; Téllez, C.; Coronas, J.; J. Mater. Chem. A, **2022**, 36, 18822-18833
- [3] Etxeberria-Benavides, M.; Karvan, O.; Kapteijn, F.; Gascon, J.; David, O.; Membranes (Basel), **2020**, 10.
- [4] David, O.; Etxeberria-Benavides, M.; Otaño, S. M.; Pineau Q., Bernaerts, K. V.; Sleczkowski, M.; EP23307022.

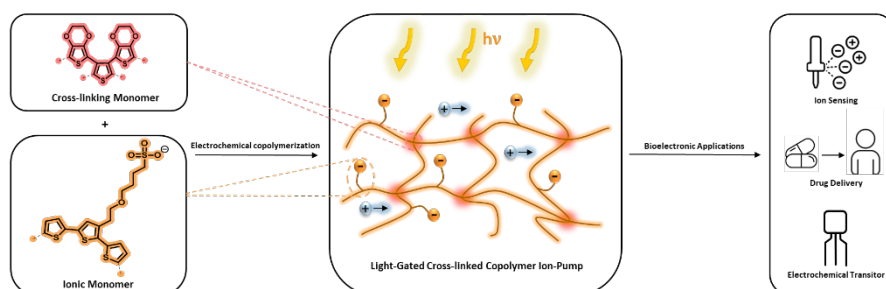
L 4-1 Ionic Cross-linked Thiophene-based Copolymers for Application in Bioelectronics

M. Trapero^{1*}, I. Abdel Aziz¹, D. Mantione^{1,2}

¹POLYMAT, University of the Basque Country UPV/EHU, Gipuzkoa, Spain

²Ikerbasque, Basque Foundation for Science, Bilbao, Spain.

Attaining ion transport with artificial molecular transport systems (AMTS) is of high interest for many bioelectronic applications, as drug delivery or ion sensing.[1,2] To drive the active transport of protons and metal ions, a potential drop is generated across an ionic membrane, which drives the ions through. While wired transport has been extensively investigated,[3,4] contactless approaches for generating the potential drop have not been studied to the same extent so far. Asymmetric light illumination, for example, generates a potential drop that pumps the ions across the membrane, allowing for contactless, low-invasive transport. Existing AMTS are typically composed of lipid or liquid membranes.^{5,6} However, these lipid or liquid membranes come with challenges such as poor efficiency, fragilness, and compatibility issues with interacting components. To overcome these limitations, ionic, cross-linked and bio-compatible polymeric membranes have been proposed. Herein, we present the synthesis and characterization of different ionic/cross-linkable thiophene-based conjugated monomers, which are then electrochemically copolymerized, obtaining ionic cross-linked polythiophenes. We obtain homogeneous films with desirable VIS light absorption and stable electrochemical properties. With these characteristics, the obtained ionic cross-linked thiophene-based copolymers have the potential to be used as light-gated ion pump systems in bioelectronic applications such as drug delivery.



General scheme of ionic and cross-linkable thiophene-based monomers which are electrochemically copolymerized to be used as light-gated ion pumps for bioelectronic applications.

Keywords Polythiophene, electropolymerization, ion-pump, ionic copolymers

References

- [1] Yoshida, T.; Shakushiro, K.; Sako, K. Ion-Responsive Drug Delivery Systems. *Curr Drug Targets* **2018**, *19* (3), 225-238.
- [2] Osaki, T.; Takeuchi, S. Artificial Cell Membrane Systems for Biosensing Applications. *Anal Chem* **2017**, *89* (1), 216-231.
- [3] Tang, C.; Bruening, M. L. Ion Separations with Membranes. *Journal of Polymer Science* **2020**, *58* (20), 2831-2856.
- [4] Dai, Q.; Zhao, Z.; Shi, M.; Deng, C.; Zhang, H.; Li, X. Ion Conductive Membranes for Flow Batteries: Design and Ion Transport Mechanism. *J Memb Sci* **2021**, *632*, 119355.
- [5] Xie, X.; Crespo, G. A.; Mistlberger, G.; Bakker, E. Photocurrent Generation Based on a Light-Driven Proton Pump in an Artificial Liquid Membrane. *Nat Chem* **2014**, *6* (3), 202-207.
- [6] Bennett, I. M.; Vanegas Farfano, H. M.; Bogani, F.; Primak, A.; Liddell, P. A.; Otero, L.; Sereno, L.; Silber, J. J.; Moore, A. L.; Moore, T. A.; Gust, D. Active Transport of Ca²⁺ by an Artificial Photosynthetic Membrane. *Nature* **2002**, *420* (6914), 398-401.

L 4-2 Mixed Ionic Electronic Conducting Polymers Based on PEDOT:PSS and Protic Ionic Liquids

P. García-Foronda¹, Ilaria Abdel Aziz¹, N. Casado^{1,2}

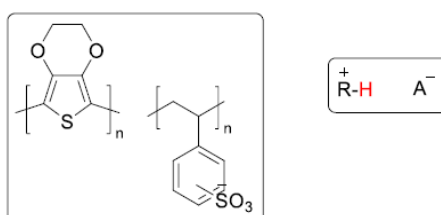
¹POLYMAT, University of the Basque Country, 20018 Donostia-San Sebastián, Guipuzkoa, Spain

²KERBASQUE, Basque Foundation for Science, Bilbao 48011, Spain

The use of conductive polymers has expanded significantly over the past 20 years. From biosensors[1] to different types of batteries[2], these polymers have been used in a wide variety of fields. The versatility of these polymers together with various modifications reported in the literature have led to an increased interest in these compounds.

One of the most commonly used conducting polymers is poly(3,4-ethylenedioxythiophene) (PEDOT) because of its high electrical conductivity[3]. The polymerization of EDOT leaves the polymer backbone with an excess positive charge, that is compensated by anions. Generally, polystyrene sulfonate (PSS) is used as counterion since improves the processability and solubility of PEDOT. There are several studies in which this dispersion is modified in distinct ways to increase conductivity. One of the previously reported ways is the treatment with aprotic and protic ionic liquids (p-IL), thus achieving a significant increase in electrical conductivity.

In this work, we present a variety of PEDOT:PSS mixtures with different p-IL in different proportions. Resistant and homogeneous membranes were obtained. Ionic and electronic conductivity tests were carried out showing good results, increasing the conductivity of the PEDOT dispersion.



Keywords: PEDOT:PSS, protic ionic liquid, electronic conductivity, electroactive polymers

Acknowledgments

Financial support from PID2023-153050OB-I00 is greatly acknowledged.

References

- [1] Picchio, M.L.; Gallastegui, A.; Casado, N.; Lopez-Larrea, N.; Marchiori, B.; del Agua, I.; Criado-Gonzalez, M.; Mantione, D.; Minari, R.J.; Mecerreyes, D. Mixed Ionic and Electronic Conducting Eutectogels for 3D-Printable Wearable Sensors and Bioelectrodes. *Adv. Mater. Technol.* 2022, 2101680.
- [2] Jia, X.; Ge, Y.; Shao, L.; Wang, C.; Wallace, G.G. Tunable Conducting Polymers: Toward Sustainable and Versatile Batteries. *ACS Sustainable Chem. Eng.* 2019, 7, 14321-14340.
- [3] Del Olmo, R.; Mendes, T.C.; Forsyth, M.; Casado, N. Mixed ionic and electronic conducting binders containing PEDOT:PSS and organic ionic plastic crystals toward carbon-free solid-state battery cathodes. *J. Mater. Chem. A* 2022, 10, 19777-19786.
- [4] Kim, M.; Lee, S.Y.; Kim J.; Choi, C.; Lansac, Y.; Ahn, H.; Park, S.; Jang, Y.H.; Lee, S.H.; Lee B.H. Protic Ionic Liquids for Intrinsically Stretchable Conductive Polymers. *ACS Appl. Mater. Interfaces* 2023, 15, 3202-3213.

L 4-3 Mass transport study for microneedle biosensors

Guillermo Conejo-Cuevas¹, Leire Ruiz-Rubio^{1,2}, José Luis Vilas-Vilela^{1,2}, Francisco Javier del Campo^{1,3}

¹ *BCMaterials, Basque Center for Materials, Applications and Nanostructures. UPV/EHU Science Park, 48940 Leioa, Vizcaya, Spain.*

² *Innovative Macromolecular Materials (Imacromat), Dpto. de Química Física, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

³ *IKERBASQUE, Basque Foundation for Science, 48009, Bilbao, Spain.*

Microneedles (MN) are a powerful platform for minimally invasive biosensing, offering painless access to interstitial fluid (ISF) and enabling continuous, real-time monitoring. MN structures are sharp micro-projections (<1 mm), typically fabricated from polymers or metals, and capable of penetrating the outer skin to reach the dermis[1]. In this study, MN-based electrochemical sensors were designed and fabricated via 3D printing; electrodes were fabricated by sputtering of thin-film Au layers through vinyl stencils, and silver-filled vias were used for electrical interconnection to the potentiostat contacts. A Prussian Blue (PB) layer was electrodeposited on the MN tips to act as an artificial peroxidase, facilitating the detection of glucose and lactate in the presence of their respective oxidase enzymes[2].

This work focuses on optimizing the enzyme immobilization matrix, a key element affecting biosensor performance. Three distinct biopolymeric matrices—chitosan (CHI), silk fibroin (SF), and methacrylated hyaluronic acid (MeHA)—were investigated for their ability to retain enzymatic activity, prevent enzyme leaching, and modulate analyte diffusion. The diffusivity of these matrices was evaluated using ferrocyanide as a model redox species on gold microelectrodes. All hydrogels were crosslinked to enhance structural stability and enzyme retention. Results highlight the critical influence of the immobilization matrix on both sensor sensitivity and dynamic range, providing insights for the development of robust, wearable MN biosensors for applications such as diabetes management.

Keywords Microneedles, interstitial fluid, enzymatic electrochemical biosensors, polymer, hydrogel

Acknowledgments

MOSINCO - MONITORIZACIÓN SIN CONTACTO DE MATERIALES COMPUESTOS DESDE SU FABRICACIÓN HASTA SU FIN DE VIDA ref. KK-2024/00037

References

- [1] Panicker, L. R.; Shamsheera, F.; Narayan, R.; Kotagiri, Y. G. Wearable Electrochemical Microneedle Sensors Based on the Graphene-Silver-Chitosan Nanocomposite for Real-Time Continuous Monitoring of the Depression Biomarker Serotonin. *ACS Appl. Nano Mater.* **2023**, *6* (22), 20601–20611. <https://doi.org/10.1021/acsnm.3c02976>.
- [2] Karyakin, A. A.; Puganova, E. A.; Budashov, I. A.; Kurochkin, I. N.; Karyakina, E. E.; Levchenko, V. A.; Matveyenko, V. N.; Varfolomeyev, S. D. Prussian Blue Based Nanoelectrode Arrays for H₂O₂ Detection. *Anal. Chem.* **2004**, *76* (2), 474–478. <https://doi.org/10.1021/ac034859l>.

L 4-4 4D Printable Electroactive and Biodegradable PEDOT:κ-Carrageenan inks for (bio)electronics

Rajat Rai¹, Antonio Dominguez-Alfaro², Salim El Hadwe², Amy T. Jin², George G. Malliaras², Miryam Criado-Gonzalez^{1,4}, Daniele Mantione^{1,3}

¹POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018, Donostia-San Sebastián, Spain

²Electrical Engineering Division, Department of Engineering, University of Cambridge, 9 JJ Thomson Ave, Cambridge, CB3 0FA, UK

³Ikerbasque, Basque Foundation for Science, Plaza Euskadi 5, Bilbao, 48009 Spain

⁴Institute of Polymer Science and Technology (ICTP-CSIC), 28006 Madrid, Spain

Over the past decade, conducting polymers (CPs) have gained prominence as electroactive inks for high-resolution 3D printing of (bio)electronic devices, particularly using digital light processing (DLP) and two-photon polymerization (2PP) [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is especially valued for its conductivity, stability, and biocompatibility. However, its typical formulation with non-degradable polystyrene sulfonate (PSS) in PEDOT:PSS dispersions requires additional photocurable polymers for light-based printing, compromising biodegradability and sustainability, critical for disposable biomedical applications [2,3]. To overcome these limitations, we developed a series of biodegradable PEDOT:biopolymer dispersions by oxidative polymerization of EDOT in the presence of naturally derived, anionically functionalized biopolymers: κ-carrageenan (CAR, sulfate groups), alginate (carboxyl groups), and inulin (hydroxyl groups). Among these, PEDOT:CAR exhibited the highest electrical conductivity (~0.1 S/cm), attributable to the high charge density and favourable interactions between PEDOT and the sulfate-rich CAR backbone. To enable light-based fabrication, CAR was further functionalized with methacrylate groups, yielding a photopolymerizable PEDOT:CAR-MA ink compatible with DLP printing. This PEDOT:CAR-MA formulation enabled the direct fabrication of architected, shape-defined conductive hydrogels with 4D functionality, exhibiting reversible swelling/deswelling behaviour, structural integrity, electrical conductivity, and enzymatic degradability. Importantly, the printed constructs supported high cell viability and demonstrated cytocompatibility with human-induced pluripotent stem cell-derived neurons (iPSC-neurons), underscoring their potential for bioelectronic interfaces. Overall, these sustainable, biodegradable PEDOT-based materials offer a compelling platform for next-generation, disposable bioelectronic devices, with demonstrated utility in soft, implantable sensors for in vivo pressure monitoring and electrocorticography (ECoG).

Keywords PEDOT, Bioelectronics, Implantable devices, Biobased, Biodegradable

References

- [1]. Criado-Gonzalez, M.; Dominguez-Alfaro, A.; Lopez-Larrea, N.; Alegret, N.; Mecerreyes, D. Additive Manufacturing of Conducting Polymers: Recent Advances, Challenges, and Opportunities. *ACS Appl. Polym. Mater.* 2021, 3, 2865–2883.
- [2]. Harris, A.R.; Molino, P.J.; Kapsa, R.M.I.; Clark, G.M.; Paolini, A.G.; Wallace, G.G. Effective Area and Charge Density of Dextran Sulphate Doped PEDOT Modified Electrodes. *Synth. Met.* 2016, 220, 394–401.
- [3]. Rai, R.; Mantione, D. The Future of Electronic Materials Is...degradable! *J. Mater. Chem. C* 2023, 11, 11803–11813.

L 4-5 Freeze–Thaw PVA Hydrogels with Crystallizable Alkyl Chains: Structure, Adhesion, and Thermal Response

Alexis Alvear^{1,2}, Mercedes Fernández², Alejandro J. Müller^{2,3}, Rebeca Hernández¹

¹ Institute of Polymer Science and Technology ICTP-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

² POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal, 3, 20018 Donostia-San Sebastián, Spain

³ IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, Bilbao, 48009, Spain

Over the last few years, there has been increasing interest in the development of hydrogels with self-healing or shape memory properties for potential applications in additive manufacturing techniques, wearable electronics, soft robotics, and biomedical devices. [1] In this context, polyvinyl alcohol (PVA), a semicrystalline polymer capable of forming physical hydrogels through freezing and thawing cycles, was chosen. PVA offers inherent advantages such as hydrophilicity, biodegradability, and biocompatibility. However, it produces physical hydrogels that are mechanically weak. [2]

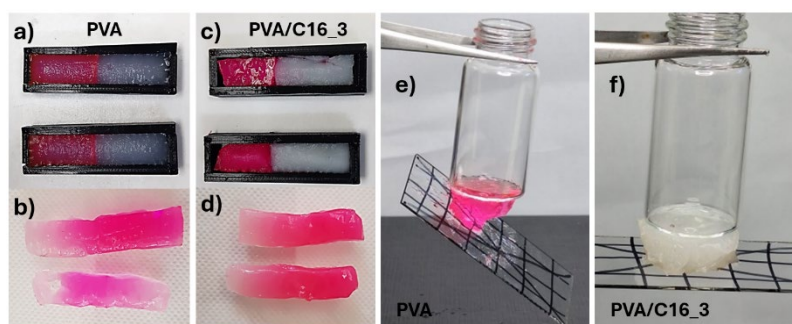


Figure 1. Representative images corresponding to hydrogel samples PVA and PVA/C16_3 (10 wt%). a) and c) cut for the self-healing test, and b) and d) after being kept at 50°C for 48 hours in a saturated vapor atmosphere. e) and f) show the capacity of the hydrogels to hold a glass slide of 5 g.

To address this limitation and enhance functionality, we employed a straightforward methodology for forming PVA gels in water by blending PVA with hexadecyl alkylamine (C16) and utilizing freeze–thaw cycles to promote gelation. [3] This simple system, in which gel formation occurs exclusively in water, demonstrates that incorporating a second, immiscible component (even in small amounts) induces crystallization of some of the PVA chains. This process promotes hydrogel formation and can significantly alter the thermomechanical properties of the resulting hydrogels, introducing additional functionalities such as self-healing and adhesive properties.

Keywords: polyvinyl alcohol, freezing-thawing cycles, crystallization induced gelation, blend hydrogels, adhesive properties, enhanced mechanical properties

References

- [1] Adelnia, H. Ensandoost R, Moonshi S.S., Gavgani J. N., Vasafi E. I., Thu Ta H. Freeze/thawed polyvinyl alcohol hydrogels: Present, past and future. *Eur. Polym. J.* **164**, 110974 (2022).
- [2] Hassan, C. M. & Peppas, N. A. Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods. *Adv. Polym. Sci.* **2000**, 153, 37–65.
- [3] Alvear A., Fernandez M., J Muller A., Hernandez R., Hexadecylamine addition promotes crystallization driven functionalities in PVA freezing-thawing hydrogels,. *Eur. Polym. J.* submitted for publication.

L 4-6 Bio-Based PU Coatings Reinforced with Nanoparticles: Active Protection in Harsh Marine Environments

R. López-Robles¹, Isabel Moreno², José Manuel Laza¹, J.L. Vilas-Vilela^{1,3}, L.Ruiz-Rubio^{1,3}

¹*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Física, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

²*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Orgánica e Inorgánica, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

³*Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.*

This work presents the development of bio-based polyurethane (PU) coatings derived from vegetable oils, aimed at offshore applications such as the protection of marine wind turbines. These coatings offer a sustainable alternative to conventional systems, which are typically formulated with petrochemical-derived substances, toxic components, and environmentally hazardous compounds, aligning with energy sector decarbonization goals and tightening environmental regulations.

The initial formulations have shown remarkable anticorrosive behavior. Electrochemical impedance spectroscopy (EIS) tests in saline medium yielded resistance values exceeding $10^7 \Omega$ reaching up to $10^9 \Omega$ surpassing the protective threshold of $10^6 \Omega$. In addition, the materials exhibit shape-memory properties, enabling structural recovery after deformation. This opens new pathways for smart coatings with self-healing potential and stimulus-responsive behavior.

Currently, metallic and metal oxide nanoparticles are being incorporated as functional fillers to further enhance anticorrosive performance, mechanical stability, and resistance to marine biofouling. This research contributes to the design of intelligent, sustainable and time-resistant protective coatings for harsh offshore environments.

Keywords/Palabras clave: bio-based polyurethane, nanotechnology, anticorrosion, cathodic protection, antifouling, smart coatings.

M 1-1 Development of Antimicrobial and Antioxidant PLA Fibers for Food Packaging Applications

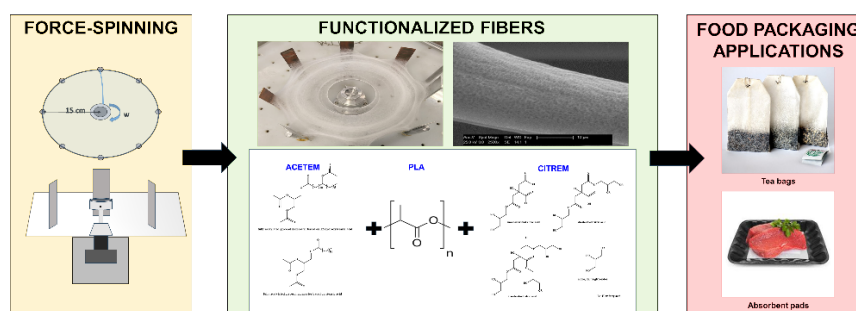
Ignacio Mena-Prado¹, Marta Fernández-García¹, Daniel López¹, Sara Limbo², Manuela Rollini², Daniele Maria Martins², Adolfo del Campo^{3*}, Alexandra Muñoz Bonilla^{1*}

¹ Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, C/ Juan de la Cierva 3, 28006, Madrid, Spain.

² DeFENS, Department of Food, Environmental and Nutritional Science, Università degli Studi di Milano, Via G. Celoria 2, 20133, Milano, Italy.

³ Institute of Cerámica y Vidrio, ICV-CSIC, C/ Kelsen 5, 28049, Campus de Cantoblanco, Madrid, Spain.

Polymeric fibers have gained attention due to their high surface area, porosity, and versatility. One of the main challenges in the food industry is to improve food safety, preserve the quality of packaged food, and extend its shelf life. "Active" packaging systems address these challenges by modifying the package environment through oxygen scavengers, moisture absorbers, antioxidants, and antimicrobial agents. Nano- and microfibers are particularly well-suited for these systems due to their high surface area, which allows them to act as efficient carriers for active compounds. Polylactic acid (PLA) fibers blended with antioxidants and antimicrobial bioplasticizers (CITREM and ACETEM) were produced using the forcesspinning technique, an alternative to electrospinning that enables higher production.



Different concentrations of PLA solutions were tested to obtain optimal fiber formation, and finally a concentration of 20% of PLA was selected. The thermal properties of the plasticized films were assessed using DSC and TGA. Antimicrobial properties were evaluated using the standard method E2149-13a against both gram-positive and gram-negative bacteria, while antioxidant properties were analyzed using Blois' method. Additionally, Raman confocal microscopy and field emission scanning electron microscopy were used to further investigate the morphology and microstructure of the samples. The results indicated that variations in PLA concentration led to instability in fiber production. Fibers containing 20% PLA exhibited a uniform diameter (approximately 20 μm) with no defects. The addition of plasticizers reduced the thermal stability of PLA while increasing crystallinity. Finally, the bioplasticizers imparted new functionalities to PLA, including antimicrobial activity and antioxidant properties. Thereby, functionalized PLA fibers hold great potential for food packaging applications, such as absorbent pads for capturing exudates in fresh products or tea bags with active properties to extend shelf life and prevent food loss.

Acknowledgement

This work was supported by the EU H2020 Project, "Characterisation and Harmonisation for Industrial Standardisation of Advanced Materials" (CHARISMA), under Grant Agreement no. 952921 and by the Ministerio de Ciencia, Innovación y Universidades (PID2022-13651OB-100), the Agencia Estatal de Investigación (AEI, Spain) and Fondo Europeo de Desarrollo Regional (FEDER, EU).

M 1-2 Synthesis and degradation of Eugenol-derived Polyamides: Advancing Towards a Circular Economy.

Maria Diaz-Galbarriatu¹, Julia Sánchez-Bodón¹, Estíbaliz Hernaez¹, A. Catarina Lopes^{1,2}, Isabel Moreno-Benítez³ and José Luis Vilas-Vilela^{1,4}

¹Innovative macromolecular Materials Group (Imacromat), Department of Physical Chemistry (UPV/EHU), 48940, Spain; ²KERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain, ³Innovative macromolecular Materials Group (Imacromat), Department of Organic and Inorganic Chemistry (UPV/EHU), 48940, Spain; ⁴BCmaterials, Basque Centre for Materials, Applications and Nanostructures, 48940, Spain

Polyamides (PA) are essential synthetic polymers used in various applications, from consumer goods to high-performance materials in technical and biomedical fields¹. They are valued for their outstanding properties, largely due to their ability to form hydrogen bonds between polymer chains². However, their stability also leads to environmental concerns, as PA microplastics accumulate in ecosystems. Moreover, given that the production of conventional polymers relies heavily on fossil fuels, which exacerbates resource depletion and climate change, there is a growing shift towards sustainable, bio-based polymers³. Hence, in this work a series of sulfur containing semiaromatic polyamides have been successfully synthesized and properly characterized. Eugenol, a natural phenolic compound, was used as starting material. Moreover, this study concludes that chemical hydrolysis is an effective method for recovering the monomer. This process enables the reuse of monomers for further polymer synthesis, contributing to a circular economy and addressing the environmental challenges posed by polyamide waste.

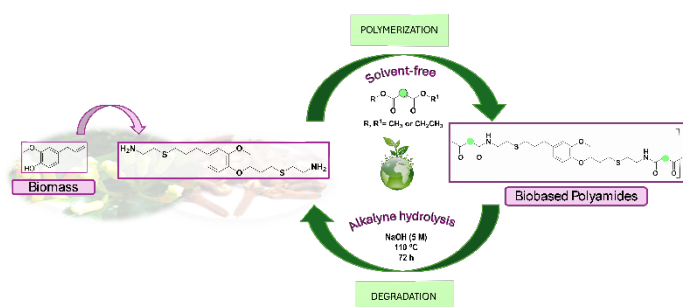


Figure 1. Synthesis and degradation schemes of biobased PAs.

Keywords: polyamides, degradation, bio-based

Acknowledgments

Government of the Basque Country (IT1756-22) and SGIker (UPV/EHU/ ERDF, EU).

References/Referencias

- [1] Kleybolte, M. M.; Zainer, L.; Liu, J. Y.; Stockmann, P. N.; Winnacker, M. (+)-Limonene-Lactam: Synthesis of a Sustainable Monomer for Ring-Opening Polymerization to Novel, Biobased Polyamides. *Macromol Rapid Commun* **2022**, *43* (17), 1–8. <https://doi.org/10.1002/marc.202200185>.
- [2] Arai, K.; Tsutsuba, T.; Wasano, T.; Hirose, Y.; Tachibana, Y.; Kasuya, K. I. Synthesis of Biobased Polyamides Containing a Bifuran Moiety and Comparison of Their Properties with Those of Polyamides Based on a Single Furan Ring. *ACS Appl Polym Mater* **2023**, *5* (5), 3866–3874. <https://doi.org/10.1021/acsapm.3c00525>.
- [3] Morales-Cerrada, R.; Molina-Gutierrez, S.; Lacroix-Desmazes, P.; Caillol, S. Eugenol, a Promising Building Block for Biobased Polymers with Cutting-Edge Properties. *Biomacromolecules* **2021**, *22* (9), 3625–3648. <https://doi.org/10.1021/acs.biomac.1c00837>.

M 1-3 Sustainable Bioplastics from Potato Peel Waste: A Circular Economy Approach Using Deep Eutectic Solvents

J Baranwal¹, D. Merino^{1,2}

¹*POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018, Donostia-San Sebastian, Spain*

²*Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain*

The widespread use of non-biodegradable, petroleum-based polymers in packaging has raised significant environmental concerns, driving the search for sustainable, circular economy-based solutions. Potato peel (PoP), the primary byproduct of potato processing, is a rich source of starch and presents a promising biomass for biodegradable material development. This study aims to valorize PoP by transforming it into bioplastics for food packaging applications.

To enhance its functionality, PoP was subjected to acidic hydrolysis and treated with a deep eutectic solvent (DES) composed of glycerol and choline chloride. The plasticization effects of DES, its individual components (choline chloride and glycerol), and thermoplastic starch films as controls were systematically investigated.

The structural and morphological properties of the developed materials were analyzed using FTIR and SEM. Additionally, their mechanical properties and interaction with water—including moisture content (MC), water solubility (WS), and water vapor permeability (WVP)—were evaluated. Thermochemical properties were assessed through TGA and DSC to determine material stability and biodegradability.

Preliminary findings indicate that DES significantly enhances the plasticization of PoP, resulting in homogeneous and flexible bioplastics. These results highlight the potential of PoP-based bioplastics as eco-friendly food packaging alternatives, reducing reliance on petroleum-based polymers and promoting waste valorization.

Keywords: Potato peel, Deep eutectic solvents, Food-waste, Bioplastics

M 1-4 PHAs en el Mediterráneo: un estudio integral desde su biodegradación hasta su biosíntesis

A. Jáuregui¹; A. Marín¹; E. Sánchez-Safont¹; J. Tena-Medialdea²; J.R. García-March²; J. Gámez-Pérez¹; L. Cabedo^{1*}.

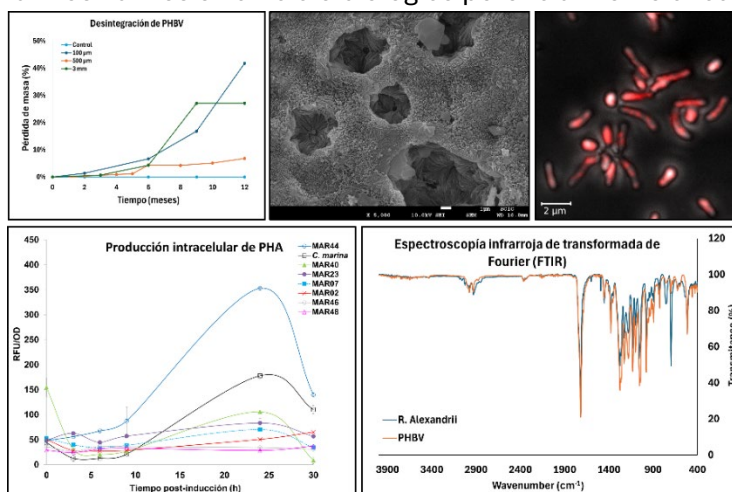
¹Grupo de Polímeros y Materiales Avanzados (PIMA), Universitat Jaume I, Castelló de la Plana

²IMEDMAR-UCV-Institute of Environment and Marine Science Research, Alicante.

La mayoría de los estudios sobre biodegradación marina de polihidroxicanoatos se realizan en condiciones de laboratorio, que no reflejan la complejidad y variabilidad de los ambientes naturales. Se diseñó un estudio *in situ* en el mar Mediterráneo durante un año para evaluar la biodegradabilidad del poli(3-hidroxiobutirato-co-3-hidroxi valerato) (PHBV) en un entorno marino real. Se monitorizó la pérdida de masa de muestras con distintos espesores [1]. Paralelamente, se analizaron los biofilms formados para identificar microorganismos biodegradadores [2], y se exploró su capacidad biosintética.

Se identificaron diferentes proteobacterias con capacidad biodegradadora del material. Además, se aisló una cepa (MAR44) que, a partir de glucosa, acumuló gránulos intracelulares de PHA (Imagen 1C). MAR44, identificada como *Roseibium alexandrii*, destacó por presentar la mayor señal de fluorescencia relativa, superando a *Cobetia marina*, utilizada como referencia positiva (Imagen 1D). El espectro de FTIR del polímero extraído mostró coincidencia con el del PHBV comercial, confirmando la identidad del biopolímero sintetizado (Imagen 1E).

Este enfoque multidisciplinar permite avanzar en la comprensión del destino ambiental de los PHAs y del papel de los microorganismos marinos nativos en un ciclo biológico potencialmente circular de los bioplásticos.



Palabras clave: Polihidroxicanoatos, biodegradación, economía circular, biofilm, biosíntesis polimérica

Agradecimientos: Trabajo financiado por los proyectos TED2021-130211B-C31 y PID2021-128749OB-C32 financiado por MCIN/AEI/10.13039/501100011033, por la Unión Europea NextGenerationEU/ PRTR y por FEDER Una manera de hacer Europa.

Referencias:

[1] Feijoo, P.; Marín, A.; Sánchez-Safont, E.; Tena-Medialdea, J.; García-March, J.R.; Gámez-Pérez, J.; Cabedo, L. Marine Degradation of Plastics in Western Mediterranean Sea: Comparison between Biodegradable and Conventional Polymers. *Polym. Degrad. Stab.* 2025, 234, 110305.

[2] Marín, A.; Feijoo, P.; de Llanos, R.; Carbonetto, B.; González-Torres, P.; Tena-Medialdea, J.; García-March, J.R.; Gámez-Pérez, J.; Cabedo, L. Microbiological Characterization of the Biofilms Colonizing Bioplastics in Natural Marine Conditions: A Comparison between PHBV and PLA. *Microorganisms* 2023, 11, 1461.

M 1-5 Development of a multilayer packaging system based on microbial polyesters and agri-food waste bioactives

E. Borselleca^{1,2}, E. Sánchez-Safont³, C. Pezzella¹, L. Cabedo³

¹Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, 80126 Naples, Italy

²Institute for Polymers, Composites and Biomaterials (IPCB), National Council of Research, Via Campi Flegrei 34, 80078 Pozzuoli, Italy

³Polymers and Advanced Materials Group (PIMA), Universitat Jaume I (UJI), Av. de Vicent Sos Baynat s/n, Castelló de la Plana, Castelló 12071, Spain

In recent years, food packaging has evolved into a key element of food preservation strategies. It plays a central role in ensuring product quality, extending shelf life, and reducing food waste along the entire supply chain [1]. At the same time, increasing environmental awareness and legislative pressure are pushing both industry and research toward the development of packaging materials that are not only functional, but also sustainable and biodegradable. A promising response to these demands lies in the use of bio-based materials derived from renewable resources or industrial byproducts. In this context, the present work contributes to a broader project aimed at the development of fully bio-based packaging prototypes specifically tailored for fresh meat applications. Accordingly, this research focuses on the integration of microbial biopolymers and agri-food waste-derived additives to obtain a sustainable multilayer packaging solution. The proposed concept includes structural and functional layers based on different types of polyhydroxyalkanoates, a family of biodegradable microbial polyesters known for their chemical diversity and tunable material properties. The sustainability of the packaging product is enhanced by the utilization of active compounds derived from spent coffee grounds. In particular, this abundant waste biomass represents the source of low molecular weight phenols, mainly caffeine and chlorogenic acid, which are obtained *via* a hydroalcoholic extraction. These compounds have already been tested for their antioxidant and antimicrobial properties [2], [3]. Hence, by integrating biopolymers and bioactive compounds derived from a common waste stream, this research proposes a circular and innovative approach to packaging design, highlighting how the synergy between biotechnology and materials science can drive the development of high-performance, sustainable solutions for food preservation.

Keywords: polyhydroxyalkanoates, biopolymers, biomass, active packaging, multilayer materials

Acknowledgments

This work was funded by PRIMA EU Program through the project 'MATE4MEAT' (Sustainable and antimicrobial MATerials for MEAT packaging).

References

- [1] S. Kumari, R. Debbarma, N. Nasrin, T. Khan, S. Taj, and T. Bhuyan, "Recent advances in packaging materials for food products," *Food Bioeng.*, vol. 3, no. 2, pp. 236–249, 2024, doi: 10.1002/fbe2.12096.
- [2] I. Corrado, R. Argenziano, E. Borselleca, F. Moccia, L. Panzella, and C. Pezzella, "Cascade disassembling of spent coffee grounds into phenols, lignin and fermentable sugars en route to a green active packaging," *Sep. Purif. Technol.*, vol. 334, no. December 2023, p. 125998, 2024, doi: 10.1016/j.seppur.2023.125998.
- [3] S. F. Mirpoor *et al.*, "Manufacture of active multilayer films made of functionalized pectin coated by polyhydroxyalkanoates: A fully renewable approach to active food packaging," *Polymer (Guildf.)*, vol. 281, no. March, p. 126136, 2023, doi: 10.1016/j.polymer.2023.126136.

M 1-6 Biodegradable and Bio-Based Foams: Influence of Processing Techniques on Swelling Behavior in Various Aqueous Media

Ekta Yadav¹, Gabriel Perli¹, Danila Merino^{1,2*}

¹*POLYMAT University of the Basque Country UPV/EHU, Centro Joxe Mari Korta Center, Tolosa Avenue, 72, 20018.Donostia-San Sebastián · Spain*

²*Ikerbasque, Baque foundation for science, 48009 Bilbao, Spain*

Conventional polymeric foams used in agriculture for seed germination, such as polyurethane and phenol formaldehyde foams, contribute significantly to environmental pollution due to their non-biodegradability, accumulation in landfills, and microplastic generation. As a sustainable alternative, biodegradable foams derived from bio-based materials are being explored to mitigate these issues. This study investigates the fabrication of bio-based foams using different compositions and varying processing methods- vacuum oven drying and microwave, crosslinking agents, and stabilizer concentrations. The foams were synthesized using grass biomass as a renewable resource and characterized for their structural, morphological, and mechanical properties. In addition, their swelling behaviour was evaluated in various aqueous media, including tap water, distilled water, and fertilizer solution. The impact of processing methods on foam morphology, porosity, and water absorption capacity was analyzed to understand the interaction of these foams with different liquid media is essential to assess their water absorption capacity and stability.

The results of this study confirm that foams were successfully obtained from both processing routes. However, the microwave-assisted method produced foams with superior pore morphology and stability. Additionally, the findings highlight the influence of processing techniques and chemical modifications on the material's swelling behaviour, achieving up to 430% water absorption when immersed in fertilizer solution media for 5h. This research contributes to the growing field of sustainable materials by offering an eco-friendly alternative to conventional polymeric foams, reducing environmental pollution, and promoting sustainable agricultural practices.

Keywords Sustainable materials, Biodegradable foam, Natural polymers, Compostable materials

M 2-1 Recycled polyols as partial substitutes in elastomeric PU formulations: characterisation and evaluation of their performance

L. Diñeiro*, M. Montero, J.L. Valentín, R. Navarro, A. Marcos-Fernández

Institute of Polymer Science and Technology (CSIC), Madrid, España

Nowadays, the versatility of polyurethanes is one of their core strengths, and places them at the forefront of leading materials across multiple sectors, i.e. footwear (adhesives), automotive (coatings and flexible foams), medical (elastomeric implants), and so on. [1] Among other notable characteristics, the simplicity of their synthesis stands out: by means of a polycondensation reaction between isocyanate and alcohol-bearing groups, the urethane bond is formed, constituting the backbone of these materials. The production of polyurethanes involves a number of additional components, including but not limited to a chain extender, a catalyst, and a plasticiser. The synergy of these ingredients is key in achieving a wide range of materials, characterised by unique morphologies and properties and, in turn, allowing the design of polyurethanes tailored to specific needs and applications.

Nevertheless, the issue of plastic accumulation and poor management is a cross-cutting concern that also extends to polyurethanes, making products that are disposed of in landfills or pollute the seas and oceans a problem that extends across all sectors. The current solution to this dilemma is one of the following: mechanical recycling, chemical recycling or energy recovery. [2] The present study focuses on chemical recycling, offering specifically an alternative to traditional glycolysis that uses polyester waste to prepare polyols, the precursors of polyurethanes, and its impact on sustainability and Circular Economy.

Therefore, the main objective of this work accounts for the design and development of tailor-made polyurethane formulations loaded with varying amounts of recycled polyols obtained after the application of a glycolysis treatment to a sample of marine poly(ethylene terephthalate) (PET). [3] Furthermore, both the structure and the properties that these new materials are endowed with are determined and tested by means of an array of classic characterisation techniques, namely Differential Scanning Calorimetry (DSC) and compression experiments, as well as some advanced techniques such as low-field Multiple Quantum Nuclear Magnetic Resonance (MQ-NMR) to study the network of the resulting polyurethanes, and the use of a Scanning Vibrating Needle Curemeter (SVNC) for the determination of the gel time of each of the synthesized samples.

Keywords: flexible polyurethanes, upcycling, sustainability, low-field NMR, chemical recycling.

Acknowledgments

The authors acknowledge the financial support given by ChemSkills and the EU (ERASMUS-EDU-2022-PI-ALL-INNO), Ministerio de Ciencia, Innovación y Universidades (PID2023-147542OB-I00, and CPP2023-010769), and CSIC for the iMOVE grant (IMOVE24205).

References

- [1] Szycher, M. Szycher's Handbook of Polyurethanes. *CRC Press*, **2012**.
- [2] Rossignolo, G.; Malucelli, G.; Lorenzetti, A. Recycling of polyurethanes: where we are and where we are going. *Green Chem.*, **2024**, *26*, 1132-1152.
- [3] Espinosa-García, K.; Navarro, R.; Ramírez, A.; Marcos-Fernández, A. New routes to difunctional macroglycols using ethylene carbonate: Reaction with BHET and degradation of PET. *Polym. Degrad. Stab.*, **2017**, *144*, 195-206.

M 2-2 Vitrímeros poli(epoxi-amina) con propiedades personalizables para la preparación de CFRCs

A. Vilanova-Pérez¹, T. Telatin², S. De la Flor¹, A. Roig^{2,3}

¹ *Universitat Rovira i Virgili, Department of Mechanical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain*

² *Universitat Rovira i Virgili, Department of Analytical and Organic Chemistry, C/ Marcel·lí Domingo 1, Edif. N4, 43007 Tarragona, Spain*

³ *Ghent University, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Polymer Chemistry Research group, Krijgslaan 281-S4, Ghent 9000, Belgium*

Una de las posibles soluciones al problema actual con los residuos plásticos son las redes covalentes adaptables. Estos materiales se basan en redes tridimensionales entrecruzadas que contienen en su estructura enlaces reversibles y dinámicos. Dichos enlaces permiten que los materiales puedan ser reciclados o reprocesados, aunque a temperatura ambiente posean las propiedades características de un termoestable, como buenas propiedades mecánicas y alta estabilidad térmica y química. Si la reacción de intercambio sigue un mecanismo asociativo, se les denomina vitrímeros por su semejanza al vidrio cuando se funde.

El objetivo de este trabajo consiste en la síntesis y caracterización de una familia de vitrímeros obtenidos a partir de diferentes oligómeros poliiminas terminados en grupos amina, a partir de la reacción entre el tereftalaldehído (TA) y dos aminas comerciales: la Jeffamina D-230 y la dietilentriamina [1]. Variando el exceso de amina es posible obtener diferentes oligómeros con distintas longitudes de cadena, lo que afecta de manera notable a las propiedades del material final. Para la obtención de los vitrímeros finales, los oligómeros fueron entrecruzados con un diepóxido cicloalifático en proporciones estequiométricas y no estequiométricas, obteniéndose cinco materiales distintos.

Todos los materiales obtenidos exhiben temperaturas de transición vítrea (T_g) en un rango de 30 a 60 °C, junto con buenas propiedades mecánicas y estabilidad térmica. Los ensayos de relajación de tensiones demostraron tiempos de relajación rápidos, mucho más notable en los materiales no estequiométricos, los cuales también presentaron una mejor resistencia a la fluencia (creep). Al final de su vida útil, los materiales pueden ser reciclados mecánicamente, conservando sus propiedades termomecánicas originales, así como degradados químicamente mediante hidrólisis o transaminación.

Otras de las propiedades evaluadas de manera cualitativa fueron la memoria de forma y la auto-soldadura, añadiendo más valor para futuras aplicaciones industriales. Finalmente, dos de los vitrímeros fueron utilizados como matriz para materiales compuestos reforzados con fibra de carbono, comprobándose una mejora en el comportamiento mecánico y manteniendo las propiedades vitriméricas.

Palabras clave: Oligómero, Poliimina, Vitrímero, Reciclabilidad, Fibra de Carbono

Referencias:

[1] Telatin, T.; De la Flor, S.; Serra, À.; Montané, X. Poly(epoxy-imine) vitrimers. Effect of the structure on the stress relaxation and creep resistance. *Polymer Testing* 2024, 135, 108465-108475.

M 2-3 Valorization of Lignocellulosic Forestry Derivatives into Functional Acrylic Polymers as Surfactants for Emulsion Polymerization

A.Tirado¹, A. Moreno¹, G. Lligadas¹, M. Galià¹, J. C. Ronda¹

¹Universitat Rovira i Virgili, Tarragona, Spain.

Growing concerns about fossil resource depletion and mounting environmental concerns has amplified interest and demand for sustainable and green materials. Consequently, much attention has been focused on integrating biomass as a renewable source of carbon to produce valuable-added chemicals. Initial efforts have been made in the preparation of biobased acrylate polymers using forestry-derived biomass and carbohydrates, being the last recently exploited in our group from solvents derived from lactic acid.^{1,2} However, biobased water-soluble acrylate polymers are still largely unexplored despite advancements in current systems. Therefore, there is a clear need to not only formulate acrylic polymers derived from renewable resources but also to design chemical synthetic routes that minimize the reliance on toxic reagents and solvents during their preparation. In this context, biobased water-soluble acrylates were synthesized from biomass-derived precursors and utilized as a key component in the preparation of sequential well-defined block copolymers. The resulting amphiphilic copolymer demonstrated promising functionality as a polymeric surfactant in aqueous emulsion polymerization of industrially relevant hydrophobic monomers, offering a method for the preparation of stable latex dispersions.

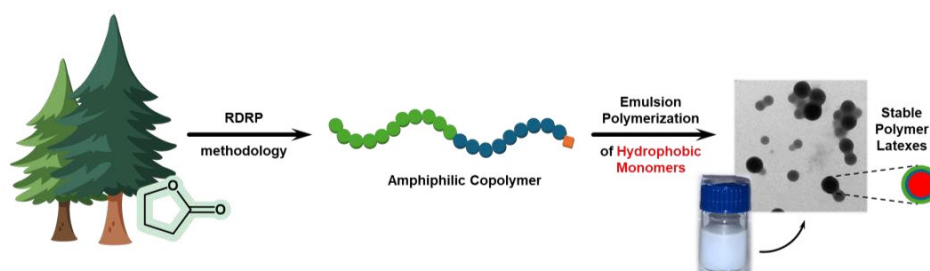


Figure 1. General overview of the use of biomass-derived copolymers for aqueous emulsion radical polymerization of hydrophobic monomers.

Keywords: Emulsion polymerization, Amphiphilic, Copolymers

Acknowledgments

This work was supported by MICIU/AEI/10.13039/501100011033 and FEDER UE through projects PID2020-114098RB-I00, PID2023-149489OB-I00 (to G. L. and M. G.), “Ramón y Cajal” contract (RYC2022-035322-I) (to A. M.) and PIPF grant 2024PMF-PIPF-40 (to A. T.).

References:

- [1] Palà, M.; Ismagilova, A.; Moreno, A.; Plaza, J.; Ronda, J. C.; Galià, M.; Vares, L.; Lligadas, G. Thermoresponsive lactate amide acrylic polymers developed from PLA bags. *Polym. Chem.* 2025, 16, 1692-1703.
- [2] Bensabeh, N.; Moreno, A.; Roig, A.; Monaghan, O. R.; Ronda, J. C.; Cádiz, V.; Galià, M.; Howdle, S. M.; Lligadas, G.; Percec, V. Polyacrylates Derived from Biobased Ethyl Lactate Solvent via SET-LRP. *Biomacromolecules* 2019, 20, 2135-2147.

M 2-4 Incorporación de neumáticos al final de su vida útil en elastómeros termoplásticos y caracterización de los productos finales

M. Narvaez*, M. Montero, R. Navarro, J.L. Valentín

Institute of Polymer Science and Technology (CSIC) Juan de la Cierva, 3 – 28006 Madrid.

La gestión de los neumáticos al final de su vida útil supone un ambicioso ambiental a nivel mundial. Los neumáticos están compuestos por diferentes materiales haciendo que su separación y eliminación sea compleja.[1] El reciclado mecánico de neumáticos al final de su vida útil proporciona tres fracciones (acero, textil y polvo de caucho). El polvo de caucho puede utilizarse en diversas aplicaciones industriales, tales como suelas de zapatos, relleno de asfaltos, parques infantiles o relleno de campos de fútbol. [2] Sin embargo, debido al Reglamento (UE) 2023/2055, se implementarán restricciones en la aplicabilidad de este material reciclado, lo que obliga a encontrar otras aplicaciones donde incorporarlo.

Por ello, la incorporación de polvo de neumático al final de su vida útil en elastómeros termoplásticos se presenta como una alternativa a considerar para el desarrollo de materiales sostenibles. Estos materiales están compuestos por una matriz termoplástica, que aporta procesabilidad al material formado, y una red elastomérica dispersa en forma de esferas distribuidas de manera uniforme, proporcionando elasticidad al producto final. [3][4] Los elastómeros termoplásticos se utilizan en una amplia gama de aplicaciones, como en automoción, electrodomésticos o en construcción (sellos, juntas, perfiles de juntas y ventanas, instrumentos de cocina, mangas de protección y puertas), entre otros. [5]

En este trabajo, se abordó la incorporación del polvo de neumático fuera de su vida útil en productos termoplásticos para promover una gestión de residuos más sostenible. Se llevaron a cabo diversos tratamientos sobre el polvo de neumático con el fin de mejorar la adherencia de la interfase entre polvo de neumático y el caucho y propiedades del producto final. Además, se estudió la reprocesabilidad y las propiedades mecánicas de los productos finales arrojando resultados competentes a nivel industrial.

Palabras clave: sostenibilidad, elastómeros termoplásticos, neumáticos al final de su vida útil

Agradecimientos

Los autores agradecen el apoyo financiero prestado al Ministerio de Ciencia, Innovación y Universidades (PID2023-147542OB-I00, CPP2023-010769, y PREP2023-001425)

Referencias

- [1] Makadia, H.K.; Siegel, S.J. Poly Lactic-co-Glycolic Acid (PLGA) as Biodegradable Controlled Drug Delivery Carrier. *Polymers* **2011**, *3*, 1377-1397.
- [1] World Business Council for Sustainable Development. End-of-Life Tires: Business opportunities and a call to action. WBCSD, **2018**.
- [2] Asaro L, Gratton M, Seghar S, Hocine NA. Recycling of rubber wastes by devulcanization. *Resources Conservation And Recycling* **2018**, *133*:250-262.
- [3] Archibong FN, Sanusi OM, Médéric P, Hocine NA. An overview on the recycling of waste ground tyre rubbers in thermoplastic matrices: Effect of added fillers. *Resources Conservation And Recycling* **2021**, *175*:105894.
- [4] Fazli A, Rodrigue D. Waste Rubber Recycling: A Review on the Evolution and Properties of Thermoplastic Elastomers. *Materials* **2020**, *13*(3):782.
- [5] Whelan D. Thermoplastic elastomers. *Elsevier eBooks* 2016, 653-703.

M 2-5 Synthesis of polyurethanes from polyols derived from bacterially-sourced polyesters.

D. Marcos-Ríos*, R. Navarro, A. Marcos-Fernández

Institute of Polymer Science and Technology (CSIC), Madrid, España

Polyurethanes (PUs) are a family of thermoplastic and thermosetting polymers that contain a significant amount of urethane (-HN-COO-) groups. These polymers are derived from isocyanates and hydroxyl-containing compounds. Through the adjustment in chemical composition and production conditions, their properties are adjustable, and can take the form of thermoplastics, elastomers and flexible foams. Their multifunctionality, flexibility and mechanical strength make them widely applicable in industries as foams, adhesives and coatings but are also present in construction materials, paints and synthetic skin [1].

Despite all the above mentioned advantages, PUs have some drawbacks, specially regarding their sustainability. PUs raise concerns at two main levels: their manufacture and their recycling. At a manufacturing level, most PUs are petroleum-based, which contribute to the depletion of increasingly scarce fossil-fuels. Furthermore, at the end of their life-cycle, PUs mostly end up as energy source in incinerators (contributing to CO₂ emissions) or buried in landfills (which contributes to soil and ecosystem pollution) [1]. To overcome these issues, the obtention of bio-based monomers as raw materials for polyurethane synthesis emerges as a valuable solution. To this end, polyhydroxyalkanoates (PHAs) are considered attractive candidates because they are microbial polyesters that some gram-positive and gram-negative bacteria are able to produce and accumulate intracellularly. They exhibit various properties depending on the monomers type and composition and have been studied as a promising substitute for petroleum-based plastics [2].

The main objective of this work revolves about the obtention of bio-based polyols derived from PHAs as raw material for the preparation of polyurethanes. To this end, we obtain polyols of an adequate molecular weight through the transesterification of the PHA polymer. We have been able to modulate the molecular weight of the resulting polyols through the control of time, temperature and catalyst. Finally, we have been able to produce and characterize PUs from these polyols. The resulting materials could be used for advanced applications while partially mitigating the stated environmental challenges that PUs face.

Keywords: bio-based polyurethanes, sustainability, polyhydroxyalkanoates.

Acknowledgments/Agradecimientos

The authors acknowledge the Spanish Ministry of Science, Innovation and Universities for the financial support (PID2023-147542OB-I00, CPP2023-010769) and Consejo Superior de Investigaciones Científicas for the project (202460E171).

References/Referencias

- [1] Delavarde, A.; Savin, G.; Derkenne, P.; Boursier, M.; Morales-Cerrada, R.; Nottelet, B.; Pinaud, J.; Caillol, S. Sustainable Polyurethanes: Toward New Cutting-Edge Opportunities. *Prog Polym Sci* **2024**, *151*, 101805, doi:10.1016/j.progpolymsci.2024.101805.
- [2] Choi, S.Y.; Cho, I.J.; Lee, Y.; Kim, Y.; Kim, K.; Lee, S.Y. Microbial Polyhydroxyalkanoates and Nonnatural Polyesters. *Advanced Materials* **2020**, *32*, doi:10.1002/adma.201907138.

M 2-6 Reshape of EoL Polyester Glass Fibre Composites

M. Camacho-Iglesias¹, L. Germán¹, R. Seoane-Rivero², A. Iturmendi¹

¹Afiliación GAIKER Technology Centre, Basque Research and Technology Alliance (BRTA), Parque Tecnológico de Bizkaia, Edificio 202, 48170 Zamudio, Spain.

²Sustainable Process Engineering Group, Department of Chemical and Environmental Engineering, University of the Basque Country (UPV/EHU), Bilbao 48013, Spain.

There is an increasing demand for lightweight composite materials in sectors such as automotive, transportation and lightweight design in general. The rise of the circular economy, along with regulatory trends towards banning the disposal of these materials highlights the need for implementing R-strategies for such materials. Consequently, it is crucial to identify new technologies that encourage the circularity of composite materials and components while ensuring environmental sustainability and acceptable economic profitability. In this work new technology for remanufacturing and reusing glass fibre polyester composite components has been developed. This new technology uses pressure at high material deformation temperature to reshape curved components into flat parts through a press moulding process.

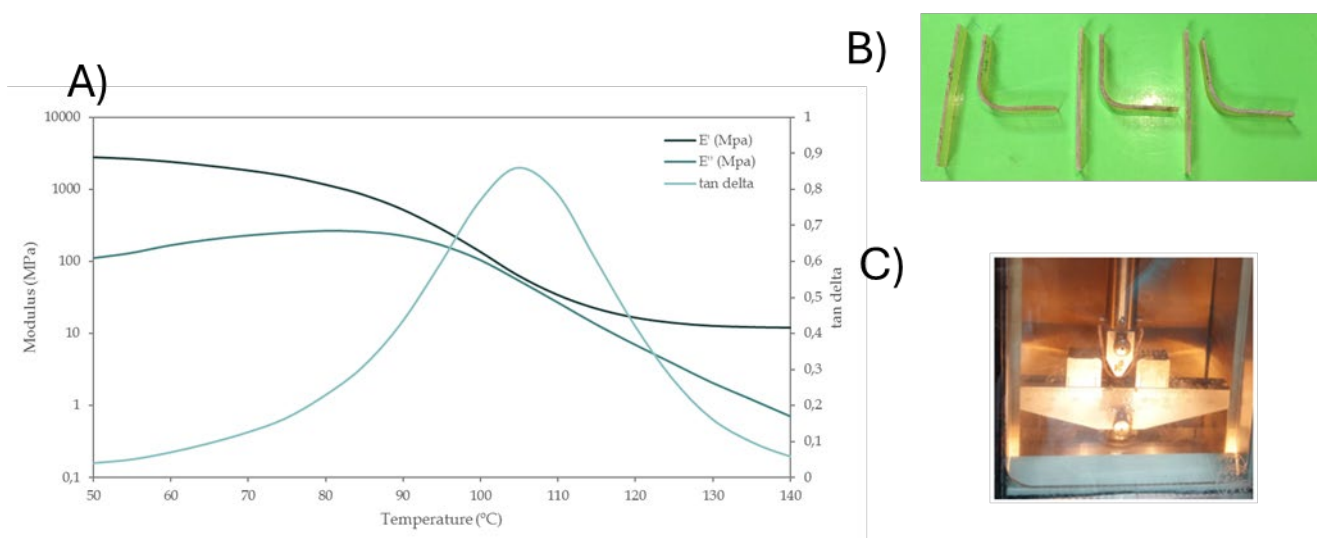


Figure 1. a) Polyester (DCPD) DMA analysis, b) crosslinked resin samples before and after reshaping and c) image of flexural test of pure crosslinked resin.

The moulding process allows transforming / the transformation of curved composites into flat parts without compromising the mechanical performance of GFC. Thus, the reshaped flat panels can be applied in different sectors such construction or transport. The study of the process involves the analysis of the viscoelastic behaviour of the crosslinked polyester resin by DMA (Dynamic Mechanical Analysis), as well as the effect of the temperature on the deformation capacity of both the crosslinked resin and the matrix reinforced with different glass fibre structures.

The shape recovery process after reshaping is a key factor to study as it is part of the reshape yield, and it is strongly affected by cooling parameters after thermodeformation.

Keywords/Palabras clave: Composite, recycling, reshape, thermoforming, polyester resin

M 3-1 Valorization of Lignin into Magnetic Biopolymer Nanoparticles for Catalytic Applications

Alberto Llopis-Lacruz, Francisco F. Pérez-Pla, Mario Culebras-Rubio, Rafael Muñoz-Espí

Institut de Ciència dels Materials (ICMUV), Universitat de València, Paterna, Spain

Lignin, the second most abundant biopolymer on Earth after cellulose, is a complex, aromatic macromolecule that has long been undervalued as a byproduct of the paper and biofuel industries. However, its unique chemical structure and renewable origin make it an attractive candidate for high-value material development. In this study, we explore an innovative strategy for lignin valorization by converting sulfonated lignin into hybrid nanoparticles through an inverse miniemulsion process. These lignin-based nanostructures not only promote circular resource use but also support the sustainable development of functional materials with tailored physicochemical properties.

The synthetic approach, partially adapted from a previously reported method by our group [1], involves the production of lignin-based hybrid nanoparticles incorporating magnetite, using a water-in-oil inverse miniemulsion method. The aqueous phase, which comprised sulfonated lignin, iron(II) chloride tetrahydrate, and iron(III) chloride hexahydrate, was emulsified into an organic phase containing polyglycerol polyricinoleate (PGPR) dissolved in a suitable non-polar solvent. High-shear ultrasonic homogenization was used to generate stable nanodroplets that encapsulated the iron salts and lignin. Upon addition of trimethylamine, magnetite formation was initiated by increasing the pH, while a diisocyanate cross-linker was simultaneously introduced to establish covalent linkages between lignin chains at the droplet interfaces. This dual-function reaction led to the formation of magnetite–lignin hybrid nanoparticles with controlled morphology and integrated magnetic functionality.

To demonstrate the potential of the prepared hybrid materials, we functionalized their surface with copper and assessed their performance in a model catalytic reaction: the reduction of 4-nitrophenol to 4-aminophenol. This transformation, relevant for both environmental remediation and pharmaceutical synthesis [2], was monitored via UV-Visible spectroscopy. Additionally, carbonization of the hybrid materials—either following or preceding copper reduction—was carried out to enhance surface reactivity. The carbonized systems exhibited superior catalytic activity, highlighting the potential of lignin-based nanomaterials for advanced applications in catalysis and environmental technology.

Keywords: heterogeneous catalysis, lignin, nanoparticle, valorization, carbonization

Acknowledgments

We thank the financial support by Generalitat Valenciana through a Consolidated Group Grant (CIAICO/2023/172).

References

- [1] Varol, H.S.; Álvarez-Bermúdez, O.; Dolcet, P.; Kuerbanjiang, B.; Gross, S.; Landfester, K.; Muñoz-Espí, R. *Langmuir*, 2016, 32, 13116-13123.
- [2] Mohami, R.; Shakeri, A.; Nasrollahzadeh, M. *Sep. Purif. Technol.* 2022, 285, 120373.

M 3-2 Crystallization behavior of Poly(3-hydroxybutyrate) systems with ATBC plasticizer and mesoporous silica, neat or ATBC modified

Cristina Pintón¹, Ernesto Pérez¹, María L. Cerrada¹, Enrique Blázquez-Blázquez¹

¹*Institute of Polymer Science and Technology, ICTP-CSIC, Madrid, Spain*

Global accumulation of petroleum-based plastics has reached critical levels, persisting in ecosystems for centuries and posing serious microplastic pollution risks to terrestrial and marine life. In this context, biodegradable polymers have emerged as promising alternatives to address this challenge. Among these, poly(3-hydroxybutyrate) (PHB) stands out for its complete microbial degradation within a few months under natural conditions after its useful life [1-2]. However, its widespread use is limited by its intrinsic brittleness and crystallization kinetics, which poses significant challenges for industrial processing.

Several approaches, such as the addition of nucleating agents, plasticizers or both, the blending of PHB with other polymers or the incorporation of suitable fillers, have been explored to overcome these limitations [3].

This work focuses on the effect of acetyl tributyl citrate (ATBC), used as a plasticizer, and of mesoporous silica particles, either neat or modified with ATBC, on the crystallization behaviour and mechanical properties of PHB. The materials studied were prepared by melt extrusion and included: (a) binary blends of PHB with different ATBC contents; (b) a binary composite of PHB with 5 wt% mesoporous silica particles; and (c) ternary systems in which the silica particles were functionalized with the same amounts of ATBC as in the binary blends. Films were then produced by compression moulding and cooled between water-cooled plates. The crystallization kinetics, thermal behaviour and mechanical performance of the resulting materials were analyzed in detail.

Thermal stability of these materials was determined by thermogravimetric analysis. This technique was also employed to assess and to confirm the actual content of minor components in the different formulations. Calorimetric results showed that ATBC retards crystallization, an effect that becomes more pronounced as its concentration increases. In addition, the melting temperature decreases as the ATBC content increases. Mesoporous silica particles acted as nucleating agents, shifting the crystallization temperature to slightly higher values. In ternary composites containing hybrid ATBC functionalized silica particles, crystallization occurred slightly faster than in the binary composite, due to the interaction between the nucleating action of the silica and the plasticizing effect of ATBC. Preliminary mechanical tests indicated a significant reduction in microhardness with the incorporation of ATBC, especially when the silica particles were functionalized with the plasticizer.

Keywords PHAs, plasticization, crystallization

Acknowledgments

This research was funded by MCIN/AEI/10.13039/501100011033, grant number PID2020-114930GB-I00. Authors are grateful to the Characterization Service and to the service of Physical-Chemistry Characterization of Polymers, both services at ICTP-CSIC.

References

- [1] Corre, Y.-M., Bruzard S., Audic J.-L., Grohens, Y., Morphology and functional properties of commercial polyhydroxyalkanoates: A comprehensive and comparative study. *Polym. Test.*, 2012, 31: 226-235.
- [2] Jihyeon K., Nevin S. G., Lindsey B. B., Jacqueline L., Kartek K. B., Shounak B., Joseph H. D., Sang Y. N., Hyun W. K., Chi Hoon P., Ghanshyam P., Carl N I., Babetta L. M., Kwan-Soo L., Biodegradation Studies of Polyhydroxybutyrate and Polyhydroxybutyrate-co-Polyhydroxyvalerate Films in Soil. *Int. J. Mol. Sci.*, 2023, 24(8):7638.
- [3] Blázquez-Blázquez, E., Barranco-García, R. Díez-Rodríguez T.M., Cerrada M.L., Pérez E., Combined Effects from Dual Incorporation of ATBC as Plasticizer and Mesoporous MCM-41 as Nucleating Agent on the PLA Isothermal Crystallization in environmentally-friendly Ternary Composite Systems. *Polymers* 2023; 15: 624.

M 3-3 Enhancing processability and properties of PLA/PBSA blends for packaging applications

I. Burgaña¹, V. Sebastián², G. Guerrica-Echevarría¹, I. Otaegi¹, N. Aranburu¹

¹POLYMAT and Department of Advanced Polymers and Materials: Physics, Chemistry and Technology (UPV/EHU), San Sebastian, Spain

²School of Engineering and Architecture (EINA), University of Zaragoza, Zaragoza, Spain

The growing use of biopolymers derived from renewable sources has led to the Polylactic acid (PLA), one of the best regarded due to its good biodegradability, mechanical properties and processability, to be highly researched. However, its low ductility limits its usage in the film production for packaging applications[1]. Blending it with Poly(butylene succinate-co-adipate) (PBSA), an aliphatic biodegradable polymer with good ductility and processability, has been studied as a potential solution to this problem[2]. Nevertheless, the film blowing process was found to be unachievable for the 80/20 PLA/PBSA blend, one of the most promising compositions, possibly due to the low compatibility between the components and the poor melt strength of the system. To overcome these issues, the incorporation of two different additives was studied, either individually or simultaneously: Paraloid BPMS 265, a melt strength enhancer; and Glyplast OLA5028, a lactic acid oligomer that can act as a chain extender. The addition of either of the additives significantly improved the processability, and films with a nominal thickness of 30 μm were fabricated successfully. The incorporation of the melt strength enhancer led to an increase in the melt strength. Ductility was also improved; however, Young's modulus and yield strength were negatively affected. In contrast, the addition of the oligomer caused an improvement of the melt strength and the Young's modulus and yield strength, whereas ductility decreased. Their simultaneous addition produced heterogeneous results attributable to the individual contributions of each additive, such as a smaller increase in ductility. The addition of natural reinforcements, such as cellulose, to polymeric blends has been widely studied over the years[3]. In this work, cellulose was added to the aforementioned blends with the aim of balancing their mechanical properties, and improving their tear strength and barrier properties. A surface modification using sunflower oil was carried out to improve the compatibility and, hence, the dispersion of the cellulose in the blends[4].

Keywords PLA, PBSA, blown-film extrusion, structure-properties relationship

Acknowledgments

The authors acknowledge the Basque Government for the grant awarded (project n. IT1503-22). I. Burgaña also thanks the University of the Basque Country (UPV/EHU) for his PhD scholarship.

References/Referencias

- [1] Diaz, C.; Kim, S.; Pao, H. Film Performance of Poly(lactic acid) Blends for Packaging Applications. *The Journal of Applied Poultry Research* 2016, 8, 43-51.
- [2] Martinez, J. PLA/PBSA biopolíester nahasteetan oinarritutako filmeak; konposizioaren eragina morfología, hesi-propietate eta propietate termiko eta mekanikoetan. Degree Final Project (UPV/EHU) 2023.
- [3] Karkhanis, S.; Stark, N.; Sabo, R.; Matuana, L. Potential of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films for improving the shelf-life of a dry food product. *Food Packaging and Shelf Life* 2021, 29, 100689.
- [4] Rathnayake, W.; Karunanayake, L.; Samarasekara, A.; Amarasinghe, D.; Sunflower oil-based MCC surface modification to achieve improved thermomechanical properties of a polypropylene composite. *Cellulose* 2020, 27, 4355-4371.

M 3-4 Sustainable and Self-Healable Rubbers: A New Perspective in Materials Science

J.C. Chicharro^{1*}, M. Hernández¹, R. Verdejo¹

¹*Institute of Polymer Science and Technology (ICTP-CSIC), Madrid, Spain.*

The widespread use of rubber in various industries, from automotive to consumer goods, has led to significant environmental concerns. Conventional rubber materials are typically derived from non-renewable petroleum-based sources and are vulcanized through irreversible chemical processes, making them difficult to recycle or degrade. As a result, end-of-life rubber products often accumulate in landfills or are incinerated, contributing to pollution and greenhouse gas emissions. The lack of efficient recycling methods and the persistence of rubber waste in the environment underscore the urgent need for sustainable alternatives that combine performance with environmental responsibility.

This work explores a novel approach to develop sustainable self-healing elastomers based on epoxidized natural rubber (ENR as the polymer matrix, using itaconic acid as a bio-based vulcanizing agent and a transesterification reaction promoter for self-healing. The focus is to achieve self-repairing properties to enhance environmental sustainability.

Traditional vulcanization methods using sulfur and radical crosslinking using dicumyl peroxide (DCP) are compared with an alternative strategy based on bio-derived compounds. Sulfur, the industry standard, is used as a benchmark, while DCP is included for its fast-curing kinetics. Itaconic acid, a bio-derived diacid, offers a sustainable alternative for vulcanization while introducing the potential for self-healing through transesterification reactions using zinc acetate.

The study details the synthesis process for the itaconic acid-based elastomers and investigates the impact of this approach on the material's mechanical properties, self-healing efficiency, and environmental footprint. A comparative analysis is presented, evaluating stress-strain behavior, healing response under mechanical damage, and other characterization techniques.

This research aims to demonstrate the feasibility of using itaconic acid for both vulcanization and self-healing in elastomers. By replacing traditional curing agents with a bio-based alternative and introducing a self-repair mechanism, the research contributes to the development of sustainable and repairable elastomers with reduced environmental impact. The findings hold promise for the advancement of green materials science and the creation of high-performance, self-healing elastomers for various applications.

Keywords: Rubber, Itaconic acid, Self-Healing.

M 3-5 Designing Sustainable TPEs: From Bio-Based Inputs to Functional Performance

Itziar Mas Giner¹, Brais Taibo Puente¹, Raquel Verdejo¹, Marianella Hernández Santana¹

¹*Institute of Polymer Science and Technology (ICTP), CSIC, Madrid, Spain.*

The thermoplastic elastomers (TPEs) industry has grown significantly, becoming key materials in sectors such as automotive, footwear, biomedicine, and consumer goods. This exponential expansion has also led to a proportional increase in waste. Elastomeric materials are typically formulated with additives such as fillers, antidegradants, and processing oils, which limit their recyclability and hinder reuse. As a result, the development of recyclable and self-healing TPEs based on natural sources or bio-based ingredients has gained increasing attention, for their potential to reduce environmental impact without compromising performance. This work focuses on the development of sustainable TPEs using natural rubber-based elastomers and bio-based fillers. The study begins with synthetic elastomers to assess the influence of processing methods. Then, a comparative analysis is carried out using three types of elastomers—polyisoprene rubber (IR), natural rubber (NR), and epoxidized natural rubber (ENR)—combined with polycaprolactone (PCL) as a biodegradable thermoplastic phase at different ratios. Cellulose and lignin, obtained from agricultural or forestry residues, are used as reinforcing agents to enhance the sustainability profile of the materials. This approach enables a systematic evaluation of how elastomer type, composition, and bio-based filler affect the structural and functional performance of the final materials.

Preliminary results demonstrate promising self-healing capabilities alongside reprocessability. In particular, the ENR compounds with cellulose are capable of recovering 80% of the mechanical performance at low deformations and 60% at the breaking point. These findings contribute valuable insights into the design of recyclable rubber materials based on renewable components, advancing the development of more circular and sustainable materials.

Keywords: Thermoplastic elastomers, Self-healing, Natural rubber, Bio-based fillers, Sustainability

M 3-6 Pectin-Based Hydrogels for the Removal of Pharmaceutical Pollutants

C. Iacovone^{1,2,3*}, F. Coin^{2,3}, S. Goyanes^{4,5}, S. Cerveny^{1,2}

¹Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, San Sebastián 20018, Spain.

²Centro de Física de Materiales (CSIC, UPV/EHU)-Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, San Sebastián 20018, Spain.

³Departamento Polímeros y Materiales Avanzados: Física, Química y Tecnología, University of the Basque Country (UPV/EHU), P. Manuel Lardizabal 3, 20018 San Sebastián, Spain.

⁴Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Física, Laboratorio de Polímeros y Materiales Compuestos, Ciudad Autónoma de Buenos Aires 1428, Argentina

⁵CONICET - Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Ciudad Autónoma de Buenos Aires 1428, Argentina

Pharmaceuticals in water poses serious risks to ecosystems and human health. Among water treatment methods, adsorption offers a practical and environmentally friendly solution for removing pollutants from wastewater[1]. Pectin, an anionic polysaccharide composed of α -(1 \rightarrow 4)-linked D-galacturonic acid (Gal) and extracted from fruit peels, has shown great potential as a tunable adsorbent for emerging contaminants, particularly heavy metals. However, its use for organic compounds is less studied [2]. This work investigates the adsorption performance of different pharmaceuticals using pectin-based hydrogels crosslinked with calcium at different stoichiometric ratios $R=[Ca^{2+}]/[Gal]$. Initially, the effect of crosslinking density on adsorption was examined, where the system with the lowest calcium content demonstrated the highest absorption capacity (Fig. 1a). Notable interactions with the pharmaceuticals are observed, with enhanced antibiotics adsorption (Fig. 1b). The highest adsorption capacity (dose: 1 g/L, pH 7) was observed for ciprofloxacin, with a removal efficiency of 90% and adsorption capacity of 45 mg/g. However, the hydrogel exhibited higher adsorption capacity, adsorbing over 110 mg/g through cumulative reuses. The hydrogel also revealed a rapid adsorption process best described by the pseudo-first-order (PFO) model (Fig. 1c), suggesting that the adsorption mechanism is predominantly driven by electrostatic interactions or physisorption. Additionally, the hydrogels allow for reuse through desorption (with contaminant recovery) and subsequent re-adsorption, where both processes maintained efficiencies above 80% after three consecutive cycles. Given the demonstrated performance, pectin-based hydrogels are promising, sustainable, and cost-effective adsorbents for water remediation applications.

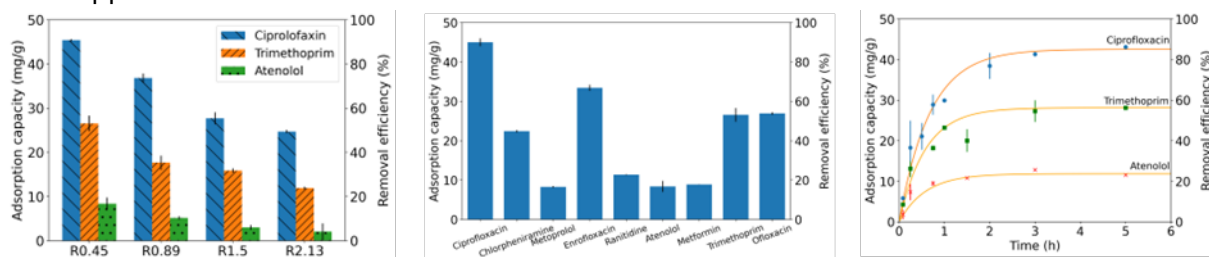


Figure 1: Adsorption capacity and removal efficiency of (a) three pharmaceuticals with the developed hydrogels, (b) several pharmaceuticals with R0.45 system, and (c) kinetics of R0.45 fitted by the PFO model. All experiments were carried out using a dose of 1 g/L and a pH of 7.

Keywords: Adsorption, Pectin, Pharmaceuticals, Water pollution

References

- [1] Kainth, S.; Sharma, P.; Pandey, O.P. Green sorbents from agricultural wastes: A review of sustainable adsorption materials. *Applied Surface Science Advances*, **2024**, *19*, 100562.
- [2] Martínez-Sabando, J.; Coin, F.; Melillo, J.H.; Goyanes, S.; Cerveny, S. A review of pectin-based material for applications in water treatment. *Materials*, **2023**, *16*(6), 2207.

M 4-1 Electrospinning of Cashew Gum/Polyvinyl Alcohol Blends. From Nanofibers to Flexible Thin Films with High Oxygen Barrier for Sustainable Food Packaging

M.Grumi^{1*}, A. Kramar¹, C. Prieto¹, L. Cabedo², J.M. Lagarón¹

¹Novel Materials and Nanotechnology Group, Institute of Agrochemistry and Food Technology (IATA), Spanish Council for Scientific Research (CSIC), Paterna (Valencia), Spain

²Polymers and Advanced Materials Group (PIMA), School of Technology and Experimental Sciences, Universitat Jaume I (UJI), Castellón, Spain

The global issue of plastic pollution and the lack of biodegradability and scarcity of petroleum sources have prompted worldwide research seeking biodegradable and renewable alternatives to fossil-based polymers for flexible packaging applications [1]. In this context, cashew gum, an agro-based, inexpensive, and biodegradable polysaccharide derived from *Anacardium occidentale* trees [2], emerges as a suitable candidate. This study focused on the development of electrospun nanofibers from cashew gum/polyvinyl alcohol blends, and different polymer ratios were considered. The obtained electrospun fiber mats were subsequently converted into thin, transparent, continuous, and flexible films through a thermal annealing post-treatment. The obtained films were characterized in terms of morphological, optical, thermal, mechanical, and water vapor and oxygen barrier properties. The films exhibited high optical clarity, transparency, and good thermal stability. Notably, they demonstrated exceptionally high oxygen barrier properties, comparable to those of conventional fossil-based, non-biodegradable plastics [3]. Oxygen barrier performance improved with increasing cashew gum content in the formulations, highlighting the role of this biopolymer in enhancing film functionality. Furthermore, outstanding elongation at break and remarkable flexibility were achieved. These results not only confirmed the great suitability of the electrospinning technique to produce cashew gum/polyvinyl alcohol-based materials, but they also positioned the obtained high oxygen barrier polysaccharide-based films as promising candidates in the sector of food packaging materials.

Keywords: high barrier biopolymers, cashew gum, PVOH, electrospinning, food packaging

Acknowledgments

This research was funded by the grant PID2021-128749OB-C31 from MCIU/AEI (10.13039/501100011033), and by ERDF A way of making Europe. M. Grumi acknowledges the MCIU for the FPI fellowship (PRE2022-103132). The authors would like to acknowledge the Joint Unit IATA (CSIC)-UJI in "Polymer Technology" and the CSIC-PTI SusPlast. The Accreditation of IATA (CSIC) as a Center of Excellence Severo Ochoa (CEX2021-001189-S), funded by MCIU/AEI/10.13039/501100011033, is also fully acknowledged.

References

- [1] Rosenboom, J.G.; Langer, R.; Traverso, G. Bioplastics for a Circular Economy. *Nat. Rev. Mater.* **2022**, *7*, 117–137.
- [2] Grumi, M.; Prieto, C.; Furtado, R.F.; Cheng, H.N.; Biswas, A.; Limbo, S.; Lagarón, J.M. On the Unique Morphology and Elastic Properties of Multi-Jet Electrospun Cashew Gum-Based Fiber Mats. *Polymers* **2024**, *16*, 1355.
- [3] Lagarón, J.M. Multifunctional and Nanoreinforced Polymers for Food Packaging. In *Multifunctional and Nanoreinforced Polymers for Food Packaging*; Lagarón, J.M., Ed.; Woodhead Publishing **2011**, *1*, 1–28.

M 4-2 Valorization of Marine Resources for the Development of Green Plastics: Sustainable Extraction and Formulation of Active and Edible Packaging

Andrés Felipe Vélez¹, Estíbaliz Hernaez¹, Leyre Pérez-Álvarez^{1,2}, Leire Ruiz-Rubio^{1,2}

¹*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Física, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

²*Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.*

The massive production and accumulation of petroleum-based plastics represent one of the most pressing challenges to environmental sustainability, particularly in the food industry. To address this issue, the European SEAREFINERY project promotes a transition toward a blue bioeconomy by encouraging the comprehensive use of marine resources—including red, green, and brown algae as well as other aquatic by-products—for the development of functional and biodegradable green plastics.

My doctoral research focuses on the sustainable extraction of biopolymers (such as alginate, chitosan, carrageenan, agar, among others) and bioactive compounds with antioxidant, antimicrobial, or functional properties from a wide variety of marine resources. To this end, both conventional methods and emerging extraction technologies are being employed, including ultrasound, microwave, and subcritical and supercritical fluids, with the aim of optimizing yield, energy efficiency, and functional quality of the extracts.

These extracted materials are being used to formulate innovative packaging solutions such as edible coatings, active films, and biodegradable nanofibers. Initial tests have shown that coatings based on chitosan and natural bio-additives (carvacrol, curcumin, phenolic extracts) significantly extend the shelf life of fresh fruits. Moreover, films developed from modified biopolymers exhibit structural and functional improvements, as confirmed by FTIR spectroscopy. Future stages will include thermal, mechanical, and biodegradability tests.

This line of research, with a strong interdisciplinary component, aims not only to create tangible solutions for the food industry but also to demonstrate the real potential of marine biopolymers as viable substitutes for petrochemical plastics. From a personal perspective, this project allows me to actively contribute to a more sustainable production model aligned with the principles of the circular bioeconomy, and it reaffirms the power of science to provide concrete alternatives to today's environmental challenges.

Keywords: marine biopolymers, sustainable extraction, green plastics, blue economy, biodegradable packaging.

Acknowledgments

The author acknowledges the support of the University of the Basque Country (UPV/EHU) and the SEAREFINERY project, funded by the SBEP (AEI and European Union), for providing the resources and framework for this research.

M 4-3 Biopolymer-Based Microgel Systems for Encapsulation of Nutrients and Microorganisms in Soil Remediation

S. Muñana-González^{1*}, A. Galdames¹, M. Ostovar¹, Estíbaliz Hernaez¹, J.L.Vilas-Vilela^{1,2}, L. Pérez-Álvarez^{1,2}, L. Ruiz-Rubio^{1,2}

¹*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Física, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

²*Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.,*

Soil bioremediation uses the metabolic activity of microorganisms to degrade environmental pollutants, offering a low-impact and cost-effective alternative to conventional remediation methods. However, its success is often limited by the bioavailability of essential nutrients and the survival of beneficial microbial communities in complex soil environments [1]. Encapsulation technologies present a promising route to overcome these limitations by enabling localized, sustained delivery of bioactive agents. Biopolymers are emerging as key materials in the development of sustainable functional systems for environmental applications [2]. In this work, we present the synthesis and characterization of microgel carriers based on natural polysaccharides, engineered for the encapsulation and controlled release of nutrients and microorganisms in soil bioremediation.

Using alginate as the primary biopolymer (chosen for its polyelectrolytic behavior, gel-forming ability under mild ionic conditions, and environmental degradability), we developed two distinct encapsulation strategies: electrostatic dripping assisted by frequency and voltage modulation, and a custom-designed oil-in-water (O/W) microfluidic system. These techniques allowed precise control over microgel size, morphology, and encapsulation efficiency, demonstrating the tunability of natural polymer-based carriers through process engineering. The resulting hydrogel systems exhibited promising characteristics for use in soil environments, including water retention, diffusion control, and mechanical integrity. Our findings highlight how biopolymer structure and crosslinking conditions directly influence the functionality of encapsulation systems, reinforcing the role of polymer science in designing eco-friendly materials for environmental biotechnology.

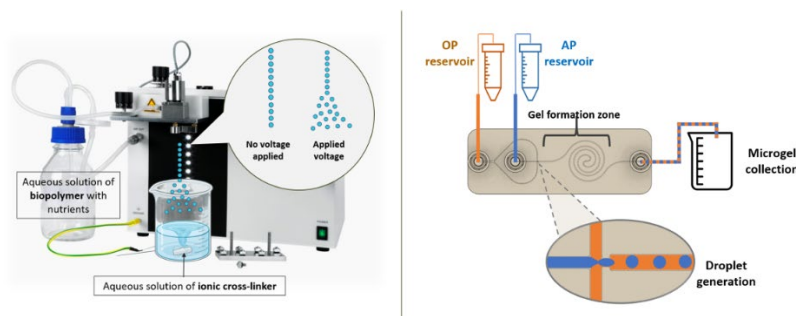


Figure 1. Microgel synthesis through electrostatic dispersion (left) and O/W microfluidic system (right).

Acknowledgments

This research was funded by the European Union's Horizon Europe (SYMBIOREM Grant agreement ID: 101060361) and Grupos Consolidados (IT1756-22).

References:

- [1] Mujtaba M. et al. 2021. Biopolymer Based Nanofertilizers Applications in Abiotic Stress (Drought and Salinity) Control. In: Jogaiah S., editor. *Advances in Nano-Fertilizers and Nano-Pesticides in Agriculture: A Smart Delivery System for Crop Improvement*. Woodhead Publishing. 85-110..
- [2] Jiménez-Arias D. et al. 2023. Encapsulation with Natural Polymers to Improve the Properties of Biostimulants in Agriculture. *Plants*. 12(1):55-74

M 4-4 Valorization of Polymeric and Agroforestry Residues and By-products (Biomass) for the Development of Materials Used in Sports Surfaces

V.D. Ortiz Miranda^{1*}, E. López Moya², M.M. Sánchez-Redondo¹, R. Moreno Martínez¹, C. Morales¹

¹IGOID-SPORTEC SL, Toledo, Spain

²University of Castilla-La Mancha, Toledo, Spain

Artificial turf sports fields are the most widely implemented surface in Europe, with over 16,000 installations and steady growth. However, they present significant environmental challenges due to their high reliance on virgin plastics and the release of microplastics. The recent EU Regulation (2023/2055) bans intentionally added microplastics, directly impacting the use of polymeric infill materials in artificial turf as of 2031.

Currently, there are no commercially viable alternatives to the use of virgin plastics in sports surfaces such as artificial turf. However, recent studies [2] and European projects such as LIFET4C and Compolive have demonstrated the potential of biobased composites that combine recycled plastics with plant biomass (cellulose, lignin, etc.) as reinforcement or additive. In this scenario, the urgent need arises to develop alternative materials based on circular economy principles. This study presents the formulation and characterization of biobased compounds made from recycled low-density polyethylene (LDPE) named ALFATEN 200 and plant biomass (olive pruning and guayule), in 10% and 20% proportions, with and without additives (0.1% graphene oxide, GrOx). Compounds in pellet form have been produced through an extrusion process using a twin-screw extruder. Thermal, mechanical, and processability properties were analyzed.

The results show that adding biomass significantly improves material stiffness (up to 281 MPa elastic modulus with 20% olive), with a proportional reduction in impact resistance (down to 15–16 kJ/m²). The GrOx additive helped partially recover that loss, reaching 48.2 kJ/m². The melt flow index increased up to 0.64 g/10 min, enhancing extrusion processing. Both rebound resilience and crystallinity slightly decreased but remained within functional ranges.

The compounds were successfully processed into pellets and components (technical infill and elastic base layers). Performance testing following FIFA and UNE-EN 17435:2022 standards showed impact absorption above 30% and a critical fall height (CFH) \geq 0.6 m, validating their suitability as functional components in sustainable sports surfaces.

Keywords: Recycled Polyethylene, Agroforestry Residues, Artificial Turf.

Acknowledgments

The results of this study are part of the support provided by PINVE-45-0023/2021 and PINVE-45-0006/2023 under the Investigo Program of the Regional Government of Castilla-La Mancha, funded by the European Union, Next Generation EU.

References

- [1] Sánchez-Sánchez, J.; García-Unanue, J.; Felipe, J. L., Jiménez-Reyes, P.; Viejo-Romero, D.; Gómez-López, M; Gallardo, L. Physical and physiological responses of amateur football players on third-generation artificial turf systems during simulated game situations. *Journal of Strength and Conditioning Research* **2016**, 30 (11), 3165-3177.
- [2] Rodríguez-Liébana, J. A.; Robles-Solano, E.; Jurado-Contreras, S.; Morillas-Gutiérrez, F.; Moya, A. J.; Mateo, Navas-Martos, F.J.; S.; La Rubia, M. D. Production and characterization of cellulose acetate using olive tree pruning biomass as feedstock. *Biofuels, Bioproducts and Biorefining* **2024**, 18, 865–882.

M 4-5 Lignin Microcapsules for Controlled Release of Plant Protection Products

Jose Huerta-Recasens¹, Julieta Cantarella-Otero^{1,2}, Amparo Cháfer³, Clara M. Gómez¹, Francisco F. Pérez-Pla¹, Mario Culebras^{1*}, Rafael Muñoz-Espí^{1*}.

¹*Institute of Materials Science (ICMUV), University of Valencia, Paterna, Valencia, Spain.*

²*School of Engineering, University of Limerick; Bernal Institute, University of Limerick, Limerick, Ireland.*

³*Research Group in Materials Technology and Sustainability (MATS), Department of Chemical Engineering, School of Engineering, Universitat de València, Burjassot, Spain.*

The growing environmental concerns linked to the intensive use of plant protection products (PPPs) and fossil-based inputs have underscored the urgent need for sustainable and innovative strategies in agriculture.¹ On the other hand, the pulp and paper industry produces millions of tons of lignin annually, a largely undervalued byproduct that is predominantly disposed of through combustion. Unlocking the potential of lignin through effective valorization pathways is therefore essential for fostering circular bioeconomy models. One of the most promising approaches is the use of lignin as a carrier material for the encapsulation of agrochemicals, which offers improved protection, enhanced stability, and controlled release of active compounds under environmentally stressful conditions.²

In this work, kraft lignin was employed as a biodegradable matrix to encapsulate difenoconazole, a widely used broad-spectrum fungicide, through spray drying. The resulting microcapsules, evaluated by scanning electron microscopy (SEM) exhibited spherical morphology, while FTIR confirmed the chemical incorporation of difenoconazole into the lignin structure. The encapsulation efficiency was evaluated by thermogravimetric analysis (TGA) and liquid chromatography coupled with mass spectrometry (HPLC-MS) analyses reached and was nearly 100% as determined. Controlled release studies conducted at various pH levels using UV-Vis spectroscopy demonstrated a pH-dependent release profile, with enhanced diffusion under alkaline conditions. The results obtained in this study confirm the potential of lignin as a renewable and functional encapsulating agent for controlled-release agrochemical formulations, offering a dual benefit: improving crop protection efficiency while valorizing an abundant industrial byproduct.

Keywords: Lignin, encapsulation, biopolymer, valorization.

Acknowledgments

The Spanish Ministry of Science, Innovation and Universities is acknowledged for financial support through the Program “Strategic Projects Oriented to the Ecological Transition and the Digital Transition” (gran no. TED2021-131134B-C21) funded by MCIN/AEI/10.13039/501100011033 and the European Union (NextGenerationEU/PRTR). The kraft-type lignin was kindly provided by ENCE Energía y Celulosa SA.

References

- [1] Alengebawy, A.; Abdelkhalek, S. T.; Qureshi, S. R.; Wang, M.-Q. Heavy Metals and Pesticides Toxicity in Agricultural Soil and Plants: Ecological Risks and Human Health Implications. *Toxics* **2021**, 9 (3), 42.
- [2] Guleria, G. et. Al. Nanotechnology for Sustainable Agro-Food Systems: The Need and Role of Nanoparticles in Protecting Plants and Improving Crop Productivity. *Plant Physiology and Biochemistry*. **2023**, 194, 533–549.

X 1-1 Controlling latex particle coagulation

S. González¹, M. Aguirre¹

¹ POLYMAT and Applied Chemistry Department, University of the Basque Country UPV/EHU, Donostia-San Sebastian, Spain

During the synthesis of polymer latexes by emulsion polymerization, stability of the polymer particles is desired avoiding coagulation during the polymerization process. However, once the polymer latex is synthesized, its control coagulation is needed to obtain polymer powders for certain applications such as additive manufacturing or impact modifiers. These powder materials can be used to create complex shapes in different fields, such as automotive, aerospace, medical biology and so on. [1]

In the coagulation experiments, the measurement of the particle size (dp) and observation of the morphology entails off-line time-consuming measurement techniques. Apart from this, to have a track of the dp during the coagulation experiment manual samples must be taken. This implies a less accurate measurement, as the particle size of the sample continues growing and the dp is no longer accurate for the time of sampling. To avoid that, in this work an in-line particle size measurement technique, the Photon Density Wave spectroscopy (PDWS) has been introduced to measure the dp during the physical-chemical coagulation experiment. By introducing a probe directly into the process reaction medium, the fibres inside each cannula will work as emission/detection points at different frequencies, making possible to obtain the dp after software calculations. [2]

In this work, the coagulation of polymethyl methacrylate (PMMA) has been performed using sodium chloride and calcium chloride. The effect of different salts and concentration, different temperatures and different salt addition speeds have been studied during the coagulation experiment. Thanks to the PDWS, it is possible to detect at which salt concentration the coagulation starts, which is helpful for a further understanding of the coagulation parameters and to reduce the amount of coagulant needed.

Keywords/Palabras clave: Colloidal dispersion, coagulation, PMMA, PDWS.

References

[1] Shi, Y.; Yan, C.; Zhou, Y.; Wu, J.; Wang, Y.; Yu, S.; Chen, Y. Polymer Materials for Additive Manufacturing—Powder Materials. In *Materials for Additive Manufacturing*; Elsevier, **2021**, 9–189. <https://doi.org/10.1016/B978-0-12-819302-0.00002-X>

[2] Aspiazu, U. O.; Paulis, M.; Leiza, J. R. Photon Density Wave Spectroscopy to Monitor the Particle Size in Seeded Semibatch Emulsion Copolymerization Reactions. *Chemical Engineering Journal* **2024**, 483. <https://doi.org/10.1016/j.cej.2024.149292>

X 1-2 Self-nucleation promotes the formation of the most stable crystal polymorph in triple polymorphic polythioethers

L. Unanue¹, J.L. Olmedo-Martínez², A.J. Müller^{1,3}

¹University of the Basque Country UPV/EHU, Donostia-San Sebastián, Spain.

²Centro de Investigación en TecnoloXías Navais e Industriais (CITENI), Ferrol, Spain.

³Ikerbasque, Bilbao, Spain.

This work analyzed the self-nucleation of three different alternating polythioether homopolymers, DMDS-*alt*-DVE, DMDS-*alt*-TEGDVE and DMDS-*alt*-BDDVE. These materials' structure consists of the same sulphur-containing part and differ in the ether functionality (see Figure 1). Previous work^{1,2} studied how the chemical structure affected the morphology and crystallization kinetics of these polythioethers and showed that these materials are polymorphic. Depending on the cooling and heating rates, up to three different polymorphs were discovered for each polythioether, the very low-temperature melting phase (VL-Tm), the low-temperature melting phase (L-Tm) and the high-temperature melting phase (H-Tm). This work studies the melt memory and how it is affected by polymorphism via self-nucleation experiments performed by Differential Scanning Calorimetry (DSC) and Polarized Light Optical Microscopy (PLOM). Figure 1 shows the self-nucleation *Domains* for each of the polymers. DSC experiments showed that self-nuclei could be formed from a particular polymorph, but they promote the crystallization of a different, more thermodynamically stable polymorph.

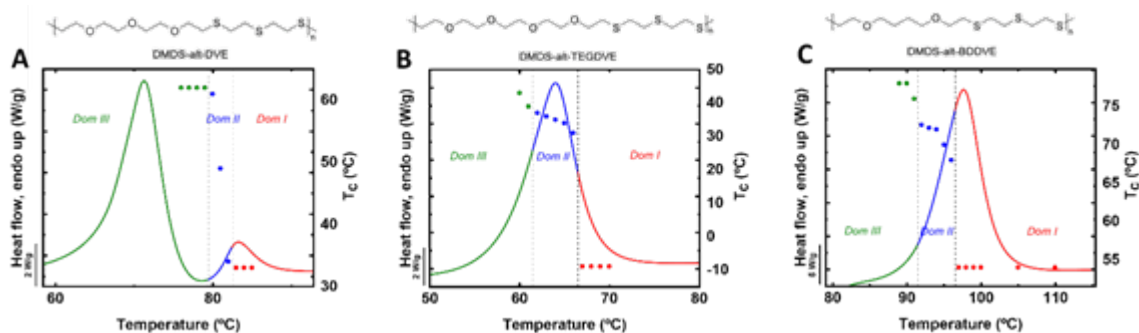


Figure 1. Chemical structure and self-nucleation *Domains* on top of non-isothermal standard DSC heating scan for: A) DMDS-*alt*-DVE, B) DMDS-*alt*-TEGDVE and C) DMDS-*alt*-BDDVE.

Keywords: self-nucleation, self-seeding, polymorphism, polythioether.

Acknowledgments

We acknowledge support from the María de Maeztu Excellence Unit CEX2023-001303-M funded by MCIN/AEI/10.13039/501100011033. In addition, this work has received funding from the Department of Education of Basque Government through grant no. IT1503-2.

References/Referencias

- [1] Pirela, V; Elgoyhen, J.; et al. Unraveling the Complex Polymorphic Crystallization Behavior of the Alternating Copolymer DMDS-*alt*-DVE. *ACS Applied Polymer Materials* **2023**, 5 (7), 5260-5269.
- [2] Pirela, V; Unanue, L.; Elgoyhen, J.; et al. Effect of chemical structure on the crystallization kinetics of triple polymorphic high-sulfur-content polythioethers. *European Polymer Journal*, **2025**, 225, 113721.

X 1-3 Biopoliésteres hiperramificados funcionalizados como aditivos sostenibles en formulaciones de PHA

I. Pisa-Ripoll^{1*}, E. Sánchez-Safont¹, B. Altava¹, J. Gámez-Pérez¹, L. Cabedo¹

¹Universitat Jaume I, Castellón de la Plana, España

Los biopoliésteres representan una alternativa sostenible a los polímeros convencionales debido a su biodegradabilidad, pero su aplicación industrial aún enfrenta limitaciones, particularmente en el caso de los polihidroxialcanoatos (PHA), cuya baja tenacidad restringe su uso. Para superar estos desafíos, una estrategia eficaz es el uso de aditivos que mejoren sus propiedades mecánicas sin comprometer el carácter biodegradable.

En este contexto, los polímeros dendríticos, y en particular, los polímeros hiperramificados (HP) destacan por su arquitectura altamente ramificada, alta densidad funcional y facilidad de síntesis, lo que les convierte en candidatos ideales como aditivos [1]. Este trabajo se centra en la síntesis, funcionalización y uso de biopoliésteres hiperramificados (HBBPE, *Hyperbranched Biopolyesters*) como aditivos biodegradables, soportados sobre celulosa microcristalina (MCC) y otras plataformas naturales [2], con el objetivo de mejorar la tenacidad de los PHA manteniendo su sostenibilidad y biodegradabilidad.

Los HBBPE se sintetizaron mediante la reacción de ácido 2,2-bis(hidroximetil)propiónico con MCC en presencia de ácido p-toluenosulfónico (p-TSA), seguida de funcionalización que permitió introducir cadenas lineales con grupos hidroxilo terminales provenientes de la caprolactona. La caracterización mediante FTIR, RMN, DSC y TGA confirmó la obtención y modificación estructural de los polímeros, así como la incorporación de caprolactona, con una mayor proporción de polímero lineal respecto a ramificado. Los compuestos obtenidos mostraron tener un efecto positivo en la mejora de la tenacidad del PHBV, evidenciada por la aparición de rotura post-cedencia y una mayor deformación plástica, además de una ligera reducción en su cristalinidad, sin comprometer su biodegradabilidad.

Este planteamiento presenta una solución innovadora y sostenible para superar las limitaciones mecánicas de los biopoliésteres convencionales, en particular su procesabilidad, y ampliando así su potencial uso en aplicaciones técnicas.

Palabras clave: polímeros hiperramificados, celulosa, tenacidad.

Agradecimientos

Trabajo financiado por MCIN/AEI/10.13039/501100011033/ y por FEDER Una manera de hacer Europa, proyecto número PID2021-128749OB-C32 y a la Cátedra UBE de Plásticos Sostenibles, proyecto número DESID/PR422-D21I63301215454711.

Referencias

- [1] Han, X.; Han, Y.; Jin, Y.; Wang, Z.; Tian, H.; Huang, J.; et al. Microcrystalline cellulose grafted hyperbranched polyester for PHBV/bio-based elastomer composites. *Int. J. Biol. Macromol.* **2023**, 242.
- [2] Piroonpan, T.; Booncharoen, K.; Pasanphan, W. Sugar-Core Synthesized Multibranching Poly(lactic Acid) and Its Diacrylate Blends as a UV LED-Curable Coating with Enhanced Toughness and Performance. *ACS Sustainable Chem. Eng.* **2022**, 10, 17027-17042.

X 1-4 Amphiphilic cyclic branched polyglycerols: synthesis and evaluation as drug carriers

E. Gómez Urreizti^{1,2} and F. Barroso-Bujans^{1,2,3}

¹Donostia International Physics Center (DIPC), Donostia-San Sebastián, Spain.

²Centro de Física de Materiales (CFM-MPC), Donostia-San Sebastián, Spain.

³KERBASQUE – Basque Foundation for Science, Bilbao, Spain.

The polymerization of glycidol (Gly) using tris(pentafluorophenyl)borane [B(C₆F₅)₃] as a catalyst is a well-studied process that yields branched cyclic structures (bcPG) on the gram scale [1,2]. However, the polymerization of cyclohexene oxide (CHO) with this catalyst has not been studied. Herein, we present our recent work on the homopolymerization of CHO and copolymerization of CHO with Gly. Copolymers with different CHO:Gly ratios were synthesized. The kinetic studies performed by *in situ* NMR showed identical polymerization rates of both comonomers confirming the formation of statistical copolymers. MALDI-TOF mass spectra of the p(CHO-*st*-Gly)₉₀₋₁₀ and p(CHO-*st*-Gly)₁₀₋₉₀ copolymers showed the exclusive formation of cyclic structures, while the PCHO homopolymer exhibited cyclic and other architectures. These results are consistent with a zwitterionic ring-expansion polymerization mechanism [3]. The T_g variation with copolymer composition showed a good agreement with the Fox equation and a T_g range from 321 K (PCHO) to 261 K (bcPG). P(CHO-*st*-Gly)₉₀₋₁₀ was further hyperbranched with Gly starting from the hydroxyl groups present in the copolymer. This hyperbranching reaction yielded an amphiphilic hyperbranched copolymer (hbPG-g-p(CHO-*st*-Gly)₉₀₋₁₀) with a predominantly hydrophobic core surrounded by hydrophilic PG branches, conferring water solubility. These structures were evaluated for their ability to load hydrophobic drugs (e.g. curcumin), evaluating the encapsulation kinetics and drug release in physiologically relevant conditions. Potential applications as a drug carrier can be attributed to these amphiphilic branched cyclic structures, where the cyclic core seems to play a key role when compared to other analogous structures.

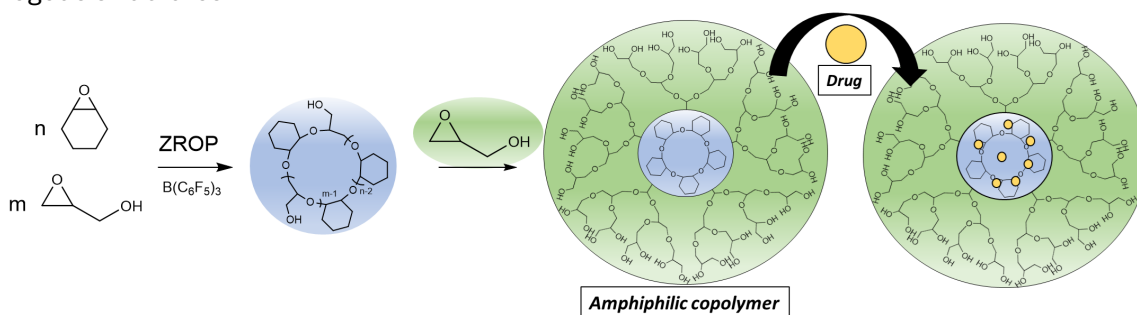


Figure 1: Schematic representation of the synthesis of amphiphilic copolymers and further hyperbranching reaction and drug loading.

Keywords: ring-opening polymerization, cyclic polymers, amphiphilic copolymers, drug release

Acknowledgments: Basque Government (IT1584-22, IT1566-22).

References:

- [1] M.A. Al Assiri, E. Gomez Urreizti et al. Reactivity of B(C₆F₅)₃ towards glycidol: The formation of branched cyclic polyglycidol structures. *European Polymer Journal* **2022**, 171, 111196.
- [2] E. Gomez Urreizti et al. Kinetics of heterogeneous polymerization of glycidol with B(C₆F₅)₃ in toluene in the absence and presence of water. *Materials Today Chemistry* **2024**, 37, 101993.
- [3] J. Ochs et al. Macrocyclic polymers: Synthesis, purification, properties and applications. *Progress in Polymer Science* **2022**, 134, 101606.

X 1-5 Tribological performance of bio-based acrylic resin coatings on mild steel and their lubricated response

P.-M. Martínez-Rubio¹, O. Platnieks², M.-D. Avilés¹, M. Jurinovs², R. Pamies¹, M. Veseta², F.-J. Carrión-Vilches¹, S. Gaidukovs²

¹Group of Materials Science and Metallurgical Engineering, Universidad Politécnica de Cartagena, Spain.

²Institute of Chemistry and Chemical Technology, Riga Technical University, Latvia.

Acrylic resins play a huge role in protective coatings on metal substrates in technological applications such as automobile and construction industries due to their color retention, chemical resistance and adhesion. However, there are technical limitations related to their mechanical properties and wear resistance that hinder their further application [1]. Recent strategies to overcome these restrictions focus on the use of wood fibers, vegetable oils and other sustainable substances to enhance their response [2].

In this work, three bio-based acrylic and methacrylic resins modified with acrylated epoxidized soybean oil were formulated as potential alternatives for conventional thermosets as protective coatings on mild steel. The coatings were evaluated in terms of thickness, surface roughness and adhesion. The wear resistance of the samples was evaluated by means of progressive load single scratch tests and multiscratch tests, analyzing the wear track via profilometry and scanning electron microscopy. The increasing content of vegetable oil induced a more ductile response, reducing the wear rate in all scenarios.

Pin-on-disk linear reciprocating tests against AISI 316L balls were performed for a more practical approach on their response, lubricating the contact with the protic ionic liquid 2-hydroxyethylammonium lactate (ML) and its dispersion with 1 wt.% graphene (MLG) for an improved tribological performance. The results were compared with a previous work with conventional epoxy resins [3], showing improved compatibility with the lubricants with reductions in the coefficient of friction above 91 % and the absence of surface damage.

Keywords: tribology, thermosets, sustainable, lubrication

Acknowledgments

The authors acknowledge MCI-AEI, Proyecto PID2021-122169NB-I00 financiado por MCIN/AEI/10.13039/501100011033/ y por FEDER Una manera de hacer Europa. P.-M. Martínez-Rubio is grateful to Fundación Séneca for the FPI grant (21574/FPI/21. Fundación Séneca. Región de Murcia (España)).

References

- [1] Jiao, C.; Sun, L.; Shao, Q.; Song, J.; Hu, Q.; Naik, N.; Guo, Z. Advances in waterborne acrylic resins: synthesis principle, modification strategies, and their applications. *ACS omega* **2021**, *6*(4), 2443-2449.
- [2] Akpan, E. I.; Wetzel, B.; Friedrich, K. A fully biobased tribology material based on acrylic resin and short wood fibres. *Tribology International* **2018**, *120*, 381-390.
- [3] Martínez-Rubio, P. M.; Avilés, M. D.; Carrión-Vilches, F. J.; Bermúdez, M. D.; Pamies, R. Characterization and tribological performance of new epoxy coatings modified with sustainable ionic liquid-graphene nanolubricants. *Progress in Organic Coatings* **2024**, *197*, 108841.

X 1-6 Polymerization of Ethylene Dioxythiophene (EDOT) with Customized Electrical Properties through an Atmospheric-Pressure Plasma-Jet

J. Sans^{1,2*}, A. Sánchez^{1,2}, A. Fontana-Escartín^{1,2}, M. Arnau^{1,2}, N. Borràs^{1,2}, and C. Alemán^{1,2*}

¹IMEM-BRT Group, Departament d'Enginyeria Química, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain

²Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, C/Eduard Maristany, 10-14, 08019 Barcelona, Spain

Plasma-assisted polymerization techniques are paying increasing attention due to its green nature, low-time consumption and versatility. Although radical polymerization is initiated due to the interaction between the plasma gas species and the precursor, the complete understanding of the polymerization mechanism remains to be very specific due the presence of fragmentation/recombination phenomena. Such competing process, which can be controlled through the plasma set up and conditions, strongly affects the final structure of the polymers, and thus, its resulting properties. In this work we report an atmospheric-pressure-jet plasma-assisted process capable of polymerizing 3,4-ethylene dioxythiophene (PEDOT) showing customized electrical properties. To elucidate the polymerization mechanism and optimize the plasma conditions, special attention has been put on the kinetics and the characterization of intermediates, including radical species and presence of different EDOT oligomers showing different colors and oxidation states. To do so, Raman microscopy, ¹HNMR and ¹³CNMR techniques have been combined with electrochemical characterization (e.g. cyclic voltammetry; CV). Interestingly, PEDOT with excellent electrical properties can be produced without the need of incorporating any doping agent or counter-ion (i.e. only the monomer or the monomer dissolved in acetonitrile) a relevant and distinctive feature as compared to electro-polymerization processes. Herein, we compare the electric performance of different plasma-polymerized PEDOT. Although the electrical properties change depending on the conditions, all samples are found in the range of the same electrical response than the reference (i.e. electro-polymerized PEDOT with lithium perchlorate), thus demonstrating the feasibility of the process reported. Finally, we have explored the possibility to produce thin-films with controlled thickness and/or discrete patterns (scanning electron microscopy analyses), further highlighting the advantages of the process reported.

Keywords: Polymerization, Plasma Technology, Advanced Materials, PEDOT, Conductivity, Electrical Properties.

Acknowledgments

This work is supported by the predoctoral program AGAUR-FI ajuts (2023 FI-100056) Joan Oró, which is backed by the Secretariat of Universities and Research of the Department of Research and Universities of the Generalitat of Catalonia, as well as the European Social Plus Fund. Authors acknowledge the Agència de Gestió d'Ajuts Universitaris i de Recerca (2021 SGR 003879) and Agencia Estatal de Investigación (PDC2023-145834-I00). This work is part of Maria de Maeztu Units of Excellence Programme CEX2023-001300-M / funded by MCIN/AEI / 10.13039/501100011033. Support for the research of C.Alemán was also received through the prize "ICREA Academia" for excellence in research funded by the Generalitat de Catalunya.

X 2-1 Quantitative characterization of reinforced rubber-silica elastomers by the combination of time-domain NMR and tensile test

M. Montero*, F. M. Salamanca, Alba Ruíz, L. Diñeiro, R. Navarro, J. L. Valentín

Institute of Polymer Science and Technology (CSIC) Juan de la Cierva, 3 – 28006 Madrid

Understanding and quantifying the separate roles of chemical cross-links and physical entanglements in filled elastomers is key for tuning their macroscopic performance. In this work, we apply Heinrich's theoretical model for the uniaxial stress [1]:

Where G_c is the cross-link modulus and G_e the entanglement contribution, δ^2 is the finite extensibility parameter, β considers the constraint release of the entanglements and will be fixed to 1 in this work. Finally, ω_d comprises the non-elastically active fraction of material measured by Multiple Quantum NMR experiments (MQ-NMR).

Additionally, Heinrich's model considers amplification (a_{s,a_d}) and the effect of the interphase between the filler surface and the polymer matrix in the crosslink modulus as follows:

Where ϕ is the volumetric fraction of fillers, G_c^n is the modulus due to chemical crosslinks and v_f denotes the filler-rubber interactions, i.e., the interphase between the polymer matrix and the fillers. It is impractical trying to obtain all those parameters only from tensile test, so we use MQ-NMR experiments to determine G_c^n . To tie molecular structure and macroscopic response, we invoke an order parameter m :

Where D_{res} is the main observable of MQ-NMR experiments, D_{stat}/k and a are known constants and m is the order parameter from Lang and Sommer model.

Thus, m provides a direct link between tensile measurements and segmental mobility measured by MQ-NMR. Remarkably, cross-link densities inferred from MQ-NMR and tensile data yield trends nearly identical to those obtained from the Payne-effect analysis.

Experiments were conducted on a natural-rubber under five reinforcing schemes: (i) unfilled; (ii) silica itself (iii) silica with monofunctional silane (grafted only to silica); (iv) silica with bifunctional silane (grafted to both silica and rubber); and (v) silane alone [2]. Compounds were mixed in two stages: first, in an internal mixer at 145 °C for 10 min (rubber + ZnO/stearic acid + silica/silane) to complete silanization; then sheeted on a two-roll mill with curing agents (CBS, DPG, S₈) [3].

RPA strain sweeps (with precycles) quantified the Payne effect; uniaxial tensile tests at 10 mm/min (after three 500 mm/min precycles) yielded m ; and low-field NMR provided D_{res} . Fitting the Heinrich model and tensile/NMR relations produced complementary measurement of G_c and G_e , all in excellent agreement with the RPA results. This dual: RPA – tensile & NMR methodology has been previously applied in our group to commercial and recovered carbon-black systems, demonstrating its broad applicability for dissecting filler–rubber interactions [4].

Keywords: rubber–silica interface; Payne effect; low-field NMR; tensile testing; Heinrich model.

Acknowledgments:

The authors acknowledge the financial support given by PTA2023-022994-I and MICIU (PID2023-147542OB-I00 and CPP2023-010769).

References:

- [1] M. Kaliske and G. Heinrich, *Rubber Chemistry and Technology*, 72 (4), **1999**, 602–632.
- [2] H.-D. Luginsland and C. Röben, *Gummi Fasern Kunststoffe*, 68, No. 11, **2015**, pp. 734–737
- [3] R. Ghosh et. al., *Polymers*, **2023**, 15, 2848
- [4] F. M. Salamanca, et. al. Assembling a theoretical framework for the characterization of reinforced elastomers considering amplification factors and filler-rubber interactions (in preparation)

X 2-2 Thermodynamic parameters of P3HT based on Flory's relation

M. Prada, J. Olmedo, M. Sanviti, J. Martín

Universidade da Coruña, Campus Industrial de Ferrol, CITENI, 15403 Ferrol, Esteiro, Spain

Regioregular poly(3-hexylthiophene) (P3HT) is one of the most studied polymers for organic solar cells (OSCs) due to its optoelectronic properties. The correlation between the performance of devices based on P3HT and the crystallinity degree highlights the need to find correct and up to date values of the thermodynamic parameters of P3HT [1]. The aforementioned necessity for these values has resulted in countless studies of the thermodynamic behaviour of P3HT and similar polymers. Different methods have been tried, ranging from the extrapolation of the equilibrium melting enthalpy from degree of crystallinity values obtained by Wide Angle X-Ray Scattering (WAXS)/Small Angle X-Ray Scattering (SAXS) experiments and Differential Scanning Calorimetry (DSC) data [2] to the use of Successive Self-Nucleation and Annealing (SSA) experiments on DSC combined with ¹³C NMR to provide a better insight of the influence of crystal size [3]. In the present work, we studied the effect of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) concentration on the crystallization behavior of P3HT by isothermal experiments performed in DSC. While this type of blend has been previously studied for P3HT [4], the use of PCBM as the diluent has not been reported before. The PCBM acts as a molecular diluent to P3HT according to the expectation of Flory-Huggins theory for polymer-diluent mixtures. By fitting our results to this theory, the value of equilibrium melting enthalpy (ΔH_0) was found (65 J/g). The equilibrium melting temperature (T_m^0) values used in this equation were calculated by the Hoffman-Weeks extrapolation, and we obtained a value for neat P3HT of 257.8 °C.

Keywords: Flory-Huggins theory, Hoffman-Weeks extrapolation, DSC, P3HT, equilibrium melting enthalpy

References

- [1] B. W. Boudouris, V. Ho, L. H. Jimison, M. F. Toney, A. Salleo, y R. A. Segalman, «Real-Time Observation of Poly(3-alkylthiophene) Crystallization and Correlation with Transient Optoelectronic Properties», *Macromolecules*, vol. 44, n.o 17, pp. 6653-6658, sep. 2011, doi: 10.1021/ma201316a.
- [2] J. Balko, R. H. Lohwasser, M. Sommer, M. Thelakkat, y T. Thurn-Albrecht, «Determination of the Crystallinity of Semicrystalline Poly(3-hexylthiophene) by Means of Wide-Angle X-ray Scattering», *Macromolecules*, vol. 46, n.o 24, pp. 9642-9651, dic. 2013, doi: 10.1021/ma401946w.
- [3] C. R. Snyder, R. C. Nieuwendaal, D. M. DeLongchamp, C. K. Luscombe, P. Sista, y S. D. Boyd, «Quantifying Crystallinity in High Molar Mass Poly(3-hexylthiophene)», *Macromolecules*, vol. 47, n.o 12, pp. 3942-3950, jun. 2014, doi: 10.1021/ma500136d.
- [4] M. Alizadehaghdam, B. Heck, S. Siegenführ, F. Abbasi, y G. Reiter, «Thermodynamic Features of Perfectly Crystalline Poly(3-hexylthiophene) Revealed through Studies of Imperfect Crystals», *Macromolecules*, vol.52,6, pp. 2487-2494, mar. 2019, doi: 10.1021/acs.macromol.8b02350.

X 2-3 Methodologies for Safe-and-Sustainable-by-Design production of polyurethane foams

E. Calleja^{1,2}, M. J. Clemente², L. Oriol^{2*}

¹Leitat technological center, Terrassa, Spain

²University of Zaragoza, Zaragoza, Spain

Conventional polyurethanes (PUs) are versatile thermoset polymers extensively used across various sectors and applications. However, their synthesis involves the use of isocyanates, which are highly toxic and pose significant health and environmental risks. At the same time, the production of isocyanates requires the use of highly hazardous phosgene, demanding highly safety requirements. Raising global awareness of environmental protection, safety and health of workers and consumers has driven the demand for more eco-friendly products. This has led to research into non-isocyanate polyurethane (NIPU) synthesis as a promising alternative.¹ NIPUs are a type of PU that are produced without using of isocyanates. Similar to their conventional polyurethane counterparts, NIPUs offer promising applications across various fields, including coatings, adhesives, foams, elastomers, and biomedical purposes.

This work aims to explore the potential of NIPUs in creating new materials similar to conventional PUs. The synthesis of NIPUs involves a two-step process: first, the synthesis of bicyclic carbonate monomers through a transesterification reaction, and second, the reaction of these monomers with amines via aminolysis to produce NIPUs. Initially, efforts were focused on the synthesis and characterization of a bicyclic carbonate, diglycerol dicarbonate (DGDC),² and determining how to utilize it to develop a new material based on NIPU. In the second step, the focus was on studying how these synthesized cyclic carbonates could be used to create final NIPUs and determine their potential application. It was seen that these monomers were used to fabricate self-blown NIPU foams.³ Different amines, catalyst and blowing agents were studied alongside DGDC in order to understand the material, assess their reactivity, optimize the foam production process, and continue the investigation of these new materials.

The absence of isocyanates in PU synthesis process reduces significantly the environmental and health risks. NIPU foams synthesis offers enormous potential for producing the next generation of greener PU foams, although the mechanisms present challenges that require further study. This advancement paves the way for more sustainable and versatile materials, promising a future where environmentally friendly PUs become the standard in various industries.

Keywords

Polyurethane, Non-isocyanate polyurethane, sustainability, synthesis, foams.

References

- [1]Mangal, M.; Supriya, H.; Bose, S.; Banerjee, T. Innovations in Applications and Prospects of Non-Isocyanate Polyurethane Bioplastics. *Biopolymers* **2023**, *114* (12), e23568.
- [2] Magliozzi, F.; Scali, A.; Chollet, G.; Grau, E.; Cramail, H. Enantioselective Crystallization of Diglycerol Dicarboxylate: Impact of the Microstructure on Polyhydroxyurethane Properties. *Macromol. Rapid Commun.* **2021**, *42* (3), 2000533.
- [3] Amezúa-Arranz, C.; Santiago-Calvo, M.; Rodríguez-Pérez, M.-Á. A New Synthesis Route to Produce Isocyanate-Free Polyurethane Foams. *European Polymer Journal* **2023**, *197*, 112366.

X 2-4 Solid-State Processing of P3HT: Effect of Temperature and Pressure on Polymer Film Formation

Paula Gallardo Santos, María Belén Montero Rodríguez, Jaime Martín Pérez

Universidade da Coruña, Grupo de Polímeros, Centro de Investigación en Tecnoloxías Navais e Industriais (CITENI), Campus Industrial de Ferrol (CIF), Rúa Mendizábal s/n, 15403, Ferrol, Spain

Poly(3-hexylthiophene) (P3HT) is a widely used semiconducting polymer in optoelectronic applications, for which solid-state processing represents a more sustainable and solvent-free alternative to conventional solution-based fabrication methods [1].

In this work, P3HT films were prepared by solid-state thermal processing, starting from the polymer in the form of fibers and without employing solvents in any stage. The influence of temperature, pressure and pressing time on the morphological and structural quality of the films obtained is explored [2,3]. Their thermal and structural behaviour was studied by differential scanning calorimetry (DSC), observing variations in the degree of crystallinity and in the thermal profile according to the processing conditions when compared to the non-processed polymer fibers.

The impact of processing conditions on the thermal and oxidative stability of P3HT is also investigated, with the aim of preserving its functionality in solid-state applications. Ongoing permeability measurements will help assess its potential integration into devices requiring barrier properties, such as organic solar cells, where P3HT is known to degrade under humid, oxygen-rich conditions [4].

This approach provides a cleaner and potentially scalable processing route for P3HT, and provides fundamental information on the stability and molecular organization of the polymer after solid-state processing.

Keywords: P3HT, semiconducting polymers, permeability, solid state processing

References

- [1] Baklar, M. A., Koch, F., Kumar, A., Domingo, E. B., Campoy-Quiles, M., Feldman, K., Yu, L., Wobkenberg, P., Ball, J., Wilson, R. M., McCulloch, I., Kreouzis, T., Heeney, M., Anthopoulos, T., Smith, P., & Stingelin, N. (2010). Solid-State Processing of Organic Semiconductors. *Advanced Materials*, 22(35), 3942-3947.
- [2] Rodrigues, A., Nabankur, D., Hilliou, L., Viana, J., Bucknall, D. G., & Bernardo, G. (2013). Low temperature solid state processing of pure P3HT fibers. *AIP Advances*, 3(5), 052116.
- [3] Kroon, R., Hofmann, A. I., Yu, L., Lund, A., & Müller, C. (2019). Thermally Activated in Situ Doping Enables Solid-State Processing of Conducting Polymers. *Chemistry of Materials*, 31(8), 2770-2777.
- [4] Hintz, H., Egelhaaf, H.-J., Lürer, L., Hauch, J., Peisert, H., & Chassé, T. (2011). Photodegradation of P3HT—A Systematic Study of Environmental Factors. *Chemistry of Materials*, 23(2), 145-154.

X 2-5 Discovering a new family of boron photocatalyst and photoinitiators

A. Leiza, H. Sardon, F. Vidal

University of the Basque Country, Donostia-San Sebastian, Spain.

Current controlled radical photopolymerization methods typically rely on organometallic photocatalysts. While effective, these systems often present challenges such as toxicity, high cost, and limited sustainability. Therefore, transitioning to metal-free photocatalytic systems is an enticing alternative that is receiving increased attention. Boron has demonstrated an excellent ability to generate radicals, a characteristic extensively utilized in organic synthesis¹ or as photoinitiators in free-radical polymerization (FRP).² However, their use in controlled radical photopolymerization, particularly in photo-based reversible addition fragmentation chain transfer (photo-RAFT) polymerization, requires further development. Importantly, while boron-sulfur bonds have shown lability under UV light,³ there is a distinct lack of research on the potential of related boron-based systems under visible light, which would allow for more energy-efficient processes. Additionally, previous attempts to utilize boron-centered catalysts have employed coordinatively saturated species,⁴ which fail to exploit the dynamic hybridization nature of boron (sp^3 and sp^2) to its fullest potential. Moreover, RAFT agents are still used separately in these systems, leading to bimolecular (or trimolecular when an external chromophore is needed) processes and slower polymerization kinetics.

In this work, we propose the design of an unprecedented family of boron-centered photocatalysts that absorb under visible light. These catalysts contain the chain transfer agent (CTA) directly bonded to the boron atom, thus creating a truly unimolecular system. This innovation promises to enhance polymerization kinetics and provide better control over the polymerization process, making use of the dynamicity of the boron hybridization nature to close the catalytic cycle. As a first step toward this ambitious goal, we report preliminary results using a commercially available reagent, Boron Subphthalocyanine Chloride (BSubPhCl) that mimics our proposed boron-based photocatalysts, setting the stage for the development of more efficient and sustainable photocatalytic systems for controlled radical photopolymerization.

Keywords: Controlled photopolymerization, organoboron photocatalyst, boron hybridization, photoRAFT, Boron Subphthalocyanine Chloride

Acknowledgments

This work was supported by the FPU (Formación de Profesorado Universitario) scholarship program (grant number: FPU23/0434).

References

- [1] Y. Sato, K. Nakamura, Y. Sumida, D. Hashizume, T. Hosoya, and H. Ohmiya, "Generation of Alkyl Radical through Direct Excitation of Boracene-Based Alkylborate," *J Am Chem Soc*, 2020, 142, 9938–9943.
- [2] B. Aubry et al., "A Second-Generation Chameleon N-Heterocyclic Carbene-Borane Coinitiator for the Visible-Light Oxygen-Resistant Photopolymerization of Both Organic and Water-Compatible Resins," *Macromolecules*, 2018, 51, 9730-9739.
- [3] S. Telitel et al., "Formation of N-heterocyclic carbene-boryl radicals through electrochemical and photochemical cleavage of the B-S bond in N-heterocyclic carbene-boryl sulfides," *J Am Chem Soc*, 2013, 135, 16938-16947.

X 3-1 Development of Eco-Friendly Semisolid Lubricants: Impact of Silica/Clay, Biopolymer and Base Oil

M. Toro-Gallego, C. Valencia, M.C. Sánchez, J.E. Martín-Alfonso, J.M. Franco

Pro2TecS – Chemical Product and Process Technology Research Center Department of Chemical Engineering and Materials Science, Universidad de Huelva, Huelva, Spain.

In recent decades, silicates have gained attention due to their unique physicochemical properties, founding new roles in composite and nanocomposite materials, extending to the nanoscale [1]. In the lubricant industry, rising concerns over pollution and increasingly stringent regulations have positioned phyllosilicates and silica as strong alternatives to traditional additives. Their outstanding lubricating properties help enhance energy efficiency and extend the lifespan of machinery. In the case of semi-solid lubricants, such as lubricating greases, biopolymer-based nanocomposites and ceramic materials can play a crucial role. However, compatibility challenges their feasibility, for which electrospinning has recently emerged as a promising technique, allowing a controlled structuring of the oil and the dispersion of the nanocomposites within the oil matrix [2].

In the present study, eco-friendly oleo-dispersion formulations were optimized by carefully selecting and balancing key ingredients: nanoclays or types of SiO₂ NPs, cellulose-derived biopolymers, and oils of diverse viscosities and origins. The rheological and tribological properties of these oleo-dispersions, along with the morphology of the produced nanocomposites were thoroughly investigated and correlated.

In conclusion, electrospun nanostructures produced from clay solutions showed a predominance of nanofibers, which results in oleo-dispersions with increased viscoelastic moduli, as well as better tribological performance than those composed of silica. Furthermore, oleo-dispersions prepared with hydrophobically modified silica nanocomposites exhibited higher viscoelastic moduli than those composed with hydrophilic silica even though nanocomposites presented similar nanoarchitectures. Overall, the rheological and tribological performance is influenced by the kind of clay or silica employed to produce the nanocomposite. In relation to the biopolymer used, higher molecular weight led to greater moduli for oleo-dispersions formed from similar nanoarchitectures. Considering the influence of oils, homogeneous dispersions were achieved when the oils had a viscosity of at least 3.5 Pa*s, regardless of their origin. Among all the oils studied, the highest viscoelastic function values were observed when combined with the nanocomposite formulated with clay. Furthermore, all processed oleo-dispersions present a tribological behaviour similar to that of traditional lubricating greases, emerging as sustainable semi-solid lubricant solutions.

Keywords: biopolymer, silica, clay, electrospinning, lubricating greases, rheology.

Acknowledgments

This work is part of the Research Project PID2021-125637OB-I00, funded by ICIU/AEI/10.13039/501100011033 and by ERDF/EU. Funding is gratefully acknowledged.

References

- [1] F. Bergaya, G. Lagaly, Chapter 1 General Introduction: Clays, Clay Minerals, and Clay Science, *Dev Clay Sci* 1 (2006) 1–18.
- [2] M. Borrego, J.E. Martín-Alfonso, C. Valencia, M.D.C. Sánchez Carrillo, J.M. Franco, Developing Electrospun Ethylcellulose Nanofibrous Webs: An Alternative Approach for Structuring Castor Oil, *ACS Appl Polym Mater* 4 (2022) 7217–7227.

X 3-2 Structure-property design in dynamic hydrogels for additive manufacturing

I. Insua^{1,2}, I. Calafel^{1,2}, R. Aguirresarobe^{1,2}, J. Nunes^{3,4}, D. Dupin³ and M. Fernández¹

¹ *Department of Polymers and Advanced Materials: Physics, Chemistry and Technology. Faculty of Chemistry, University of the Basque Country (UPV/EHU). Donostia-San Sebastián. Spain.*

² *Polymat. Donostia-San Sebastián. Spain.*

³ *Cidetec. Basque Research and Technology Alliance (BRTA). Donostia-San Sebastián. Spain.*

⁴ *IIS Biogipuzkoa. Donostia-San Sebastián. Spain.*

The adaptability and responsiveness of hydrogels for regenerative medicine is significantly enhanced through dynamic covalent chemistry. This powerful tool allows for the incorporation of reversible bonds, such as thiol-disulfide exchange reactions into covalent networks. Consequently, these dynamic hydrogels, can selectively reform their networks in response to specific conditions.[1] The mechanical stability and responsiveness to external stimuli provided by the dynamic covalent bonds make them very promising materials with self-healing properties, injectability, and suitability for additive manufacturing.[2]

This study investigates the dynamic response of hydrogels formulated with thiol-functionalized hyaluronic acid and 4-arm-PEG with coordination dynamism given by metals. Our aim is to understand how tuning the metal coordination affects the properties of these hydrogels, with the ultimate goal of optimizing their performance for 3D printing applications. The characterization revealed that the hydrogel network, while exhibiting good macroscopic mechanical stability at rest, transitions to a liquid-like state under strain, thus improving its deformability and printability. The rheological response depends on the type of mechanism that governs, either covalent dynamic network or coordinative dynamism interactions.

The soft-solid characteristics and the self-healing behaviour of the network were confirmed through large amplitude oscillatory shear measurements. Furthermore, superposition experiments, combining steady and oscillatory shear, allowed for the detection and quantification of flow-induced acceleration of the network's relaxation modes.

Keywords: 3D printing, rheology, dynamic hydrogel.

Acknowledgments This work was supported by the Basque Government through the "Predoctoral Program for the Training of Non-Doctoral Research Staff".

References

[1] Tran, V. T. et al. Multifunctional poly(disulfide) hydrogels with extremely fast self-healing ability and degradability. *Chem. Eng. J.* 2020, 394, 124941.

[2] Zegota, M. M. et al. Dual Stimuli-Responsive Dynamic Covalent Peptide Tags: Toward Sequence-Controlled Release in Tumor-like Microenvironments. *J. Am. Chem. Soc.* 2021, 143, 17047–17058.

X 3-3 Diseño de Tintas Biomateriales Basadas en Hidrogeles Granulares Reticulados Químicamente para Impresión 3D

Jorge Mercado-Rico¹, Luis Pérez-Pérez^{1,2}, José María Alonso², Raúl Pérez-González², Virginia Sáez-Martínez², Aroa Mascaraque-León³, Mónica Echeverry-Rendón³, Rebeca Hernández¹

¹ Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), 28006 Madrid, España

² i+Med S. Coop. Parque Tecnológico de Álava, 01510 Vitoria-Gasteiz, España

³ Instituto IMDEA Materiales, Technoetafe, , 28906 Getafe, Madrid, España

Los hidrogeles granulares están demostrando ser una opción prometedora en la impresión 3D por extrusión debido a sus excepcionales propiedades fisicoquímicas. Formados por microgeles organizados de manera compacta, estos materiales permiten una extrusión precisa y controlada, además de tener una gran capacidad para recuperar su estructura, lo que es esencial para asegurar que las impresiones 3D no se deformen y conserven su forma durante el proceso [1]. Muchos de estos hidrogeles están basados en polímeros de origen natural, como polisacáridos y proteínas, que actúan como tintas biomateriales, abriendo nuevas posibilidades en el campo de la biomedicina [2]. Dado que la mayoría de tintas biomateriales a base de hidrogeles son geles físicos, nuestro desafío en este trabajo fue desarrollar tintas biomateriales a base de hidrogeles químicos, debido a que suelen presentar mejores propiedades mecánicas. En este estudio, proponemos un enfoque innovador basado en la impresión por extrusión 3D de hidrogeles reticulados químicamente obtenidos a partir de polímeros naturales con el objetivo de aumentar las propiedades mecánicas y de estabilidad de los hidrogeles resultantes[3]. Para ello, se modificaron químicamente pectina de alto grado de metoxilación (HM) y ácido hialurónico con Bis (3-aminopropil) amina (APA)[4], introduciendo grupos amina con el objetivo de formar hidrogeles al ser reticulados con genipina a diferentes concentraciones molares. La elección de la pectina no solo responde a su capacidad gelificante, sino también a su origen vegetal, económico y sostenible, al tratarse de un polisacárido ampliamente disponible y derivado de residuos agroindustriales como cáscaras de frutas, haciendo que el material sea más sostenible y accesible. Posteriormente se realizaron tintas biomateriales a través de la dispersión de estos geles granulados en una solución de polímero pre-entrecruzada, permitiendo la fabricación de andamios poliméricos mediante impresión 3D por extrusión con alta estabilidad hidrolítica y respuesta al pH. Finalmente, se evaluó la citotoxicidad in vitro de los materiales seleccionados acorde la norma ISO 10993-5 comprobándose su biocompatibilidad.

Palabras clave: hidrogeles granulares, polisacárido, pectina, tintas biomateriales, impresión 3D por extrusión.

Agradecimientos.

Esta investigación ha sido financiada por los proyectos PID2020-113045GB-C22 y PID2023-149734NB-C21 financiado por la MCIN/AEI/10.13039/501100011033, la convocatoria “Doctorados Industriales” (DIN2019-010868) y el proyecto DIGIMATER-CM (TEC-2024/TEC-102) financiado por la Comunidad de Madrid.

Referencias

- [1] C.Daly, Andrew. Granular Hydrogels in Biofabrication: Recent Advances and Future Perspectives. *Advance Healthcare Materials* 2024, 13, 25.
- [2] Hernandez-Sosa, A.; Mercado-Rico, J.; et al. Composite nano fibrillated cellulose-alginate hydrogels: Effect of chemical composition on 3D extrusion printing and drug release. *Polymer* 2024, 298.
- [3] Mercado-Rico, J.; Pérez, L.A.; et al. Design of Biomaterial Inks Based on Chemically Crosslinked Granular Hydrogels for 3D Printing. In preparation.
- [4] Kunkit, N.; Deekaiam, T.; et al. Physical hydrogels prepared from cationically modified pectin with tunable sol-gel phase transition behaviors. *International Journal of Polymeric Materials and Polymeric Biomaterials* 2021, 70, 131-141.

X 3-4 3D printing ternary blends of poly (butylene succinate), polylactide and poly (butylene adipate-co-terephthalate)

Pablo López Matanza¹, Manoli Zubitur², Agurtzane Mujica¹, Ricardo A. Pérez-Camargo¹, Alejandro. J. Müller^{1,3}

¹POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry, and Technology, Faculty of Chemistry, UPV/EHU, Donostia-San Sebastián, Spain,

²Chemical and Environmental Engineering Department, Polytechnic School, University of the Basque Country (UPV/EHU), Donostia-San Sebastián, Spain

³IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain

Poly(butylene succinate) (PBS) is a significant biodegradable polymer; however, its high crystallinity (X_c) creates hurdles for 3D printing, leading to prevalent issues like warping and deformation, common complications when working with semicrystalline materials. In this study, we formulated ternary blends of biodegradable polyesters by combining PBS with poly (butylene adipate-co-terephthalate) (PBAT) and poly (L-lactide) (PLLA) in various ratios to improve printability. We thoroughly evaluated the blends' properties before and after printing, employing advanced methods such as differential scanning calorimetry, polarized light microscopy, scanning electron microscopy, synchrotron radiation X-rays, and rheological and mechanical analysis. Our results indicated that these blends could be effectively printed, even with a significant PBS proportion, exhibiting warping and deformation levels comparable to or less than PLA, a commonly used printable material. The qualities of the blends varied based on their morphology and composition, leading to the development of printable PBS-based blends with a range of characteristics. This research lays the groundwork for promising advancements in the 3D printing of semicrystalline biodegradable polyester blends.

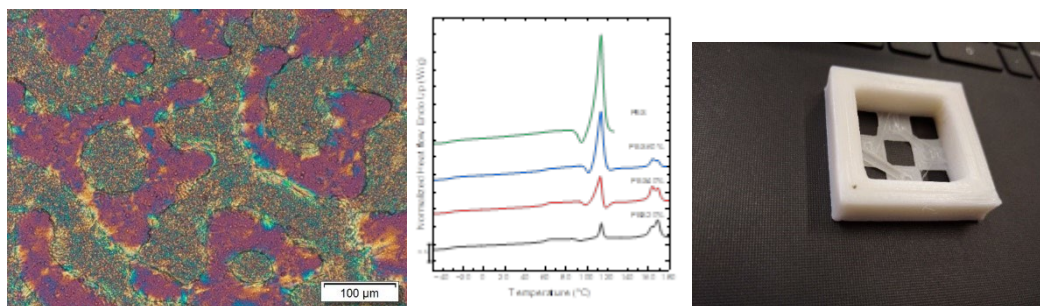


Figure 1: DSC first heating scans (at 20 °C/min), PLOM micrograph showing the blend morphology, and 3D printed part prepared with PLA, PBAT, and PBS ternary blend.

Keywords: 3D Printing, FDM, PBS.

Acknowledgments: We acknowledge the support of the Basque Government through grants IT1503-22 and PIBA_2023_1_0017. R.A.P-C is supported by the ADAGIO-H2020-MSCA COFUND-2020 program (101034379).

References:

[1] Candal, M. V., Calafel, I., Aranburu, N., Fernández, M., Gerrica-Echevarria, G., Santamaría, A., & Müller, A. J. (2020). Additive Manufacturing, **2020**, 36, 101408.

X 3-5 Carbon Nanotube Coatings Enabling the Conversion of Polyacrylonitrile Fibers into Carbon Fibers via Microwave Carbonization

N. Cárdenas^{1,*}, C. M. Gómez¹, R. Muñoz-Espí¹, M. Collins², M. Culebras¹

¹ Institut de Ciència dels Materials (ICMUV), Universitat de València, Valencia, Spain

² University of Limerick, Limerick, Ireland

Carbon fiber reinforced polymers (CFRPs) play a pivotal role in industries requiring lightweight and high-strength materials, including aerospace, automotive, and renewable energy. Although polyacrylonitrile (PAN)-based carbon fibers dominate the market due to their superior properties, traditional production methods involve extremely high energy consumption, mainly during the carbonization stage at temperatures exceeding 1000 °C. Recently, microwave (MW) heating has emerged as a sustainable alternative, offering benefits such as energy efficiency and lower environmental impact. However, the inherently low dielectric properties of PAN fibres limit their ability to absorb microwave energy directly, necessitating innovative strategies to facilitate their conversion to carbon fiber (CF) via microwave heating.¹ To overcome this challenge, this work focuses on the use of carbon nanotube (CNT) coatings to enhance the microwave responsiveness of PAN fibers. By employing a layer-by-layer (LBL) deposition technique, multi-walled carbon nanotube (MWCNT) suspensions were applied to create uniform, conductive layers on the fiber surfaces. The impact of multiple coating cycles and fiber surface pre-treatments, including plasma and corona activation, was examined to optimize coating adhesion, dispersion, and overall performance.

Scanning electron microscopy (SEM) and Raman spectroscopy, among other characterization techniques, were utilized to assess coating quality, morphology, and distribution of the nanostructures. The preliminary results suggest that both the number of coating cycles and the surface treatment methods are crucial for achieving stable and uniform coatings. Plasma and corona treatments improved the distribution of the nanostructures on the fiber surface.

Keywords: Polyacrylonitrile (PAN) fibres, Multi-Walled Carbon Nanotubes (MWCNT) surface coating, carbon fiber production, microwave-assisted carbonization

Acknowledgments

This work has been supported by the European Union's Horizon Europe research and innovation program under the project "Carbon Fiber Production Via Low Energy Microwave Absorption (CARBOWAVE)", grant agreement number 101192581.

References

[1] Stróżyk¹, M. et. Al. Decreasing the Environmental Impact of Carbon Fibre Production Via Microwave Carbonisation Enabled by Self-assembled Nanostructured Coatings. *Adv. Compos. Hybrid Mater.* **2024**, *7*, 39.

X 3-6 Optimización del proceso de infusión VARI para laminados de fibra de carbono con resina termoplástica

D. Martín-Crespo, S. González-Tomé, R. Verdejo, M.A. López-Manchado

Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), Juan de la Cierva, 3, 28006, Madrid.

El proceso de infusión de resina asistida por vacío (VARI) es una técnica económica y versátil, ampliamente utilizada en la industria para la fabricación de materiales compuestos estructurales de altas prestaciones con una alta fracción en volumen de fibra. Este proceso consiste en la impregnación de las fibras con una resina de baja viscosidad, generalmente termoestable, dentro de un molde bajo vacío. La dificultad de reciclar los materiales compuestos con resina termoestable, ha impulsado en los últimos años, la búsqueda de alternativas más sostenibles, como las resinas termoplásticas. Entre ellas, destacan las resinas termoplásticas reactivas de baja viscosidad, basadas en mezclas de monómeros u oligómeros que polimerizan en presencia de un iniciador. Su principal ventaja es que se pueden procesar con las mismas técnicas empleadas para las resinas termoestables [1].

Este trabajo describe la optimización del proceso de infusión de una resina termoplástica acrílica, Akelite, patentada por el grupo de Compuestos Poliméricos del CSIC [2]. El análisis se centró en variables de proceso, como el nivel de vacío, y variables de polimerización, como la temperatura y el porcentaje de catalizador. Además, se monitorizó en tiempo real la reacción de polimerización mediante análisis dieléctrico, con el fin de optimizar los tiempos del proceso. Se fabricaron laminados de cuatro capas de fibra de carbono UD 12K con un gramaje de 340 g/m² y un espesor de 45 μm mediante VARI utilizando un molde plano calefactado. Los laminados se evaluaron mediante ensayos de tracción, flexión en tres puntos y cizallamiento interlaminar (ILSS) (Tabla), comparando los resultados con los obtenidos con una resina epoxi comercial. Se desarrolló un método sencillo y escalable, por inmersión del laminado en un disolvente común, que permite recuperar la fibra y la resina en óptimas condiciones. Finalmente, se fabricó un laminado con material completamente reciclado con propiedades mecánicas similares a las del original.

Tabla. Propiedades mecánicas de los test realizados a los laminados con resina Akelite y Epoxy.

Test	Akelite		Epoxy	
	Longitudinal	Transversal	Longitudinal	Transversal
Flexión				
σ (MPa)	980 ± 40	78 ± 4	957 ± 67	90 ± 5
E (GPa)	55 ± 6	5.1 ± 0.5	59 ± 7	6.6 ± 0.8
ILSS (MPa)	59 ± 6		50 ± 3	

Palabras clave: VARI; material compuesto; sostenibilidad

Agradecimientos

Este proyecto ha recibido financiación del programa de investigación e innovación Horizonte Europa de la Unión Europea en virtud del acuerdo de subvención nº 101148066. Los autores agradecemos la financiación del Ministerio de Ciencia, Innovación y Universidades de España a través del proyecto coordinado SUCCESS BLADE (TED2021-130201B-C31), cofinanciado por NextGenerationEU, Unión Europea).

Referencias

[1] Bodaghi M, Park CH, Krawczak P. *Reactive Processing of acrylic-based thermoplastic composites: A mini-review*. *Frontiers in Materials* 2022; 9: 931338. [2] Verdejo R, López-Manchado MA, Santiago A. *Polímeros reforzados con fibras basados en matrices termoplásticas*, (2022). WO2022079336A1, CSIC.

X 4-1 Morphological Control of PBSA/PLA Microfibrillar Composites for packaging applications

Johan Garcia, Itxaso Calafel, Itziar Otaegi, Gonzalo Guerrica-Echevarria, Nora Aranburu

POLYMAT and Department of Advanced Polymers and Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country (UPV/EHU). Manuel de Lardizabal 3, 20018, Donostia-San Sebastian, Spain.

Research on biopolymers has gained significant attention in recent years due to their potential to address several pressing environmental challenges. Unlike commonly used conventional petroleum-based plastics, some biopolymers are biobased and biodegradable, making them more sustainable alternatives for single-use applications. However, finding a single biopolymer featuring a good balance of processability and properties is challenging. In this scenario, blending different biopolymers, such as polylactic acid (PLA) and polybutylene succinate-co-adipate (PBSA), has proven to be a straightforward approach to develop a new family of biopolymers displaying a combination of desirable properties [1]. Nonetheless, as is the case of conventional polymer blends, PLA and PBSA are immiscible, and hence, a good microstructure control is essential to achieving optimal performance [2]. A particularly interesting strategy involves engineering these blends into microfibrillar composites (MFCs) where one polymer forms reinforcing microfibrils within the matrix. This morphology can significantly enhance mechanical performance [3].

Hence, this research focuses on the development of in situ MFCs based on PBSA/PLA blends. First, a rheological approach was used as a predictive tool for PLA microfibril formation under specific operating conditions, in order to select the most suitable commercial PLA grade and processing conditions for PBSA/PLA MFCs manufacturing. Then, MFCs were processed using two different methods: (1) cold drawing and (2) hot stretching. In each case, the processing conditions (temperature and draw-ratio) were optimized to induce PLA microfibril formation and the effect of the developed microstructure on the mechanical, thermal, and barrier properties was assessed.

Keywords: Microfibrillar reinforced composites, PLA, PBSA

References

- [1] B. Palai, S. Mohanty, and S. K. Nayak, "Synergistic effect of polylactic acid(PLA) and Poly(butylene succinate-co-adipate) (PBSA) based sustainable, reactive, super toughened eco-composite blown films for flexible packaging applications," *Polym. Test.*, vol. 83, p. 106130, 2020, doi: <https://doi.org/10.1016/j.polymertesting.2019.106130>.
- [2] K. Friedrich, M. Evstatiev, S. Fakirov, O. Evstatiev, M. Ishii, and M. Harrass, "Microfibrillar reinforced composites from PET/PP blends: processing, morphology and mechanical properties," *Compos. Sci. Technol.*, vol. 65, no. 1, pp. 107–116, 2005, doi: <https://doi.org/10.1016/j.compscitech.2004.06.008>.
- [3] P. Taepaiboon, J. Junkasem, R. Dangtungee, T. Amornsakchai, and P. Supaphol, "In situ microfibrillar-reinforced composites of isotactic polypropylene/recycled poly(ethylene terephthalate) system and effect of compatibilizer," *J. Appl. Polym. Sci.*, vol. 102, no. 2, pp. 1173–1181, Oct. 2006, doi: <https://doi.org/10.1002/app.24402>.

X 4-2 Lignin, SCG and Ox-SCG influence on FDM printability and electrical conductivity of PLA/MWCNT composites for electronic devices

Silvia Lage-Rivera^{1*}, Ana Ares-Pernas¹, María-José Abad¹, M. Sonia Dopico-García¹, Carlos M. Costa^{2,3}, Nelson Miguel Macedo Silva Pereira^{2,3}, Senentxu Lanceros-Méndez^{2,4,5}

¹Universidad da Coruña, Campus de Industrial de Ferrol, CITENI, Grupo de Polímeros, Campus de Ferrol 15403, Ferrol, Spain

²Physics Centre of Minho and Porto Universities (CF-UM-UP) and Laboratory of Physics for Materials and Emergent Technologies, LapMET, University of Minho, 4710-057 Braga, Portugal

³Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, Portugal

⁴BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

⁵IKERBASQUE, Basque Foundation for Science, 48009, Bilbao, Spain

The expansion of FDM (fusion deposition modeling) 3D-printing in electronics requires the development of novel materials with certain electrical properties and suitable processability for applications in electronics and sensing. Moreover, it is essential the transition to bio-based polymers and composites to reduce the dependence on fossil-derived materials.

Within this work, novel FDM-printable composites were developed by a combination of solvent-casting and melt-mixing method, using PLA as a bio-based matrix, MWCNT as a conductive filler (reaching the electrical threshold at 5wt.% [1]), and bio-based additives (3 wt.% of, lignin, spent coffee grounds or SCG [2], and oil-extracted from them). The composites were characterized in terms of MWCNT dispersion, thermal stability, viscoelastic behavior, mechanical and electrical performance and 3D printability. SCG proved to be the most effective additive, enhancing PLA/MWCNT conductivity up to $1.4 \pm 0.1 \text{ S cm}^{-1}$ and improving its mechanical performance.

PLA/MWCNT/SCG filaments were used to 3D print flexible sensors, using a PLA substrate (Figure 1A). The sensors were subjected to electromechanical tests to evaluate their performance as gyroscopic devices. Last, a proof-of-concept device was assembled by integrating the printed sensor with an accelerometer and an Arduino board (Figure 1B–C), demonstrating the feasibility of fully 3D-printed, low-cost and highly customizable sensing systems.

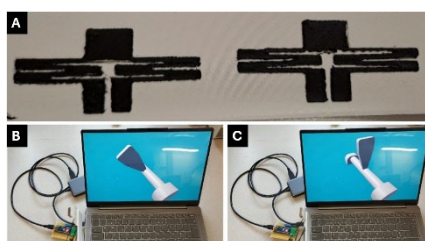


Figure 1. (A) 3D-printed sensors, (B, C) rotation of the sensor.

Keywords: FDM, conductive polymer composite, bio-additives, lignin, SCG, Ox-SCG

References

- [1] Lage-Rivera, S.; Ares-Pernas, A.; Becerra Permy, J. C.; Gosset, A.; Abad, M.-J. Enhancement of 3D Printability by FDM and Electrical Conductivity of PLA / MWCNT Filaments Using Lignin as Bio-Dispersant. *Polymers* **2023**, 15.
- [2] Lage-Rivera, S.; Ares-Pernas, A.; Dopico-García, M. S.; Covas, J.; Abad, M.-J. Comparing lignin and spent coffee grounds as bio-fillers in PLA 3D-printable filaments. *Polymer Composites* **2024**, 1-14.

X 4-3 Lignin's Thermal Fingerprint: Guiding Sustainable 3D Printing through TGA-FTIR of Isolated and Acylated Variants

C. Quintero Rodríguez^{1*}, M. Bodor², A. Lasagabáster Latorre³, S. Dopico-García¹, M. José Abad¹

¹ *Universidade da Coruña, Campus de Industrial de Ferrol, CITENI-Grupo de Polímeros, Ferrol, Spain*

² *"Dunarea de Jos" University of Galati, Dept. of Materials and Environmental Engineering, Galați, Romania*

³ *Dpto Química Orgánica I, Facultad de Óptica y Optometría, Universidad Complutense de Madrid, Spain*

Lignin is a natural, abundant and renewable aromatic polymer with great potential as a source of biomaterials and precursor chemicals. However, its structural complexity and thermal behavior vary considerably depending on its origin, the extraction method used and the chemical modifications to which it has been subjected[1].

In this study, a comparative analysis was carried out by TGA-FTIR of several types of lignin, investigating how both its extraction method and its subsequent functionalization affect its thermal properties[2,3]. Lignins from industrial processes and others extracted in the laboratory were analyzed. In particular, two commercial lignins and two lignins obtained in the laboratory from Bétula Park using extraction methods based on organic solvents (Acetosolv) and deep eutectic solvents (DES) have been studied. In addition, the latter two were also investigated after chemical modification by acylation.

The results confirmed differences in the chemical structure of the lignins, which were directly reflected in variations in their thermal behavior, with distinct gas evolution profiles depending on the origin, extraction method, and acylation. The conclusions obtained will allow optimizing the use of lignins in pyrolysis processes to obtain graphite-like carbon that may be of interest as an additive in printable compounds for electronics applications [4,5].

This work is part of one of our group's main current research areas, which focuses on the valorization of lignin in new sustainable formulations for DLP 3D printing.

Keywords: TG-FTIR, lignin, pyrolysis, DLP-3D

References

- [1] Ali, S.; Rani, A.; Dar, M. A.; Qaisrani, M. M.; Noman, M.; Yoganathan, K.; Asad, M.; Berhanu, A.; Barwant, M.; Zhu, D. Recent advances in characterization and valorization of lignin and its value-added products: challenges and future perspectives. *Biomass* **2024**, 4(3), 947-977.
- [2] Zhang, M.; Resende, F. L.; Moutsoglou, A.; Raynie, D. E. Pyrolysis of lignin extracted from prairie cordgrass, aspen, and Kraft lignin by Py-GC/MS and TGA/FTIR. *Journal of Analytical and Applied Pyrolysis* **2012**, 98, 65-71.
- [3] Sobiesiak, M.; Podkościelna, B.; Sevastyanova, O. Thermal degradation behavior of lignin-modified porous styrene-divinylbenzene and styrene-bisphenol A glycerolate diacrylate copolymer microspheres. *Journal of Analytical and Applied Pyrolysis* **2017**, 123, 364-375.
- [4] Celzard, A.; Marêché, J. F.; Payot, F.; Furdin, G. Electrical conductivity of carbonaceous powders. *Carbon*, **2002**, 40(15), 2801-2815.
- [5] Kane, S.; Hodge, D. B.; Saulnier, B.; Bécsy-Jakab, V. E.; Dülger, D. N.; Ryan, C. Role of sodium sulfate in electrical conductivity and structure of lignin-derived carbons. *Journal of Analytical and Applied Pyrolysis* **2024**, 181, 106600

X 4-4 Improving the Anti-Corrosion Efficiency and Electrical Functionalization of Sustainable Bio-Epoxy Coatings from Epoxidized Soybean Oil and Tannic Acid with Carbonaceous Nanofillers.

R. Tejjido^{1,2}, L. Ruiz-Rubio^{1,2}, Pedro Costa⁴, Luís Amorim⁴, Leyre Pérez-Álvarez^{1,2}, Q. Zhang^{2,3}, S. Lanceros-Mendez^{2,3,4}

¹*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Física, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

²*BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, Leioa, Spain.*

³*IKERBASQUE, Basque Foundation for Science, Plaza Euskadi, 5, 48009 Bilbao, Spain.*

⁴*Physics Centre of Minho and Porto Universities (CF-UM-UP) and LaPMET – Laboratory of Physics for Materials and Emergent Technologies, University of Minho, 4710-057, Braga, Portugal.*

Epoxy resins (ERs) are the most common way of protecting metallic surfaces against the effects of corrosion [1]. Widely used commercial paints are synthesized from the reaction between petroleum derived products: Bisphenol A and Epichlorohydrin. Environmental concerns around these resins' sustainability, together with their potential to release toxic substances [2], leaves two main challenges to be addressed: the use of more renewable precursors and the improvements in their microstructure to provide higher protection and resilience. Therefore, we present our work on developing fully bio-based epoxy resin coatings from two natural substances, epoxidized soybean oil (ESO) and Tannic Acid (TA) [4]–[6], doped with different carbon-based nanofillers, such as graphene oxide (GO), reduced GO (rGO) and carbon nanotubes (CNTs). Furthermore, we assessed the possibility to provide these resins with electrical properties. Thus, bio-epoxy resins were obtained (bulk materials, coatings, self-standing films) by mixing the initial components with different epoxy-to-hydroxyl molar ratios and up to 5 wt.% of the selected carbonaceous filler. Characterization techniques included dynamical mechanical analysis (DMTA), tensile tests and rheological experiments. Their functionalities, were characterized by means of electrochemical and electrical techniques, such as electrochemical impedance spectroscopy and polarization curves. Results obtained, assessed the viability of these bio-based thermosets for a wide range of applications, regarding their specific mechanical properties, while displaying superior anti-corrosion resistance (corrosion rates = 10^{-8} - 10^{-6} m/year). Thus, this research could open alternative ways for developing more sustainable and economic formulations for multifunctional ERs.

Keywords/Palabras clave: anti-corrosion, bio-based composites, thermosetting coatings, epoxidized soybean oil, tannic acid, graphene oxide, carbon nanotubes, electrochemistry.

References:

- [1] C. Verma et al., "Epoxy resins as anticorrosive polymeric materials: A review," *React. Funct. Polym.* **2020**, 156, 9, 104741.
- [2] F. A. M. M. Gonçalves, M. Santos, T. Cernadas, P. Ferreira, and P. Alves, "Advances in the development of biobased epoxy resins: insight into more sustainable materials and future applications," *Int. Mater. Rev.* **2022**, 67, 2, 119–149.
- [3] M. Schwaiger et al., "Bioinspired fracture toughness enhancement of a fully bio-based epoxy resin," *Polym. Test.* **2023**, 124, 6, 108098.
- [4] C. Di Mauro, S. Malburet, A. Genua, A. Graillet, and A. Mija, "Sustainable Series of New Epoxidized Vegetable Oil-Based Thermosets with Chemical Recycling Properties," *Biomacromolecules* **2020**, 21, 9, 3923–3935.
- [5] R. Tejjido, L. Ruiz-Rubio, S. Lanceros-Méndez, Q. Zhang, and J. L. Vilas-Vilela, "Sustainable Bio-Based Epoxy Resins with Tunable Thermal and Mechanical Properties and Superior Anti-Corrosion Performance," *Polymers (Basel)* **2023**, 15, 20.
- [6] R. Tejjido et al., "Exploring anti-corrosion properties and rheological behaviour of tannic acid and epoxidized soybean oil-based fully bio-based epoxy thermoset resins," *Prog. Org. Coatings* **2024**, 196, 5.

X 4-5 Sustainable Biopolymer-Based Coatings for Corrosion and Fouling Protection in Offshore Structures

Y. Y. Plasencia-Cerdeña¹, A. Catarina Lopes^{1,2}, José Manuel Laza¹, Isabel Moreno³, E. Hernaez¹, L. Ruiz-Rubio^{1,4}

¹*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Física, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

²*IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain,*

³*Innovative Macromolecular Materials (Imacromat), Dpto. de Química Orgánica e Inorgánica, Universidad del País Vasco UPV/EHU, 48940 Leioa, Spain.*

⁴*Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.*

The main objective of this research is the development of bio-based epoxy composite coatings for offshore corrosion and fouling protection of steel. Although steel is widely used in construction and energy sectors due to its excellent mechanical properties [1], it is highly susceptible to corrosion, particularly in marine environments[2]. In such environments, steel structures are exposed to harsh conditions, including high salinity, oxygen availability, and electrical conductivity, which accelerate corrosion mechanisms[3].

To address these challenges, bio-epoxy thermosetting resin matrices have been prepared by reacting epoxidized soybean oil (ESO) with tannic acid (TA), in controlled epoxy-to-hydroxyl molar ratios[4]. These materials exhibit antioxidant properties and a hydrophobic character, making them suitable for use as protective barrier coatings. In line with sustainability goals and circular economy principles, industrial demoulding waste rich in bentonitic content was incorporated as a low-cost, functional filler. The anticorrosion performance of the developed coatings was evaluated using electrochemical impedance spectroscopy (EIS), showing impedance values ranging from $10^{5.5}$ and $10^9 \Omega \cdot \text{cm}^2$, surpassing the commonly accepted threshold for effective protective coatings ($>10^6 \Omega \cdot \text{cm}^2$) in most cases.

Keywords: Bio-based epoxy coatings, corrosion protection, antifouling, epoxidized soybean oil (ESO), tannic acid (TA), demoulding waste, sustainable fillers, marine environments, offshore structures.

References

- [1] Ramezanzadeh, M.; Bahlakeh, G.; Ramezanzadeh, B.; Rostami, M. Mild Steel Surface Eco-Friendly Treatment by Neodymium-Based Nanofilm for Fusion Bonded Epoxy Coating Anti-Corrosion/Adhesion Properties Enhancement in Simulated Seawater. *Journal of Industrial and Engineering Chemistry* 2019, 72, 474–490.
- [2] Wang, D.; Bierwagen, Gordon. P. Sol–Gel Coatings on Metals for Corrosion Protection. *Prog Org Coat* 2009, 64 (4), 327–338.
- [3] Speight, J. G. Corrosion. In *Subsea and Deepwater Oil and Gas Science and Technology*; Elsevier, 2015; pp 213–256.
- [4] Tejjido, R.; Ruiz-Rubio, L.; Lanceros-Méndez, S.; Zhang, Q.; Vilas-Vilela, J. L. Sustainable Bio-Based Epoxy Resins with Tunable Thermal and Mechanic Properties and Superior Anti-Corrosion Performance. *Polymers (Basel)* 2023, 15 (20), 4180.

J 1-1 Sustainable polymers derived from itaconic acid for biomedical applications

A. Funes-López¹, R. Cuervo-Rodríguez², A. Muñoz-Bonilla¹, M. Fernández-García¹

¹Instituto de Ciencia y Tecnología de Polímeros, CSIC, Madrid, España.

²Universidad Complutense de Madrid, Madrid, España

The synthesis of polymers from renewable sources is a highly relevant research area due to the need to reduce dependence on petroleum-derived plastics. In this study, we present a sustainable polymeric system based on the copolymerization of two monomers: MTA, a monomer derived from a vitamin B1 (sulfurol) component,[1] and PrI,[2] a naturally sourced itaconic acid derivative. The chemical versatility of itaconic acid allowed us to introduce functional groups susceptible to *click* chemistry, enabling the incorporation of natural antimicrobial and antioxidant molecules (Sulfurol and Menthol). Additionally, the polymers were designed with varying positive charge densities, which directly influence their bioactive properties. To assess the properties of the copolymers, several evaluations were performed. Firstly, their antimicrobial activity against Gram-positive and Gram-negative bacteria was determined using minimum inhibitory concentration (MIC) assays,[2] yielding values ranging from 500 to 8 µg/mL depending on the copolymer and the tested microorganism. Secondly, their antioxidant capacity was evaluated through DPPH radical scavenging,[3] showing activity at a polymer concentration of 0.25 mg/mL, with TEAC values quantified in the range of 0.4–0.6 µmol/mg. Finally, the biocompatibility of the materials was assessed with Normal Human Dermal Fibroblasts Adult using Alamar Blue assay. The results confirmed cell viability in the presence of the copolymers, supporting their potential for applications in contact with biological tissues.

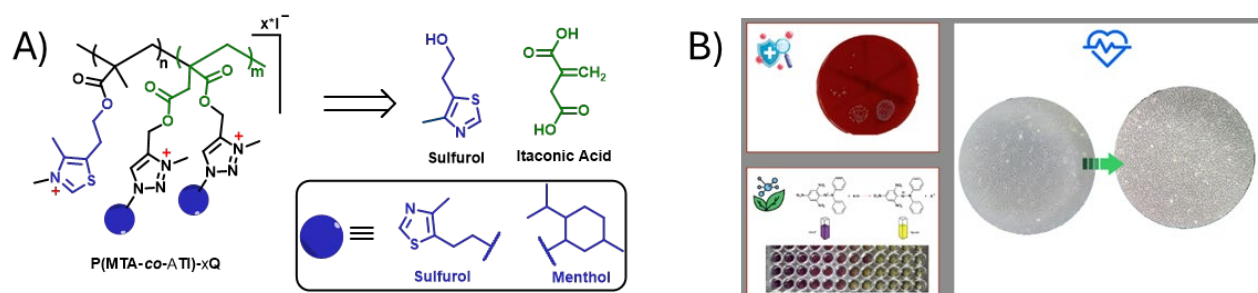


Figure 1. A) Schematic retrosynthesis of polymers. B) Evaluation of bioactive properties

Keywords: Sustainable polymers, itaconic acid, sulfurol, antimicrobial, antioxidant, biocompatible

Acknowledgments

A. Funes gratefully acknowledges the financial support received from MICINN through project PID2022-136516OB-I00.

References

- [1] Hevilla, V., Sonseca, A. et al. Photocuring of aliphatic-lineal poly(glycerol adipate) with a monomer bearing thiazolium groups as a promising approach for biomedical applications. *Eur. Polym. J.* **2023**, 186, 111875
- [2] Chiloeches, A., Funes, A. et al. Biobased polymers derived from itaconic acid bearing clickable groups with potent antibacterial activity and negligible hemolytic activity. *Polym. Chem.*, **2021**, 12, 3190-3200;
- [3] Rumpf, J., Burger, R. et al. Statistical evaluation of DPPH, ABTS, FRAP, and Folin-Ciocalteu assays to assess the antioxidant capacity of lignins. *Int. J. Biol. Macromol.* **2023**, 233, 123470.

J 1-2 Development and characterization of modified chitosan scaffolds for tissue engineering applications.

C. Muñoz-Núñez^{1*}, K. Deshpande², S. Trujillo², A. Muñoz-Bonilla¹, M. Fernández-García¹

¹Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), C/Juan de la Cierva 3, 28006 Madrid, Spain

²INM-Leibniz Institute for New Materials, Saarbrücken, Germany

In recent years, interest in developing effective strategies to counteract tissue damage caused by aging, injuries, or diseases has grown significantly. Tissue engineering has emerged as a promising approach for tissue regeneration, relying on scaffolds that replicate the structure and function of the extracellular matrix. Among the various materials explored, biopolymers, particularly chitosan (CS), have gained considerable attention. This natural polymer, obtained through the deacetylation of chitin from crustacean exoskeletons, is highly valued for its biocompatibility, biodegradability, and its capacity for chemical modification to enhance its properties. The development of biocompatible scaffolds with great physicochemical properties, remarkable cell adhesion and biological response are crucial for tissue engineering applications[1]. In this study, CS scaffolds were designed and characterized, focusing on their mechanical behavior, fibroblast proliferation, and immunomodulatory effects. The incorporation of a CS derivative (CS-MelmB) into the scaffold, along with reinforcement using chitin nanowhiskers (Nw), are studied. The scaffolds exhibited an interconnected porous structure, facilitating nutrient diffusion and cell infiltration.

Rheological analysis confirmed a predominantly viscous behavior at low frequencies, indicative of a transition toward a more elastic structure. After fibroblasts were seeded on the scaffolds, proliferation assays revealed that during the first few days, the cells initially appeared rounded but progressively spread on the scaffold[2]. This reflected enhanced adhesion and interaction over time, correlating with improved cell-scaffold integration (Figure 1). Additionally, immunological studies using macrophages demonstrated the low immunogenicity of the scaffolds. Initially, activation of the nuclear factor kappaB (NF-κB) was similar to lipopolysaccharide (LPS) stimulation. However, secretion of cytokine IL-6 remained low.[3] This suggests an early immune activation without leading to prolonged inflammatory response.

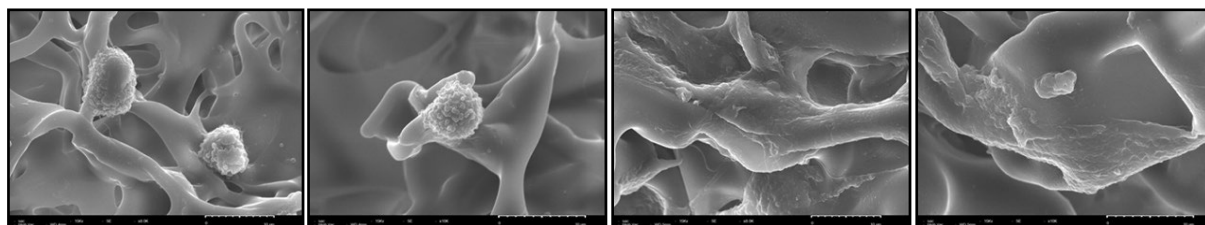


Figure 1: SEM images of Normal Human Dermal Fibroblasts, Adult (NHDF-Ad) growth for 24h (left) and 3 weeks (right) on CS scaffolds

Keywords: Chitosan, scaffolds, fibroblast, proliferation, macrophages

Acknowledgments

This work was funded by MICINN (PID2022-136516OB-I00). C. Muñoz-Núñez acknowledges MICINN for the FPI fellowship: PRE2020-093596.

References

- [1] Madhally, S. V. & Matthew, H. W. T. Porous chitosan scaffolds for tissue engineering. *Biomaterials* **20**, 1133–1142 (1999).
- [2] Jhala, D. *et al.* Biomimetic polycaprolactone-chitosan nanofibrous substrate influenced cell cycle and ECM secretion affect cellular uptake of nanoclusters. *Bioact. Mater.* **4**, 79–86 (2019).
- [3] Nawrotek, K. *et al.* Controlling the Spatiotemporal Release of Nerve Growth Factor by Chitosan/Polycaprolactone Conduits for Use in Peripheral Nerve Regeneration. *Int. J. Mol. Sci.* **23**, 2852 (2022).

J 1-3 Encapsulación y liberación de proteínas a partir de hidrogeles covalentes dinámicos basados en iminoboronatos

Ma. Sofia Navarrete Burgos,^{1,2} Santiago Sarasa,^{1,2} Silvia Hernández-Ainsa,¹ Jesús del Barrio.^{1,2}

¹Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50018, Spain

²Departamento de Química Orgánica, Universidad de Zaragoza, Zaragoza 50009, Spain

La encapsulación y liberación de sustancias utilizando hidrogeles covalentes dinámicos representa una estrategia innovadora en la terapia dirigida y la entrega localizada de especies terapéuticas. [1] Durante el proceso de liberación juegan un papel importante tanto las propiedades del hidrogel (propiedades de transporte y reológicas, por ejemplo) como las condiciones físicas o químicas del entorno (temperatura, pH, agentes competitivos, etc.). [2] En este trabajo, se han preparado hidrogeles covalentes dinámicos basados en iminoboronatos (PEG-4arm-FPBA) (**Figura 1a**) y se ha encapsulado como sustancia modelo una proteína, la Inmunoglobulina G (IgG), que porta el marcador fluorescente Atto594. Mediante espectroscopia de fluorescencia, se ha investigado la cinética de liberación de IgG (**Figura 1b**), su dependencia con la concentración del hidrogel y con la presencia de agentes que modifican el grado de reticulación de la red, así como la respuesta frente a sustancias químicas y metabolitos como la glucosa. Igualmente, se ha estudiado el grado de erosión del hidrogel y su contribución a las tasas de liberación de IgG. Estos resultados contribuirán al desarrollo de hidrogeles covalentes dinámicos como biomateriales para la entrega localizada de fármacos.

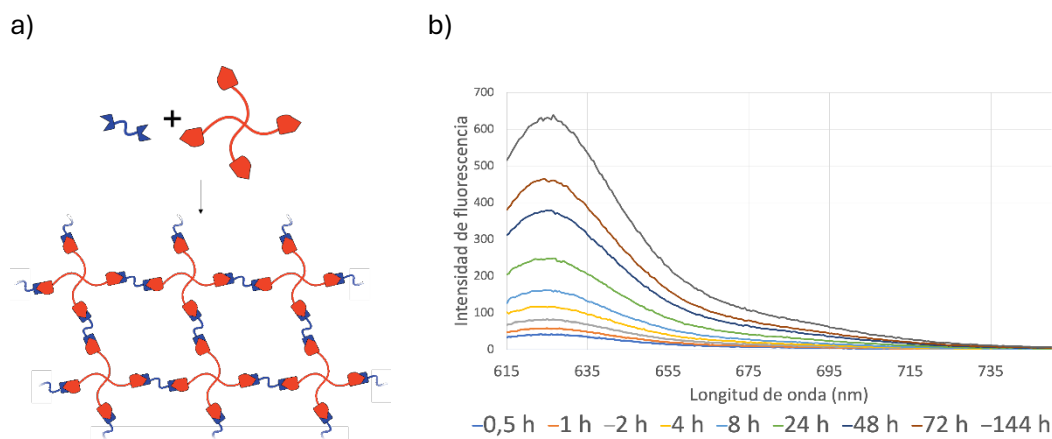


Figura 1. a) Esquema que representa la formación del hidrogel entre el polímero de 4 brazos de PEG, que contiene el FPBA, y el agente reticulante; b) Cinética de la liberación del IgG-Atto594 por medidas de fluorescencia.

Palabras clave: encapsulación, hidrogel, enlaces covalentes dinámicos, iminoboronatos.

Referencias

[1] Marco-Dufort, B.; Willi, J.; Vielba-Gomez, F.; Gatti, F.; Tibbitt M. W.; Environment Controls Biomolecule Release from Dynamic Covalent Hydrogels. *Biomacromolecules*, 2021, 22(1), 146-157.

[2] Yesilyurt, V.; Webber, M. J.; Appel, E. A.; Godwin, C.; Langer, R.; Anderson, D. G.; Injectable Self-Healing Glucose-Responsive Hydrogels with pH-Regulated Mechanical Properties. *Adv.Mater.* 2016, 28, 86-91.

J 1-4 Studying the viscoelastic properties of the human tear film: microrheology of complex polymer solutions

A. Cardil,^{1*} M. Fernandez,² I. Calafel,² I. Martínez-Soroa,^{3,4} A. Pérez Sarriegui,^{3,4} J. Ramos,¹ A. Acera,^{5,6} and J.F. Vega¹

¹BIOPHYM, Department of Macromolecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid

²POLYMAT and Department of Polymers and Adv. Mat., UPV/EHU, Donostia-San Sebastián, Spain

³Miranza Begitek Clinic, Plaza Teresa de Calcuta 7, 20012 Donostia-San Sebastián, Spain

⁴Donostia University Hospital, Paseo Dr. Beguiristain s/n, 20014 Donostia-San Sebastián, Spain

⁵Department of Cell Biology and Histology, GOBE, UPV/EHU, Leioa 48940, Spain

⁶Ikerbasque, Basque Foundation for Science, Bilbao 48001, Spain

Light scattering techniques based on the Einstein-Stokes approach [1,2] have become a powerful tool to investigate the viscoelastic properties of soft materials, such as polymer solutions, biological systems and cross-linked networks [3,4]. Dynamic light scattering in the single scattering mode microrheological approach (DLS μ R) presents several advantages over the previous diffusing wave spectroscopy based techniques, and has become subject of extensive research [5]. This technique allows the study of very small sample volumes, as low as 12 μ L. Furthermore, DLS μ R is able to measure the dynamics of these systems in a broad time range, making possible the analysis of the wide hierarchy of phenomena typical of biological materials. An overview of the DLS μ R measurement process is shown in Figure 1. The main focus of this study is researching, using passive microrheology, the viscoelastic properties of artificial and natural human tears. Hyaluronic acid (HA) is one of the most used bio-polymers for the manufacture of lubricating eye drops. The viscosity of HA solutions is influenced by the molecular characteristics and concentration of the polymer solution. There is, however, a lack of knowledge about the viscosity of human tears. Commercial lubricant eyedrops exhibited behaviours consistent with unentangled semidilute solutions. A linear relationship could be established between the molecular weight and the concentration on HA in the artificial eyedrops and their Newtonian viscosities. Additionally, this study successfully measured the viscoelastic behaviour of human tears, which exhibited a characteristic non-Newtonian behaviour, with a significant increase in the relaxation time compared to the artificial tears with similar values of the Newtonian viscosity. Microrheological measurements have shown promise in order to design solutions with a viscoelastic behaviour mimic that of the natural tear film. Complex mixtures of polymers with different chain flexibilities present a more complex relaxation spectrum, paving the way towards the design of better eye-drops and a deeper understanding of the viscoelastic properties of polymer solutions.

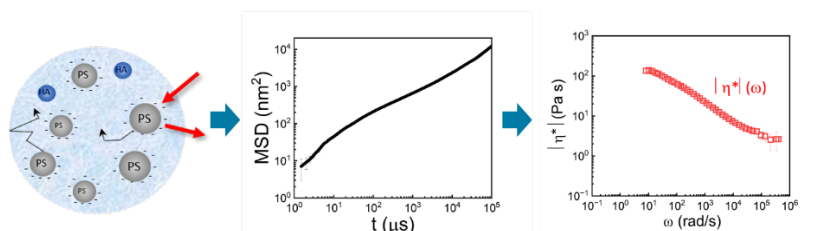


Figure 1. Diagram of a microrheological experiment. From DLS μ R measurements, MSD is obtained and calculated.

Keywords: Rheology, passive microrheology, bio-fluids, polymer solutions

Acknowledgments Project PIE202250E035

References

- [1] Einstein, A. On the Electrodynamics of Moving Bodies. *Annalen der Physik*. **1905**, *17*, 449.
- [2] Mason, T.G., Weitz, D.A. *Phys. Rev. Lett.* **1995**, *74*, 1250.
- [3] Dsgupta, B.R., Tee, S.Y., Crocker, C., Frisken, B.J., Weitz, D.A. *Phys. Rev. E*. **2002**, *65*, 51505.
- [4] Xu, J., Viasnoff, V., Wirtz, .A.. *Rheol Acta*. **1998**, *37*, 387.
- [5] Krajina, B.A., Tropini, C., Zhu, A., et al., *ACS Cent. Sci.* **2017**, *12*, 1294

J 1-5 Polyelectrolytes for Fluorescence-Based Detection of Serum Protein Composition Changes in Liquid Biopsy Cancer Diagnostics

M. Val-Carreres^{*1}, A. Nogueras¹, D. Ortega², O. Abian², L. Oriol¹, T. Sierra¹

¹Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Facultad de Ciencias, Zaragoza 50009, Spain.

²Institute of Biocomputation and Physics of Complex Systems (BIFI), Joint Units IQFR-CSIC-BIFI, and GBsC- CSIC-BIFI, Universidad de Zaragoza, Facultad de Ciencias, Zaragoza 50018, Spain.

Fluorescence liquid biopsy (FLB) is a non-invasive technique for early cancer detection via disease-specific biomarkers in body fluids.[1] However, low biomarker concentration and non-specific molecules hinder accurate diagnosis based on fluorescence differences linked to changes in protein-contents owing to the presence of tumours. To enhance FLB sensitivity and selectivity, our study explores polymeric nanoparticles (NPs) that concentrate such changes via protein corona (PC) formation. We recently reported that the interaction of NPs and serum proteins can modify the natural fluorescence of the latter, making the NPs- fluorescence spectroscopy tandem a useful, non-invasive and user-friendly tool to detect changes in blood serum composition and be used in liquid biopsy.[2]

In this work, we prepared cationic or zwitterionic NPs via self-assembly of amphiphilic block copolymers (BCs) based on pluronic. Using click chemistry, pluronic® F-127 was conjugated both to i) allyl-terminated dendrons (D_{G_x}, being dedron generation x=1,2,3) through azide-alkyne coupling, followed by guanidinium functionalization via thiol-ene reaction (Figure 1a); and ii) the zwitterionic group 2-(2-methylprop-2-enoyloxy)ethyl 2-(trimethylammonio)ethyl phosphate via thiol-Michael addition (Figure 1b). NPs were prepared by micellization in water, as confirmed by TEM and DLS. Fluorescence studies ($\lambda_{ex} = 280$ nm) targeting tryptophan residues in serum protein assessed interactions between NPs and proteins in commercial blood serum. These findings highlight the potential of NP-assisted fluorescence spectroscopy as a promising tool for cancer diagnostics by detecting fluorescence changes in PC composition.

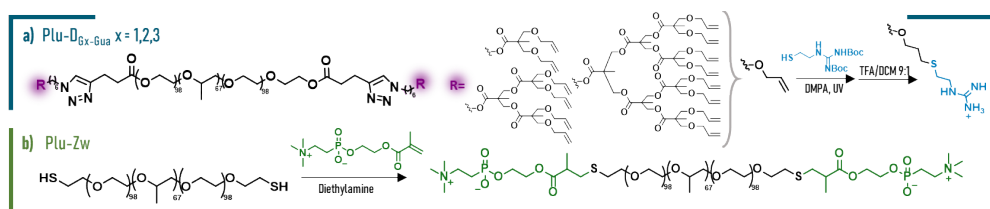


Figure 1. Schematic representation of a) dendritic-linear-dendritic BCs containing peripheral guanidinium moieties (Plu-DG_x-Gua) and b) BCs with terminal zwitterionic groups (Plu-Zw)

Keywords: Fluorescence liquid biopsy, Dendron, Protein corona, Click chemistry

Acknowledgments

Financial support from Ministerio de Ciencia e Innovación (Project PID2021-126132NB-I00; FPI fellowship of MVC, PRE2022-104437) and Gobierno de Aragón (Project LMP93_21; Research group 47_23R) is acknowledged.

References

- [1] Kaniyala Melanthota, S. *et al.* Types of spectroscopy and microscopy techniques for cancer diagnosis: a review. *Lasers Med. Sci.* **2022**, 37 (8), 3067-3084.
- [2] Morcuende-Ventura, V. *et al.* Fluorescence Liquid Biopsy for Cancer Detection Is Improved by Using Cationic Dendronized Hyperbranched Polymer *Int. J. Mol. Sci.* **2021**, 22, 6501.

J 1-6 3D-Printable Gelatin-based Hydrogels with tunable mechanical and degradation behaviour for Tissue Engineering

Ane García-García^{1,2}, Leire Ruiz-Rubio^{1,2}, Unai Silván^{2,3}, José Luis Vilas-Vilela^{1,2}, Senentxu Lanceros-Mendez², Leyre Perez-Álvarez^{1,2}

¹Innovative Macromolecular Materials Group (Imacromat), Department of Physical Chemistry (UPV/EHU), 48940, Spain

²BCmaterials, Basque Centre for Materials, Applications and Nanostructures, 48940, Spain

³IKERBASQUE, Basque Foundation for Science, Leioa

Over the past decade, 3D printing has emerged as a widely recognized and extensively studied technology in the field of tissue engineering because it enables the precise fabrication of dynamic three-dimensional (3D) scaffolds that mimic the mechanical and biological properties of the ECM. In order to produce 3D-printed scaffolds, numerous bio-inks have been widely studied. Among them, hydrogels are very attractive materials due to their good biocompatibility, soft tissue-like properties and water-filled networks, which allow the passage of oxygen, nutrients and metabolites [1]. Extrusion-based 3D printing has garnered significant attention due to its simplicity, scalability, and ability to print a diverse range of bio-inks [2]. For this technique, photocrosslinkable hydrogels are especially advantageous, as they allow precise spatial and temporal control over gelation during the printing process. Specifically, photopolymerizable hydrogels derived from peptide-based polymers such as gelatin have garnered significant attention due to their capacity to form 3D structures. Moreover, the ability to modulate the mechanical properties and degradability of these hydrogels is crucial for supporting dynamic cell behaviour and ensuring the success of engineered tissue constructs in physiological environments. Hence, in this work, methacrylated gelatin was employed to prepare 3D-printable hydrogels with modulated mechanical properties and degradability.

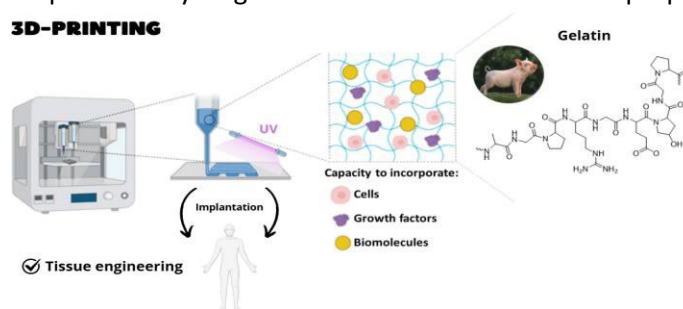


Figure 1. 3D printing of photopolymerizable gelatin-based hydrogels for tissue engineering.

Keywords/Palabras clave: gelatin, hydrogels, degradation, 3D-printing

Acknowledgments

This work (Grant No. PID2022-138572OB-C42) is a research project funded by MCIN/AEI/10.13039/501100011033, FEDER UE and the Department of Health of the Basque Government (ref. 2024333042).

References/Referencias

- [1] Alexa, R.L.; Iovu, H.; Ghitman, J.; Serafim, A.; Stavarache, C.; Marin, M.M.; Ianchis, R. 3D-Printed Gelatin Methacryloyl-Based Scaffolds with Potential Application in Tissue Engineering. *Polymers (Basel)*. **2021**, *13*, 1–17, doi:10.3390/polym13050727.
- [2] Li, X.; Zheng, F.; Wang, X.; Geng, X.; Zhao, S.; Liu, H.; Dou, D.; Leng, Y.; Wang, L.; Fan, Y. Biomaterial Inks for Extrusion-Based 3D Bioprinting: Property, Classification, Modification, and Selection. *Int. J. Bioprinting* **2022**, *9*, doi:10.18063/IJB.V9I2.649.

J 2-1 Analysing the potential of laser femtosecond technology for the mass production of Cyclic Olefin Copolymer microfluidic devices for biomedical applications

Irene Varela Leniz¹, Taieb Bakouche², Malen Astigarraga¹, Florent Husson², Ane Miren Zaldua¹, Laura Gemini², José Luis Vilas-Vilela^{3,4}, Leire Etxeberria¹

¹ Leartiker S. Coop, Xemein Etorbidea 12A, 48270 Markina-Xemein, Bizkaia, Spain

² ALPhANOV, Institut d'optique d'Aquitaine, Rue François Mitterrand, 33400 Talence, France

³ Macromolecular Chemistry Research Group (labquimac), Department of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48940 Leioa, Spain

⁴ BC Materials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

Microfluidic devices have attracted increasing attention due to their great potential across a wide range of advanced applications. Among their key advantages are the significant reduction in reagent consumption, faster sample processing, and the simplification of laboratory workflows [1]. However, transitioning microfluidic prototypes to commercial-scale production still faces challenges, primarily due to the complexities of manufacturing them in large quantities. These challenges stem largely from the need to maintain precise tolerances while using cost-efficient production methods [2]. Precision micromilling is widely used for mould inserts but is costly and slow for complex, high-resolution microfeatures at scale [3,4]. In contrast, femtosecond laser (fs-laser) technology has gained attention as a highly accurate and efficient alternative for micromachining applications [5].

This study examines the use of femtosecond laser micromachining to create injection mould inserts for mass production of thermoplastic microfluidic devices. A reference design was used to optimize laser parameters for high structural resolution and surface quality, aiming to reduce production time and cost. Microstructures were replicated using two medical-grade Cyclic Olefin Copolymers (COC), E-140 and 8007S-04. Dimensional accuracy and surface finish were evaluated with SEM and confocal microscopy, and bonding tests assessed surface suitability for microfluidic applications. The optimized process reduced insert fabrication time by up to 90% compared to micromilling. Surfaces were exceptionally smooth, with average roughness of 64.6 nm for the metal insert and 71.8 nm and 72.9 nm for COC E-140 and 8007S-04, respectively. While further improvements are needed to match the precision of traditional methods, the significant time savings and high-quality results demonstrate strong potential for large-scale microfluidic device manufacturing.

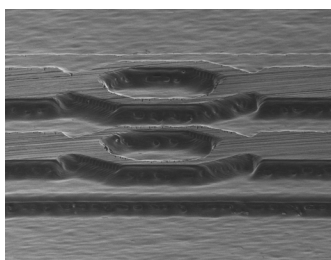


Figure 2. SEM image of the structures replicated in COC E-140 by injection moulding.

Keywords: microfluidics, thermoplastics, laser processing, injection moulding, surface analysis

References

- [1] Berlanda, S.F.; Breitfeld, M.; Dietsche, C.L.; Dittrich, P.S. *Anal. Chem.* 2021, 93, 311–331.
- [2] Cong, H.; Zhang, N. *Biomicrofluidics* 2022, 16, 021301.
- [3] Chang, W.-L.; Luo, X.-C.; Ritchie, J.M.; et al. *Proc. Inst. Mech. Eng. Part B J. Eng. Manuf.* 2011, 225, 458–462.
- [4] Lu, Y.; Liu, B.; Zhang, Z.; Guo, M.; Wang, J.; Wang, C. *Int. J. Adv. Manuf. Technol.* 2023, 127, 3665–3680.
- [5] Malinauskas, M.; Žukauskas, A.; Hasegawa, S.; et al. *Light Sci. Appl.* 2016, 5, e16133–e16133.

J 2-2 Natural polysaccharide based hydrogels for cardiac tissue repair

A. Taboada^{1*}, R. Bouza¹, M. Rico¹

¹ CITENI, Grupo de Polímeros, Campus Industrial de Ferrol, Universidade da Coruna, Ferrol, Spain

Cardiovascular diseases (CVDs) remain the leading cause of mortality globally, with their prevalence expected to rise due to an aging population. Ischemic heart disease, often resulting in myocardial infarction (MI), is the primary cause of cardiovascular deaths. The current treatments improve patients' quality of life but do not repair the loss of cardiac cells [1].

Cardiac tissue engineering, particularly using hydrogels, emerges as a promising therapeutic strategy. Hydrogels, composed of highly biocompatible materials, mimic the cardiac extracellular matrix and support cell growth and tissue regeneration, offering advantages such as minimal invasiveness, reduced recovery times, and localized delivery of cells and growth factors [2].

Highly biocompatible dynamic hydrogels are developed using collagen and chitosan, reinforced to promote cell adhesion and proliferation, particularly for cardiomyocytes, fibroblasts, and adipocytes. The synthesis and gelation process of these hydrogels is analyzed according to the effects of different crosslinking agents [3]. In addition, green graphene is included as an organic reinforcement to improve mechanical strength and electrical conductivity. Although research on graphene for biomedical applications is growing, its integration into collagen and chitosan hydrogels remains unprecedented. The aim of this work is to develop dynamic hydrogels incorporating graphene to enhance their mechanical strength without compromising other functional properties [4].

Keywords: Cardiac tissue engineering, Hydrogel, Chitosan, Collagen and Green Graphene.

References

- [1] Gil-Cabrerizo, P.; Scacchetti, I.; Garbayo, E. & Blanco-Prieto, M. J. Cardiac tissue engineering for myocardial infarction treatment. *Eur J Pharm Sci* **2023**, 185, 106439.
- [2] Gorain, B. *et al.* Carbon nanotube scaffolds as emerging nanoplatform for myocardial tissue regeneration: A review of recent developments and therapeutic implications. *Biomedicine & Pharmacotherapy* **2018**, 104, 496–508.
- [3] Sánchez-Cid, P. *et al.* Effect of different crosslinking agents on hybrid chitosan/collagen hydrogels for potential tissue engineering applications. *Int J Biol Macromol* **2024**, 263, 129858.
- [4] Kaviani, S.; Talebi, A.; Labbaf, S. & Karimzadeh, F. Conductive GelMA/alginate/polypyrrole/graphene hydrogel as a potential scaffold for cardiac tissue engineering; Physicochemical, mechanical, and biological evaluations. *International Journal of Biological Macromolecules* **2024**, 259.

J 2-3 Biofunctional PLLA via Amoxicillin Immobilization through Amino-yne Click Chemistry

J. Sanchez-Bodon^{1*}, M. Diaz-Galbarriatu¹, A. Galdames¹, L. Ruiz-Rubio^{1,2}, E. Hernaez-Laviña¹, J.L. Vilas-Vilela^{1,2}, I. Moreno-Benitez³

¹Imacromat, Dept. of Physical Chemistry (UPV/EHU), Leioa, Spain; ²BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU, Science Park, 48940 Leioa, Spain; ³Imacromat, Dept. of Organic and Inorganic Chemistry (UPV/EHU), Leioa, Spain

Poly-L-lactic acid (PLLA) is a biodegradable polyester commonly used in orthopedic and dental applications. However, its hydrophobic and crystalline nature can lead to unwanted microbial contamination and biofilm formation.[1] To address this, surface functionalization strategies have been explored in the last years. One promising approach is the amino-yne click reaction, a catalyst-free and spontaneous reaction that proceeds under mild conditions. Compared to other click reactions, it uses readily available amines and forms β - aminoacrylate linkages, which are cleavable in mildly acidic environments, allowing stimulus-responsive behavior.[2] In this work, the amino-yne click reaction was employed to immobilize amoxicillin onto PLLA surfaces. The process included alkaline hydrolysis for surface activation, amidation with ethylenediamine, functionalization with propiolic groups, and subsequent amoxicillin conjugation. A model experiment using tryptophan, a fluorescent amino acid, validated the methodology. Surface characterization techniques—XPS, ATR-FTIR, SEM, and water contact angle analysis—confirmed successful immobilization and preserved substrate integrity on both immobilizations.[3] This surface modification approach enhances PLLA's antimicrobial properties and extends its potential in drug delivery and stimulus-responsive behavior.

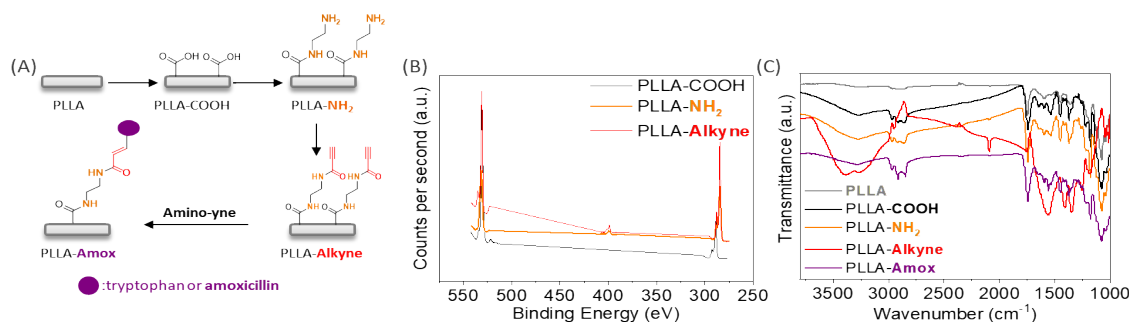


Figure 1. A) schematic representation of PLLA surface functionalization and amoxicillin immobilization, (B) total XPS spectra of PLLA-COOH, PLLA-NH₂ and PLLA-Alkyne, (C) FTIR-ATR spectra of pristine and functionalized PLLA

Keywords: click reaction, amino-yne, bioconjugation

Acknowledgments

This research was funded by the Basque Government (ELKARTEK program, Department of Development and Infrastructures of the Basque Country, KK-2023-00016); Grupos Consolidados IT1756-22; Ministerio de Ciencia e Innovación (MCIN)/Agencia Estatal de Investigación (AEI) (MCIN/AEI/10.13039/501100011033; and the Basque Government (IT1639-22).

References

- [1] Khouri, N.G.; Bahu, J.O.; Blanco-Llamero, C.; Severino, P.; Concha, V.O.C.; Souto, E.B. Polylactic acid (PLA): Properties, synthesis, and biomedical applications – A review of the literature. *J. Molec. Struc.* **2024**, *1309*, 138243.
- [2] Zhang, J.; Zhang, Z.; Wang, J.; Zang, Q.; Sun, J. Z.; Tang, B.Z. Recent progress in the applications of amino-yne click chemistry. *Polym. Chem.* **2021**, *12*, 2978-2986.
- [3] Sanchez-Bodon, J.; Diaz-Galbarriatu, M.; Sola-Llano, R.; Ruiz-Rubio, L.; Vilas-Vilela, J.L.; Moreno-Benitez, I., H.K.; Siegel, S.J. Catalyst-Free Amino-Yne Click Reaction: An Efficient Way for Immobilizing Amoxicillin onto Polymeric Surfaces. *Polymers* **2024**, *16*, 246.

J 2-4 3D Printing of Responsive Polymeric Bioinks for Bacterial Detection

Ana M. Muñoz-Mateo^{1,2}, Francesca Perin¹, Clara García-Astrain^{1,3}

¹Basque Center for Macromolecular Design and Engineering – POLYMAT FUNDAZIOA, 20018 Donostia-San Sebastián, Spain

²Department of Applied Chemistry and Polymeric Materials, University of the Basque Country (UPV/EHU), 20018 Donostia-San Sebastián, Spain

³Ikerbasque Basque Foundation for Science, 48013 Bilbao, Spain

Antimicrobial resistance (AMR) is a major global health concern, demanding alternatives beyond traditional drug development. Alongside new antibiotics, there is an urgent need for tools that allow precise detection and monitoring of bacterial behavior. Bioprinting offers a promising solution by enabling the fabrication of 3D in vitro models that closely mimic the in vivo microenvironment, including tissue structure and cell-bacteria interactions. Furthermore, this technology allows the integration of biosensors into bioinks, facilitating real-time, in situ monitoring of bacterial infections.^[1,2] Among infection monitoring sensors, conjugated polymers (CPs) stand out for their opto-electronic properties, showing colorimetric and fluorescent changes in response to bacteria or biomarkers. Polydiacetylenes (PDAs) are a unique group of CPs that combines highly ordered backbones with customizable side chains. Polymerization of self-assembled diacetylene monomers forms blue vesicles (non-fluorescent) that shift to red (fluorescent) upon exposure to microorganisms or biomolecules.^[3] In this work, by combining sensors with hydrogel-based bioinks we aim to create bioprinted 3D cells models for bacterial infection monitoring (Figure 1). Gelatin methacrylate (GelMa), hyaluronic acid methacrylate (HAMA) and alginate methacrylate (AlgMa) are proposed as viable hydrogels options due to their excellent biocompatibility, biodegradability, low cytotoxicity and printability. As PDAs, 10,12-pentacosadiynolic acid (PCDA) is proposed for its commercial availability and extensive study in sensing applications. Hydrogels incorporating PCDA were characterized in terms of their rheological properties, biocompatibility and fluorescence response. Preliminary results show that PCDA vesicles successfully incorporates into the different hydrogel formulations whereas GelMA-based formulations give the better sensing response, exhibiting the expected blue-red transitions in response to external stimuli. Additionally, the formulated bioink supports the fabrication of basic 3D structures.

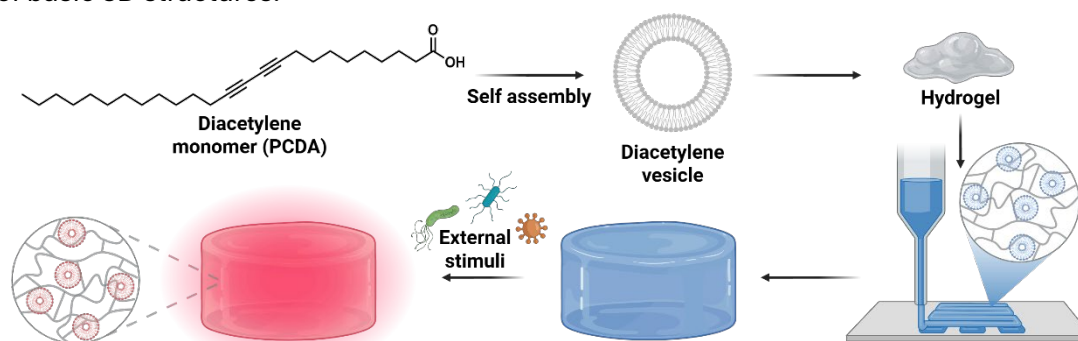


Figure 1. General scheme of printed bioink with incorporated PCDA vesicles.

Keywords: biosensors, hydrogels, 3D models, bioprinting

References

- [1] Thomas J. Hall et al. A call for action to the biomaterial community to tackle antimicrobial resistance. *Biomaterials Science* **2020**, 8, 4951-4974.
- [2] Jianye Y. et al. 3D Bioprinting in Cancer Modeling and Biomedicine: From Print Categories to Biological Applications. *ACS Omega* **2024**, 9, 44076-44100.
- [3] Xiaomin Q.; Brigitte S. Recent Developments in Polydiacetylene-Based Sensors. *Chemistry of Materials* **2019**, 31, 1196-1222.

J 2-5 Design of polysaccharide-based copolymers with potential biomedical applications

M. I. Peñas^{1,2}, L. Rubatat¹, S. C. M. Fernandes¹, M. Save¹

¹IPREM - Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux, Université de Pau et des Pays de l'Adour (IPREM-UPPA), Hélioparc Pau Pyrénées, 2 avenue du Président Angot, 64053 Pau, France

²UPPA - Université de Pau et des Pays de l'Adour, Avenue de l'Université - BP 576 - 64012 Pau, France

Although plastic manufacturing is making significant efforts toward plastic recycling and promoting a circular economy, a large portion of plastic waste is still not properly recovered and continues ending-up into landfills and the ocean, causing substantial environmental damage [1]. Consequently, current researches focus to develop biodegradable and recyclable materials, using bioplastics such as polylactic acid (PLA) and polycaprolactone (PCL) emerging as potential candidates to replace fossil-fuel derived plastics. However, their biomedical applications remain limited due to slow degradation rates and poor mechanical properties. Moreover, their polymeric matrix hinders biodegradation by restricting water and enzymatic activity [2]. To address these limitations, we propose the development of novel copolyesters based on polysaccharides. The polysaccharide phase within the polyester matrix could enhance the rate of degradation by allowing water permeation, as well as improving the mechanical properties and conferring the materials with antimicrobial capabilities.

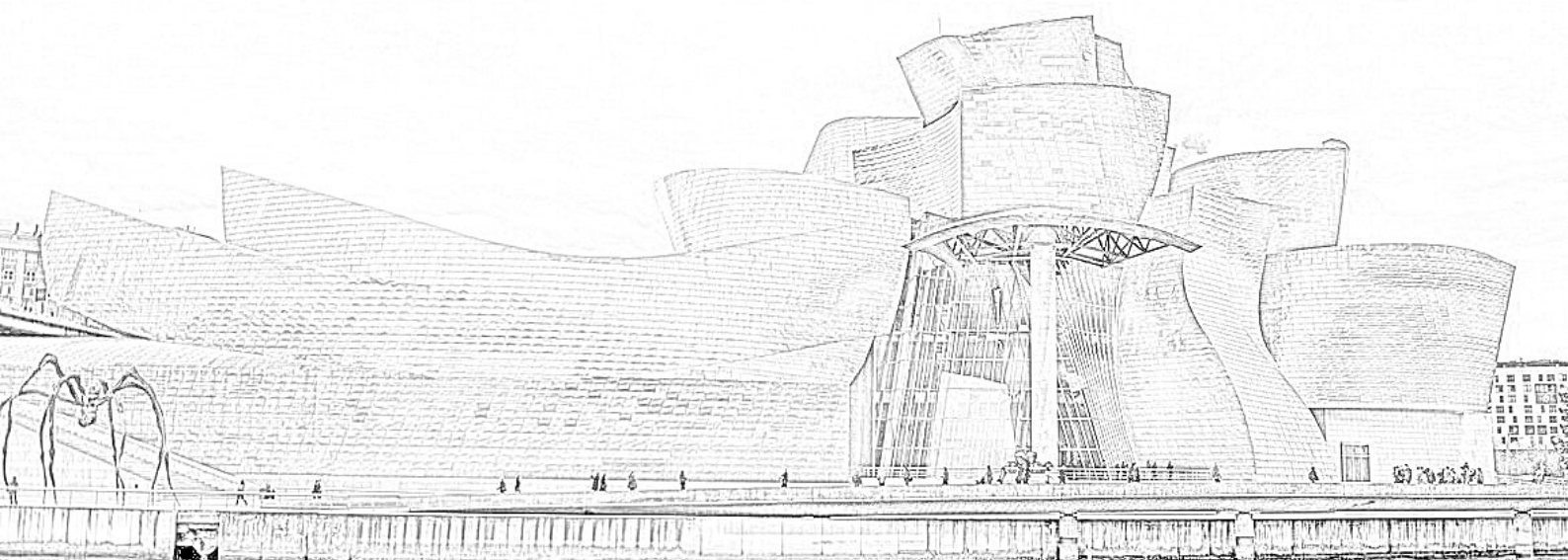
For such purpose, and as a preliminary approach, we performed a thiol-Michael coupling reaction has been carried out between a polysaccharide and an (oligoethylene glycol) acrylate. Dextran has been selected as the polysaccharide component, due to the well-known feasibility of functionalization compared to other polysaccharides [3]. The functionalization of dextran has been done via reductive amination at its chain-end, introducing an active site. As the second component, two different oligoethylene glycols were employed with acrylate and methacrylate chain-ends. The so-obtained copolymers have been characterized by NMR, FTIR-ATR, AFM, and SAXS/WAXS, in order to study their self-assembly behavior. Future work will focus on synthesizing new copolyesters with functionalized PCLs instead of the oligoethylene glycol.

Keywords: block copolymers, self-assembly, thiol-Michael addition, polysaccharides

References

- [1] Kim, J.; Park, S.; Jung, S.; Yun, H.; Choi, K.; Heo, G.; Jin, H. J.; Park, S.; Kwak, H. W. Biodegradation Behavior of PolybutyleneSuccinate (PBS) Fishing Gear in Marine Sedimentary Environments for Ghost Fishing Prevention. *Polymer Degradation and Stability* **2023**, *216*, 110490.
- [2] Kurowiak J.; Klekiel, T.; Będziński, R. Biodegradable Polymers in Biomedical Applications: A Review—Developments, Perspectives and Future Challenges. *International Journal of Molecular Sciences* **2023**, *24* (23), 16952.
- [3] Chen, S.; Alves, M. H.; Save, M.; Billon, L. Synthesis of amphiphilic diblock copolymers derived from renewable dextran by nitroxide mediated polymerization: towards hierarchically structure honeycomb porous films. *Polymer Chemistry* **2014**, *5*, 5310.

Innova





BCMaterials, Centro Vasco de Materiales, Aplicaciones y Nanoestructuras, es un centro de investigación autónomo lanzado en junio de 2012

por Ikerbasque, la Fundación Vasca para la Ciencia y la Universidad del País Vasco (UPV/EHU) como centro de investigación de Materiales, Aplicaciones y Nanoestructuras. El centro está incluido en la red BERC (Basque Excellence Research Centers) y su misión es generar conocimiento sobre la nueva generación de materiales, convirtiendo este conocimiento en soluciones y dispositivos (multi)funcionales para el beneficio de la sociedad.

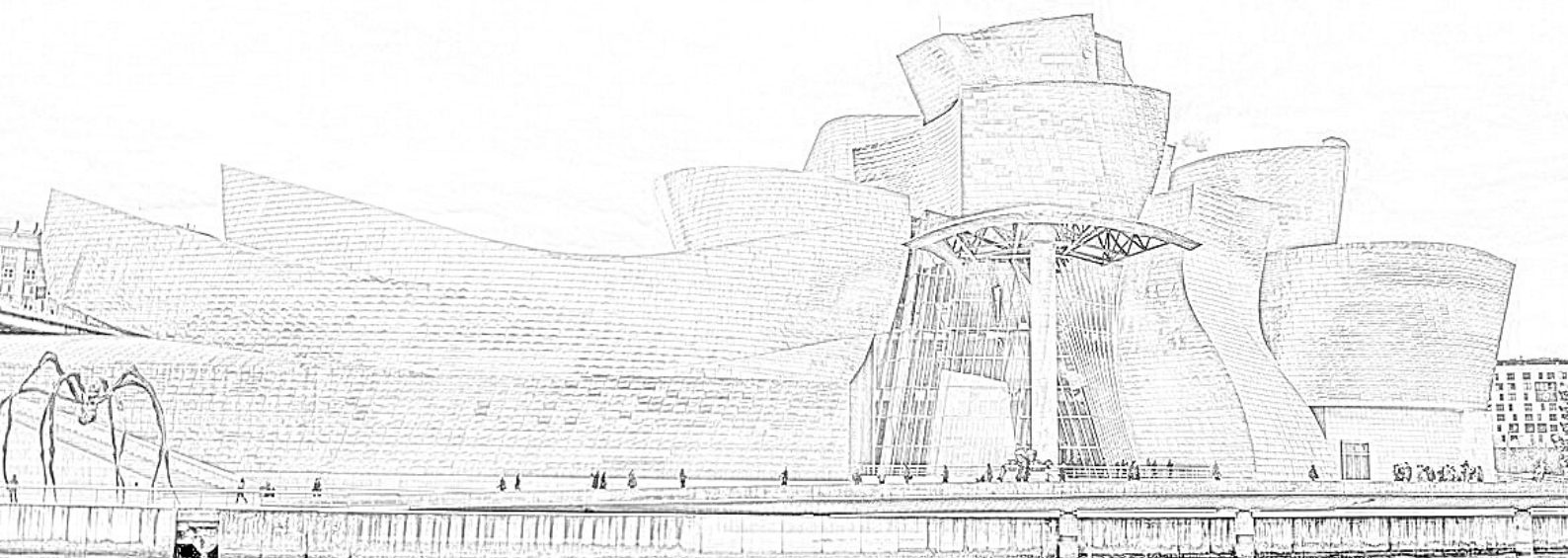
BCMaterials desarrolla, evalúa, comprende e implementa materiales para sensores y actuadores que son críticos para el Internet de las Cosas y la Industria 4.0. Lleva a cabo investigaciones sobre materiales para aplicaciones biológicas y biomédicas avanzadas, así como materiales para energía (tanto de generación como de almacenamiento), entre otros campos paradigmáticos que están configurando los impulsos tecnológicos modernos.

Su compromiso con la sociedad abarca no solo la investigación, el desarrollo y la transferencia de tecnología, sino también la divulgación y la formación de la nueva generación de grandes científicos.



TEKNIKER es un centro tecnológico especializado en fabricación avanzada, ingeniería de superficies, ingeniería de producto y TICs aplicadas a la industria. Su misión es impulsar el crecimiento y el bienestar de la sociedad mediante la I+D+i, contribuyendo de forma sostenible a la competitividad del tejido empresarial.

Sus principales líneas de investigación abarcan desde procesos de fabricación convencionales y no convencionales en diferentes escalas (macro, micro y nano), hasta mecatrónica, ingeniería de precisión y gestión de la producción industrial. En el ámbito de la ingeniería de superficies, trabaja con tecnologías físico-químicas, tribología, materiales para energía y el comportamiento de materiales y fluidos en uso.



En cuanto a las TICs, TEKNIKER desarrolla soluciones innovadoras en analítica predictiva, visión artificial, interacción hombre-máquina, redes de sensores, sistemas ciber-físicos, electrónica de bajo consumo y actuadores electromagnéticos, entre otros. Todo ello con el objetivo de transformar la industria a través de tecnologías inteligentes y sostenibles.

tecnalia

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

mejorar su competitividad, impulsar un crecimiento sostenible y elevar la calidad de vida de las personas. Lidera en España la participación en el programa Horizon Europe y destaca por su elevada solicitud de patentes europeas.

Con un equipo de 1.500 personas apasionadas por la tecnología, TECNALIA promueve una cultura de innovación, anticipación y mejora continua. Su modelo de colaboración se basa en la confianza, la excelencia y el compromiso social, abordando retos complejos mediante soluciones multitecnológicas.

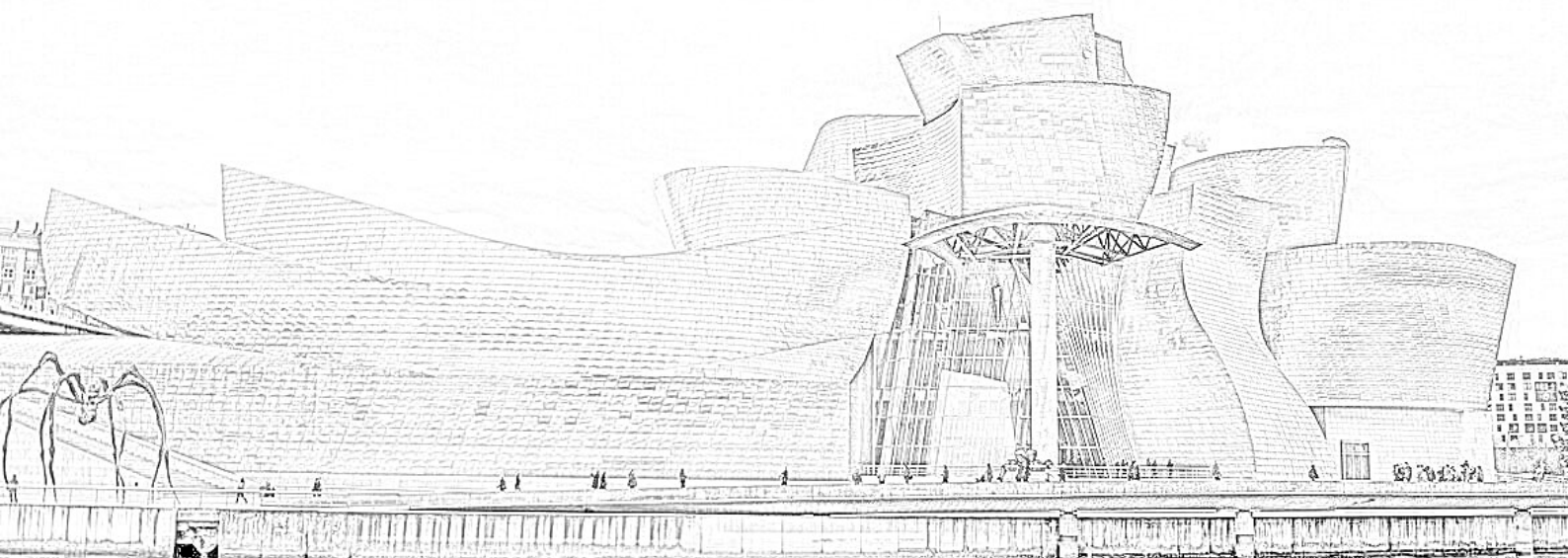
Sus principales ámbitos de actuación incluyen la fabricación inteligente, transición energética, salud, movilidad sostenible, economía circular y digitalización. En TECNALIA, la innovación es más que una meta: es una actitud transformadora.

TECNALIA es el mayor centro de investigación aplicada y desarrollo tecnológico de España, y un referente en Europa, integrado en la Basque Research and Technology Alliance. Su objetivo es transformar la investigación tecnológica en prosperidad, colaborando estrechamente con empresas e instituciones para

Leartiker

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

LEARTIKER es un centro tecnológico que centra su actividad en dos áreas clave: la tecnología de alimentos y la tecnología de polímeros. Su objetivo es generar valor para el tejido empresarial mediante proyectos de I+D y una transferencia efectiva del conocimiento.



En el área de tecnología de alimentos, destaca el trabajo de su centro lácteo, especializado en el desarrollo de nuevos quesos y derivados lácteos, así como en el diseño de alimentos saludables y sostenibles, desde la concepción hasta su lanzamiento al mercado.

En cuanto a la tecnología de polímeros, LEARTIKER investiga nuevos materiales poliméricos biocompatibles destinados al ámbito de la salud, especialmente para su aplicación en dispositivos médicos. Además, impulsa soluciones para el transporte sostenible, desarrollando estructuras poliméricas ligeras, fiables y silenciosas, cuya eficacia se valida mediante técnicas avanzadas de digitalización.

LEARTIKER contribuye así al desarrollo de productos innovadores y sostenibles, adaptados a las necesidades actuales del mercado.

