Index of Contents

Committees

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Scientific Program

Sessions & Topics

🟦 **Plenary, Keynotes & Round Table**

🟧 **Flash Sessions**

🟥 **Advances in polymer synthesis and Characterization.**

🟩 **Structure and properties of polymers, theory and simulation**

🟪 **Polymers for biomedical and nanomedical applications, hydrogels, electrospinning.**

⬜ **Block copolymers, multiphase polymers, blends, nanocomposites and nanohybrids.**

🟩 **Polymers for energy, optoelectronics and smart applications.**

🟨 **Polymer recycling, bio-based and biodegradable polymers, circular economy.**

🟦 **Rheology, processing, additive manufacturing and mechanical properties of polymers.**

Monday September 16th (Espacio Maldonado – C/ Serrano, 104)

7:30 – 8:30	**REGISTRATION**
8:30 -9:00	**Welcome & opening**
CHAIR	David Mecerreyes
9:00 - 9:40	**Plenary Lecture:** PL-01 – Luis Oriol
9:40 - 10:00	**Keynote Presentation:** KN-01 – Jaime Martín
CHAIR	Jaime Martín & Eva Maya
10:00 – 10:10	O-01
10:10 – 10:20	O-02
10:20 – 10:30	O-03
10:30 – 10:40	O-04
10:40 – 10:50	O-05
10:50 – 11:00	O-06
11:00 – 11:30	**COFFEE + Posters**
CHAIR	Horacio Salavagione & José María Lagarón
11:30 – 11:40	O-07
11:40 – 11:50	O-08
11:50 – 12:00	O-09
12:00 – 12:10	O-10
12:10 – 12:20	O-11
12:20 – 12:30	O-12
12:30 – 12:40	O-13
CHAIR	Luis García
12:40 – 13:00	**Flash Session** **F01-F06**
13:00– 14:30	**LUNCH – Gourmet Voucher**

CHAIR	Luis Rojo
14:30 – 15:10	**Plenary Lecture:** PL-02 - Manuela Gomes
15:10-15:30	**Keynote Presentation:** KN-02 – Marcelo Calderón
CHAIR	Marcelo Calderón & Sergio Martín
15:30 – 15:40	O-14
15:40 – 15:50	O-15
15:50 – 16:00	O-16
16:00 – 17:00	**COFFEE + Posters**
CHAIR	Julieta Páez & José Alberto Méndez
17:00 – 17:20	**Keynote Presentation:** KN-03 - Julieta Paez
17:20 – 17:30	O-17
17:30 – 17:40	O-18
17:40 – 17:50	O-19
17:50 – 18:00	O-20
18:00 – 18:10	O-21
18:10 – 18:20	O-22
18:20 – 18:30	O-23
18:30 – 18:40	O-24
18:40 – 18:50	O-25
18:50 – 19:00	O-26

20:00	**Welcome Reception** National Museum of Natural Sciences (MNCN-CSIC)

National Museum of Natural Sciences

C/ Jose Gutierrez Abascal 2

Tuesday September 17th (Espacio Maldonado – C/ Serrano, 104)

8:30 -9:00	**REGISTRATION**	
CHAIR	Javier Carretero	
9:00 - 9:40	**Plenary Lecture:** PL-03 – Michel Armand	
9:40 - 10:00	**Keynote Presentation:** KN-04 - Marta Liras	
CHAIR	Marta Liras & Saul Vallejos	Isabel Quijada & Virginia Rivero
10:00 – 10:10	O-27	O-40
10:10 – 10:20	O-28	O-41
10:20 – 10:30	O-29	O-42
10:30 – 10:40	O-30	O-43
10:40 – 10:50	O-31	O-44
10:50 – 11:00	O-32	O-45
11:00 – 11:30	**COFFEE + Posters**	
CHAIR	Carmen Mijangos & Beatriz Merillas	J.C. Rodríguez Cabello & José Alberto Berrocal
11:30 – 11:40	O-33	O-46
11:40 – 11:50	O-34	O-47
11:50 – 12:00	O-35	O-48
12:00 – 12:10	O-36	O-49
12:10 – 12:20	O-37	O-50
12:20 – 12:30	O-38	O-51
12:30 – 12:40	O-39	O-52
CHAIR	Luis García	
12:40 – 13:00	**Flash Session** **F07-F12**	
13:00– 14:30	**LUNCH - Maldonado**	

CHAIR	Pilar Tiemblo
14:30 -14:50	**Round Table**
15:10-15:30	**Keynote Presentation:** KN-05 – Amparo López-Rubio
CHAIR	Amparo López-Rubio & Mercedes Jiménez
15:30 – 15:40	O-53
15:40 – 15:50	O-54
15:50 – 16:00	O-55
16:00 – 17:00	**COFFEE + Posters**
CHAIR	Milagros Piñol & Juan López Valentín
17:00 – 17:20	**Keynote Presentation:** KN-06 – Juan López-Valentin
17:20 – 17:30	O-56
17:30 – 17:40	O-57

18:30 – 19:30	**Cultural Visit** Royal Botanical Gardens of Madrid (RJB-CSIC)

Royal Botanical Gardens of Madrid
Plaza de Murillo 2

REAL JARDÍN
BOTÁNICO

Wednesday September 18th (Espacio Maldonado – C/ Serrano, 104)

8:30 -9:00	**REGISTRATION**
CHAIR	Miryam Criado
9:00 - 9:40	**Plenary Lecture:** PL-04 – George Malliaras
9:40 - 10:00	**Keynote Presentation:** KN-07 – Ana Beloqui
CHAIR	Ana Beloquí & Daniel Domingo
10:00 – 10:10	O-58
10:10 – 10:20	O-59
10:20 – 10:30	O-60
10:30 – 10:40	O-61
10:40 – 10:50	O-62
10:50 – 11:00	O-63
11:00 – 11:30	**COFFEE + Posters**
CHAIR	Auxi Prieto & Laura Peponi
11:30 – 11:40	O-64
11:40 – 11:50	O-65
11:50 – 12:00	O-66
12:00 – 12:10	O-67
12:10 – 12:20	O-68
12:20 – 12:30	O-69
12:30 – 12:40	O-70
CHAIR	Luis García
12:40 – 13:00	**Flash Session** **F13-F19**
13:00– 14:30	**LUNCH - Gourmet Voucher**

CHAIR	Rebeca Hernández
14:30 -14:50	**Keynote Presentation:** KN-08 – Carlos Sánchez-Somolinos
CHAIR	Carlos Sánchez & Rebeca Hernández
14:50 – 15:00	O-71
15:00 – 15:10	O-72
15:10-15:30	O-73
	O-74
15:30 – 15:40	O-75
15:40 – 15:50	O-76
15:50 – 16:00	O-77
16:00 – 17:00	**COFFEE + Posters**
CHAIR	Elisabeth Engel & Juan Rodríguez
17:00 – 17:20	**Keynote Presentation:** KN-09 – Elisabeth Engel
17:20 – 17:30	O-78
17:30 – 17:40	O-79

18:00 – 19:30	**GEP General Assembly**

20:45	**Gala Dinner**

Restaurante Descaro

Plaza España 6

Thursday September 19th (CSIC Auditorium – C/ Serrano, 117)

8:30 -9:00	**REGISTRATION**
CHAIR	María Rosa Aguilar
9:00 - 9:40	**Plenary Lecture:** PL-05 – Auxi Prieto
9:40 - 10:00	**Keynote Presentation:** KN-10 – Alexandra Muñoz
CHAIR	Alexandra Muñóz & Marina Galia
10:00 – 10:10	O-80
10:10 – 10:20	O-81
10:20 – 10:30	O-82
10:30 – 10:40	O-83
10:40 – 10:50	O-84
10:50 – 11:00	O-85
11:00 – 11:30	**COFFEE**
CHAIR	Luis Oriol & Ester Verde
11:30 – 11:40	O-86
11:40 – 11:50	O-87
11:50 – 12:00	O-88
12:00 – 12:10	O-89
12:10 – 12:20	O-90
12:20 – 12:30	O-91
12:30 – 12:40	O-92
12:40 – 13:00	**Closing Ceremony**

CSIC Auditorium
C/ Serrano 117

Index of Abstracts

Plenary lectures

PL-01 - *Controlled polymerization and click chemistry approaches to smart block copolymers.* Luis Oriol Langa (Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza)

PL-02 - *Recreating tendon structure and biomechanical environment using magnetic 3D Bioprinting.* Manuela E. Gomes (School of Medicine and Biomedical Sciences, University of Porto,)

PL-03 - *Polymer electrolytes, the key to solid-state batteries*. Michel Armand (CIC Energigune Basque Research and Technology Alliance (BRTA),)

PL-04 - *Conducting Polymers for Bioelectronic Medicine*. George Malliaras (University of Cambridge)

Keynotes

KN-01 - *New Insights Into The Structural Organization Of Semiconducting Polymers For Photovoltaics.* Jaime Martín Pérez (Universidade da Coruña)

KN-02 - *Multiresponsive Nanogels For Mucosal Drug Delivery.* Marcelo Calderón (POLYMAT, University of the Basque Country)

KN-03 - *Thiol-Mediated Dynamic Covalent Hydrogels With Tunable Viscoelasticity For 3d Cell Culture.* Julieta Paez (University of Twente)

KN-04 - *Conjugated Porous Polymers And Covalent Organic Frameworka As Well As Hybrid Thereof For Solar Fuels Production.* Marta Liras Torrente (IMDEA Energy)

KN-05 - *Revalorización De Residuos Agroindustriales Para El Desarrollo De Nuevos Materiales Biodegradables.* Amparo López Rubio (IATA-CSIC)

KN-06 - *Improving Polymer Circularity Through Chemical Recycling Strategies*. Juan López Valentin (Institute of Polymer Science and Technology, CSIC)

KN-07 - *Thin Nanogel Dressing Of Biomolecules To Approach Smart Applications.* Ana Beloqui Elizazu (POLYMAT, University of the Basque Country)

KN-08 - *Advancing Soft Robotic Functions Through Additive Manufacturing Of Liquid Crystal Elastomers*. Carlos Sánchez Somolinos (INMA-CSIC)

KN-09 - *3D Bioprinting Biomimetic Breast Cancer Models Using Decellularized extracellular matrices.* Elisabeth Engel (Institute for Bioengineering of Catalonia)

KN-10 - *Antimicrobial Cationic Polymers Based On Thiazole Rings, A Component Of Vitamin B*. Alexandra Muñoz Bonilla (ICTP-CSIC)

Oral Presentations

O-01 - *Water-Soluble Cyclic Polymers With Potential Biomedical Applications.* Fabienne Barroso Bujans (Donostia International Physics Center)

O-02 - *Itaconic Acid: A Versatile Biobased Building Block For The Replacement Of (Meth)Acrylic Acid In Photocurable Formulations For 3D Printing*. Mirko Maturi (Universidad de Cadiz)

O-03 - *Transforming Commodity Plastic PVC Into Efficient Catalytic Single-Chain Nanoparticles*. Ester Verde Sesto (Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center (MPC))

O-04 - *CRISPR-Mediated Transcriptional Activation Technology (CRISPRa) As An Opportunity For Enhancing Elastin Like Recombinamers (ELRs) Expression In Bacteria*. Viktoriya Chaskovska (University of Valladolid)

O-05 - *Conducting Polymers Effect In The Volume Phase Transition Of Thermosensitive PNIPAAm-Based Hydrogels*. Joan Torras Costa (Universidad Politècnica de Catalunya)

O-06 - *A Novel And Self-Consistent Physical Framework To Characterize Molecular Structure And Dynamics Of Reinforced Rubbers Based On A Combination Of Experimental Techniques.* Fernando Martín Salamanca (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-07 - *Self-Healing Supramolecular Polyurethanes Based On Multiple Hydrogen Bonds.* Rodrigo Navarro Crespo (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-08 - *Detailed Morphology Of ABS Latex Nanoparticles Revealed By Mathematical Model And HAADF-STEM Tomography.* Shaghayegh Hamzehlou Gholipour (POLYMAT, UPV/EHU)

O-09 - *Efecto De La Velocidad De Enfriamiento En Las Transiciones De Fase De Sistemas Basados En Ácido Poliláctico Con Nucleantes Poliméricos.* Rosa Barranco García (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-10 - *Structural And Crystalline Characterization Of Even-Odd Nylons Obtained From Pimelic Acid.* Matteo Arioli (Departament d'Enginyeria Química, Universitat Politècnica de Catalunya)

O-11 - *Modelos Atomísticos Y De Grano-Grueso Para La Modelización De Disoluciones De Polisacáridos De Origen Bacteriano.* Javier Ramos Díaz (IEM-CSIC)

O-12 - *Relationship Between PLA Structure And Wettability Properties.* María Hernández Rivas (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-13 - *Grafting Of A Photocrosslinkable Coumarin-Based Methacrylate To PLA For 3D Printing Purposes.* José Alberto Méndez González (Universitat de Girona)

O-14 - *Engineering An Immunocompetent Gut On A Chip Model With Controlled Permeability Using Synthetic Polymers.* Ana Mora Boza (Georgia Institute of Technology)

O-15 - *New Generation Of Iodinated Embolic Liquid: A Success Case In The Laboratory-To-Clinic Translation Of Polymeric Medical Devices..* Raquel Palao Suay (Group of Biomaterials, Institute of Polymer Science and Technology)

O-16 - *Multifunctional Curcumin-Based Polymer Coating: A Promising Platform Against Bacteria, Inflammation And Coagulation.* Julia Sánchez Bodón (UPV/EHU)

O-17 - *Sustainable Polylactic Acid (PLA)/Sargassum Bioplastics Prepared Using SBS.* Effect Of Sargassum Content On Morphology And Mechanical Properties. Dania Olmos Díaz (Universidad Carlos III de Madrid)

O-18 - *A Highly Oxygenated Biomimetic Hydrogel With A Predictive Oxygen Durability Model To Enhance Post-Transplantion Cellular Survival.* Daniel Domingo Lopez (Anatomy and Regenerative Medicine Institute (REMEDI), University of Galway)

O-19 - *Degradable Hydrogel Antifouling Coatings Derived From Lactic Acid-Based Solvent.* Marc Palà Sánchez (Universitat Rovira i Virgili)"

O-20 - *Fibras Electrohiladas Avanzadas Dopadas Con Nanopartículas De Cobre Para La Eliminación De Pesticidas En Agua.* Ana Isabel Quilez Molina (BioEcoUVA Research Institute on Bioeconomy)"

O-21 - *Advancements In NOx Abatement Techniques Using Impregnated Porous Biopolymeric Aerogel.* Kåre Gunnar, Erling Tjus (IVL Swedish Environmental Research Institute)

O-22 - *Polymer-Inorganic Nanoparticle Hybrid Tandems As Selective Metal Sensors.* Isabel Quijada Garrido (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-23 - *Epoxidized Soybean Oil Based Thermoset As Matrix For Functional Materials.* Agnieszka Tercjak (UPV/EHU)

O-24 - *Polymer Based Thermoelectric Materials.* Mario Culebras Rubio (Universitat de Vale`ncia)

O-25 - *Sustainable Lignin-Based Hydrogels: Synthesis And Functionalization Of Ionic Thermoelectric Materials.* Nazish Jabeen (University of Valencia)

O-26 - *Nanoencapsulation Of Alkanes For Thermally Active Polymer Coatings.* Luis Fernando Jiménez-Hernández (Universitat de Vàlencia)

O-27 - *Development Of Lignosulfonate Blends For Carbon Precursors.* Anne Beaucamp (University of Limerick)

O-28 - *Correlation Between Thermal Insulation Properties And Structure In PLA Aerogels..* Jaime Lledó Martín (Universidad de Valladolid)

O-29 - *Ion Conducting Polymers Of Intrinsic Microporosity (PIMs) As Selective Membranes For Redox Flow Batteries.* Juan Carlos Martínez López (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-30 - *Trimetallic Lignin-Based Carbon Nanofibers As High-Performance Electrodes For Supercapacitors.* Hamid - Hafizi (University of Limerick)

O-31 - *Diaminomaleonitrile-Based Polymers As Emerging Multifunctional Materials.* Marta Ruiz Bermejo (Centro de Astrobiología, CAB (CSIC-INTA))

O-32 - *Structural Control Of Semiconductor Polymer D18 Used In Organic Photovoltaics..* Jesika Asatryan (UDC)

O-33 - *Ordering Of Polymeric Nanoparticles In PEO-Based Solid Polymeric Electrolytes.* Jorge L. Olmedo Martínez (POLYMAT, UPV/EHU)

O-34 - *Exploring Oxygen Reduction Reaction Electrocatalysis Using Covalent Organic Frameworks.* Marcos Martínez Fernández (Universidad Complutense de Madrid)

O-35 - *Hetero-Functionalization Of Polyitaconates For Developing Improved Polymer Dielectrics: Merging Sulfones With Bulky/Rigid Cycles..* Sebastian Bonardd Salvador (Materials Physics Center)

O-36 - *Thermal And Dielectric Stability Of Self-Crosslinkable Polypropylene Functionalized With Thermo- Or Photo-Active Groups.* José Manuel Gomez-Elvira González (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))"

O-37 - *Impact Of Molecular Weight On The Solid State Structure In Semiconducting Polymers For Photovoltaics.* Matteo Sanviti (Universidade da Coruña)

O-38 - *Understanding Li6.*24La3Zr2Al0.24O11.98 Effect On Poly(Ionic Liquid)-Based Hybrid Electrolytes For High Voltage Solid-State Lithium Batteries. CARLOS VILLACIS SEGOVIA (POLYMAT, UPV/EHU)

O-39 - *Anisotropic Composites Of Conjugated Polymers And Polymer-Wrapped Carbon Nanotubes For Thermoelectric Applications.* Xabier Rodríguez Martínez (Institute for Physical Chemistry, Heidelberg University)

O-40 - *Recyclable Thermally Conductive Vitrimers Using Sequential Stress-Relaxation Profiles.* Sasan Moradi (Universitat Politècnica de Catalunya)

O-41 - *Synthesis And Characterization Of Sustainable Thermoplastic Polyurethane Containing Recycled Bis(2-Hydroxyethyl) Terephthalate For Advanced Applications.* Mercedes Santiago Calvo (FUNDACIÓN CIDAUT)

O-42 - *Using Indentation To Study The Creep Behaviour Of Sustainable Polyurethane Adhesives.* Araceli Flores Aguilar-Amat (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-43 - *Revalorización De Residuos Post-Consumo De RPET-O: Efecto De La Compatibilización Reactiva En La Integridad Mecánica Estructural De Mezclas PP/RPET-O.* Orlando Santana Pérez (Universitat Politécnica de Catalunya - Centre Català del Plàstic)

O-44 - *The Development Of Remotely-Triggered Reversible Polyurethane Adhesives By Addition Of Radiation Absorbing Nanoparticles.* Horacio Salavagione (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-45 - *Desarrollo De Termoestables Epoxídicos Con Enlaces Dinámicos Covalentes De Imina Para Compuestos Sostenibles De Fibra De Carbono.* Cristina Monteserin Vilela (TEKNIKER)

O-46 - *Pre-Clinical Evaluation Of A New Class III Biodegradable Stent For The Treatment Of Urethral Stricture.* Laura Rubio Emazabel (Polimerbio SL)

O-47 - *Chemoresponsive Behavior In Dynamic Polymer Networks.* Jesús del Barrio Lasheras (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))

O-48 - *Stimuli-Responsive Dendritic Hydrogels: Tuning The Macroscopic Properties From The Nanoscale.* Sandra García Gallego (University of Alcalá, Department of Organic and Inorganic Chemistry and Research Institute in Chemistry “Andrés M. del Río” (IQAR))"

O-49 - *Preparation Of Silver Nanoparticles (AgNPs) Using Beta Chitosan Suspensions.* Saeedeh Pouri (Pluridisciplinar.UCM)

O-50 - *Degradable Amino-Yne Hydrogels: Study Of β-Aminoacrylate Crosslink Cleavage.* Sara Bescós Ramo (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))

O-51 - *Mass Production Of Multicellular Spheroids With 3D Printed Low-Attachment Polyurethane Microwell Arrays.* Pedro Jesús Navarrete Segado (IMDEA Materiales)

O-52 - *Conductive Tissue Engineered Scaffolds For Spinal Cord Injury Repair.* Aleksandra Serafin Serafin (University of Limerick)

O-53 - *Fully Natural And Functional Porous Sorbents For Sustainable Materials Manufactured Via Polymer Processing Techniques.* Antonio Capezza (KTH Royal Institute of Technology)

O-54 - *Oxime Metathesis: Tuneable And Versatile Chemistry For Dynamic Networks.* Marta Ximenis Campins (POLYMAT, UPV/EHU)

O-55 - *Nanocellulose-Based Cryogels For Sustainable Cultural Heritage Conservation.* Erlantz Lizundia Fernandez (Life Cycle Thinking Group, Department of Graphic Design and Engineering Projects, Faculty of Engineering in Bilbao, University of the Basque Country (UPV/EHU))

O-56 - *Recyclable Photoresins For Light-Mediated Additive Manufacturing: Loop 3D Printing.* Xabier Lopez de Pariza Sanz (POLYMAT, UPV/EHU)

O-57 - *Polimerización En Superficie De Agro-Residuos Para Fabricación Aditiva De Materiales Compuestos Sostenibles.* Alberto Sanz de León (Universidad de Cádiz)

O-58 - *Injectability Of Macro-Hydrogels: Development Of Hyaluronic Acid Granular Formulations.* Luis Andrés Pérez Pérez (I+Med)

O-59 - *Biomimetic Linear-Dendritic Hybrids For Adhesion: Dendritic Effect And Skin Adhesion.* Alexandre Lancelot (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))

O-60 - *Surface-Functionalized Thermoplastic Elastomers And Human Stem Cells: A Combinatorial Approach For Nerve Tissue Engineering.* Sara Martín Colomo (Cell Therapy, Stem Cells and Tissues Group, Biobizkaia Health Research Institute, 48903)

O-61 - *Fibrous PLA/Fe3O4 Nanocomposite Materials Prepared By Solution Blow Spinning And Electrospinning: A Comparative Study Of Their Mechanical Behavior.* Francisco Javier González Benito (Universidad Carlos III de Madrid)

O-62 - *PH-Responsive Amphiphilic Homopolyacetal Derived From Green Solvent Cyrene.* Javier Delgado Lijarcio (Universitat Rovira i Virgili)

O-63 - *Surface Modification Of PLA-Based Electrospun Nanofibers Mats With Hydrophilic Polymers..* Valentina Salaris (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-64 - *Comprehensive Structural Characterization Of Devulcanized Rubber Derived From End-Of-Life Tires..* Zenen Zepeda Rodríguez (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-65 - *Impact Of Aliphatic Glycol Chain Length In Polycaprolactone Based Random Copolyesters.* Juan Torres Rodríguez (POLYMAT, UPV/EHU)

O-66 - *Síntesis De Biopoliesteres A Partir De CO2 Y Furfural.* Eva M Maya Hernandez (Instituto de Ciencia de Materiales de Madrid)

O-67 - *Improving PLA Performance With Biobased Plasticizers: Technological Assessment And Raman Spectroscopy Analysis..* Ignacio Mena Prado (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-68 - *Análisis Comparativo Entre Moldeo Por Inyección Y Compresión Aplicado A Matrices Bioplásticas Para Fines Hortícolas.* Daniel Castro Criado (Universidad de Sevilla)"

O-69 - *Exploration And Synthesis Of Novel Polyols Obtained From Bio-Based Diols.* Ane Olazabal Abarrategui (Polykey Polymers)

O-70 - *Silica Based Particles As Carriers Of Additives For Enhancing The Protection Of Recycled Materials.* Enrique Blázquez Blázquez (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-71 - *Detección De La Tensión De Tracción En Compuestos Reforzados Con Fibra De Vidrio Con Microhilos Ferromagnéticos Integrados.* Rafael Garcia-Etxabe (GAIKER Technology Centre, Basque Research and Technology Alliance (BRTA))

O-72 - *Propiedades Viscoelásticas De Las Lágrimas Humanas Y Artificiales: Una Visión Microrreológica.* Juan Francisco Vega (Instituto de Estructura de la Materia (CSIC))

O-73 - *Improved Polyurethane Based Adhesives For Satin XPS-Sandstone Insulation Panels.* Álvaro Miguel Ortega (Universidad de Burgos)

O-74 - *Synthetizing Sustainable Thermosetting Polymers: The Role Of Different Vegetable Oils.* Esperanza Cortés Triviño (Pro2TecS-Chemical Product and Process Technology Centre, University of Huelva)

O-75 - *Toward Self-Driving Laboratory For The Design Of Multifunctional Nanocomposites.* Maciej Haranczyk (IMDEA Materiales)

O-76 - *High Resolution Molds, Sacrificial In Aqueous Media, Obtained By Vat Photopolymerization 3D Printing.* Pedro Liz Basteiro (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

O-77 - *Optimizing the processing parameters of PEEK additive manufacturing through design of experiments.* Lucia Doyle (IMDEA Materiales)

O-78 - *3D bioprinted scaffolds using fibrillar collagen bioinks for Tissue Engineering: New approaches in cardiac and cartilage tissue regeneration..* Teresa Zuñiga (Viscofan S.A.)

O-79 - *Hydrogel-Based 3D Printed Cancer Models For SERS Sensing And Imaging.* Clara García Astrain (POLYMAT, UPV/EHU)

O-80 - *Impresión 3D De Filamento Fundido De Policaprolactona Cargada Con Resina Epoxi Reciclada.* Iker Razquin Martin (POLYMAT, UPV/EHU)

O-81 - *PHBV Films Loaded With PHA Microparticles For Packaging Applications.* María Belén Montero Rodríguez (Universidade da Coruña)

O-82 - *Aplicación De Los PHA Al Sector Del Envasado: Mejoras En La Usabilidad Y Control De La Biodegradación.* Luis Cabedo Mas (Universitat Jaume I)

O-83 - *Recycling Ground Tyre Rubber Via Their Blending With Natural Rubber Matrix For Elastocaloric Applications.* Nicolas Candau (Universitat Politècnica de Catalunya)

O-84 - *Recycled Polyolefin Blends And Ground Tire Rubber (GTR): From Post-Consumer Waste To 2nd Generation Functional Materials.* Itziar Otaegi Tena (POLYMAT, UPV/EHU)

O-85 - *Functionalization Of Polymer Nanoparticles With Catalytically Active Organic And Metallorganic Moieties.* Rafael Muñoz-Espí (Universitat de València)

O-86 - *Double-Shelled Hollow Particles Based On Polyester Grafted Bacterial Cellulose For Trapping Bioactive Cargoes.* Virginia Rivero Buceta (Polymer Biotechnology Group, Biological Research Centre Margarita Salas, Spanish National Research Council (CIB-CSIC))

O-87 - *Using Nanoparticles Of Sepiolite For Designing Advanced Polystyrene Cellular Materials.* Luis Eduardo Alonso Pastor (Cellular Materials Laboratory (CellMat), Universidad de Valladolid)

O-88 - *Optimization Of Processing Conditions And Themal/Mechanical Properties For PEEK/PEI Multilayered Blends And Their CF Composites..* Juan Pedro Fernández Blázquez (IMDEA Materiales)

O-89 - *Improving Na-O2/Air Batteries: Overcoming Oxygen Crossover And Future Challenges With Solid-State Polymer Electrolytes (SSPE)..* Mohamed Yahia (CIC-EnergiGUNE)

O-90 - *Determination Of Betalain Content In Cooked Beetroots Using Smart Polymers.* Carlos Sedano Labrador (Universidad de Burgos)

O-91 - *Poly (Methyl Methacrylate) Foaming By One Step Process With ScCO2 And Water.* Aránzazu Redondo Hernangómez (BioEcoUVA Research Institute on Bioeconomy)

O-92 - *Advancements And Characterization Of Polymer Gel Electrolytes For Sodium Batteries.* Ángela Campo Peña (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

Flash presentations

F-01 - *Long Term-Dispersible And Metal-Free-Single-Chain Nanoparticles (SCNPs).* Ainara Ruiz Bardillo (Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center (MPC))

F-02 - *Kinetic Study Of The Bulk Thermal Polymerisation Of Malononitrile Dimer By Differential Scanning Calorimetry.* Juan Francisco Ruiz Guerron (Instituto Nacional de Técnica Aeroespacial)

F-03 - *Plasma-Derived Fibrin Hydrogels With Perfusable Microchannels For Vascularized Skin Tissue Engineering Applications.* Alejandro Hernández Sosa (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

F-04 - *Materials Based On Modified PLA With Biocide Properties For The Production Of Certified Filters For PPEs And Air-Conditioning Systems.* Noelia Esteban Hernández (IU CINQUIMA, University of Valladolid)

F-05 - *Biocompatibility, Antibacterial And Antioxidant Potentials Of Microfluidic-Assisted Cannabidiol-Loaded PLGA Nanoparticles.* Pedro Luis Echevarria Torres (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

F-06 - *TrHCross® synthesized using SARE® technology: The Best Commercial Viscosupplement for Knee Osteoarthritis Supported by In-Vitro Evidence.* Laura (RED MARFIL)

F-07 - *Long-Term Oxygen Reduction Reaction Electrocatalysis Using Robust Amide-Linked Fluorinated Covalent Organic Frameworks.* Miguel Jiménez Duro (Universidad Complutense de Madrid)

F-08 - *Sustainable Core-Shell Structures Derived From Lignin For Sodium-Ion Batteries.* Judith Miralda Jalle (Stokes Laboratories, School of engineering, University of Limerick)

F-09 - *Covalent Organic Frameworks Based On Multi-Component Synthesis For Photoconductivity.* Marta Gordo Lozano (Dept. of Organic Chemistry. Faculty of Chemistry, Complutense Univ. of Madrid)

F-10 - *Encapsulation Of Organic Phase Change Materials In Poly(3,4-Ethylenedioxythiophene) Nanoparticles For Enhanced Thermal Energy Storage Coatings.* Inés Adam Cervera (Institut de Ciència dels Materials de la Universitat de València (ICMUV))

F-11 - *Formulation Of Antibacterial Cream Containing Imidazolium-Terminated Carbosilane Dendrimers For Wound Treatment.* Rebeca Lozano García (Department of Organic and Inorganic Chemistry, Research Institute in Chemistry “Andrés M. del Río” (IQAR), University of Alcalá (UAH))

F-12 - *Aqueous Seeded RAFT Polymerization For The Preparation Of Self-Assemblies Based On 2,6-Diacylaminopyridine For Biomedical Applications.* Miriam Abad Andrés (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))

F-13 - *Lignin-Based Magnetically Separable Catalysts For The Degradation Of Nitroaromatic Pollutants.* Alberto Llopis Lacruz (Universitat de València)

F-14 - *Effect Of Bio-Based Sizing On The Interface Of Carbon Fibre-Reinforced Composites.* Clotilde Techoueyres (University of Limerick)

F-15 - *Wet Spinning Of Lignin Based Precursors Fibres For Carbon Fibre Production.* Rougé Jean (University of Limerick)

F-16 - *Lignin-Based Encapsulation Of Agrochemical Compounds By Spray Drying.* Jose Huerta-Recasens (Universitat de Valencia)

F-17 - *DLP 3D Printing Of Reprocessable Semi-Interpenetrating Networks Based On High Molecular Weight Latexes.* Jon Ayestarán Uriarte (POLYMAT, UPV/EHU)

F-18 - *Nuevo Accesorio De Limpieza Y Preparación De Muestra En Ensayos De Reológica De Cizalla.* Cesar del Rio (TA INSTRUMENTS)

F-19 - *Desarrollo De Polímeros De Fuentes Renovables Con Propiedades Mejoradas Para Su Aplicación En Sectores Industriales De Alto Consumo Y Valor Añadido.* Red Marfil

Poster presentations Session 01 (September 16th)

P-01 - *Development Of Low-Density Foams From Liquid Biopolymers And Bio Additives To Stabilize The Cellular Structure.* Clara Amezúa Arranz (Universidad de Valladolid)

P-02 - *The Use Of Biodegradable Polyester Matrices For Magnetic Nanocomposites.* Eider Matxinandiarena (POLYMAT, UPV/EHU)

P-03 - *Development And Characterization Of Electrospun Films Of Biopolyesters Blends Of Application Interest In Food Packaging.* Sara Añón Peral (Instituto de Agroquímica y Tecnología de Alimentos (IATA) - CSIC)

P-04 - *Producción Acuosa De Hilos Para Textil A Partir De Nano/Microcelulosa Y Biopolímeros.* Ane Rivas Zuñiga (CIC-nanoGUNE)

P-05 - *Novel Roofing Binders And Their Application In Eco-Friendly Construction.* Clara Delgado-Sánchez (Pro2TecS - Universidad de Huelva)

P-06 - *The Mesophase Of PLA In Materials With ATBC And MCM-41.* Ernesto Pérez Tabernero (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-07 - Cellulose Nanocrystal Enabled Shear-Thinning Inks With Embedded Au Nanoparticles For 2D Printed Photothermia Applications. Marta García Castrillo (BCMaterials, Basque Center for Materials, Applications and Nanostructures)

P-08 - Exploring Boron-Based Materials As A Promising Platform For The Development Of Dynamic Materials. Jacopo Teotonico (POLYMAT, UPV/EHU)

P-09 - Chemical Recycling To Monomer Of Polyamide 6 With Sulfonic Acids. Marta Mestre Membrado (POLYMAT, UPV/EHU)

P-10 - *High-Performance Elastomeric Compounds Made From Recycled Materials Obtained From End-Of-Life Tires.* Marina Montero Escrivá (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-11 - *Degradable Alternating Copolymers By Radical Copolymerization Of 2-Methylen-1,3-Dioxepane And Crotonate, And Tertpolymerization With Industrial Monomers..* Alice Marchand (POLYMAT, UPV/EHU)

P-12 - *Design And Characterization Of Biobased Polymers From Vegetal Proteins.* Laura Matesanz Niño (Fundación CIDAUT)

P-13 - *Estudio De Films Basados En Residuos De Filamentos De Poli (ácido Láctico) De Impresoras 3D Con Nanopartículas De Cobre.* Gabriel Pinto Cañón (Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid (UPM))

P-14 - *Films Tricapa Sostenibles A Base De RPLA/Caseinato/RPLA Reforzados Con Celulosa Bacteriana De Kombucha Fermentada En Residuos De Café Para Envase Activo De Alimentos.* Simón Faba (Departamento de Ingeniería Química Industrial y del Medio Ambiente, Escuela Politécnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid (ETSII-UPM))

P-15 - *A Closed-Loop Process To Transform Mixed Plant Biomass Waste Into Cellulose Acetate Bioplastic As Innovative Growing Substrates In Plant Cultivation.* yuan yuan chen (Technological University of the Shannon)

P-16 - *Transformación De Lignina En Filtros Solares Fotoadaptativos.*. Gonzalo Rotea San Luis (Roka Furadada)

P-17 - *Valorización De Residuos De Corcho En Polímeros: Hacia Materiales Compuestos Más Sostenibles.* María Del Carmen García Laynez (Universidad de Cádiz)

P-18 - *Depolimerización Del Polimetacrilato De Metilo A Temperaturas Moderadas.* Gema Marcelo Alejandre (Universidad de Alcalá)

P-19 - *Biocomposites Based On PHBV With PHA Microparticles As Fillers For Packaging Applications.* Anja Schmidt (Universidade da Coruña)

P-20 - *Preparation Of Films Potentially Applied To Agroindustry From Discarded 3D Printing Material Based On Poly(Lactic Acid) And Iron Particles.* Ángel Agüero Rodríguez (Instituto Universitario de Tecnología de Materiales, Universitat Politécnica de Valéncia, IUTM-UPV)

P-21 - *Síntesis De Poliuretanos Sin Isocianato Mediante Fijación De CO2.* Nahikari Martin Larrañaga (POLYMAT, UPV/EHU)

P-22 - *Preparation And Characterization Of Biocomposites Reinforced With Novel Green Graphene.* Danny Moncada Villalobos (Universidade da Coruña)

P-23 - *Matrices Biodegradables A Partir De Un Subproducto Proteico Para La Liberación Controlada De Nutrientes Y Agua A Los Cultivos.* Mercedes Jiménez Rosado (Universidad de León)

P-24 - *Functionalized Starch-Based Materials For Food Packaging Applications.* Pedro Francisco Muñoz Gimena (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-25 - *Análisis Y Polimerizabilidad De MMA Reciclado Químicamente.*. Lucía Parra Oliva (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-26 - ARE GREEN METHODS SUITABLE FOR CHITIN DEPROTEINIZATION?. Daniel Alonzo Durante Salmerón (Department of Chemistry in Pharmaceutical Sciences)

P-27 - *Sustainable Polymers For A Better Environment: Chitosan-Based Coatings Embedded With Activated Carbon For Water Remediation.* Minghao Yi (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-28 - *PLA Platform Membranes For Applications As 3D SLIPS.* Clemente Rodríguez Gómez (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-29 - *Recycled Vs Virgin PET: Distinct Features And Properties.* Nuria García (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-30 - *Characterization and Biomedical Applications of Electrospun PHBV Scaffolds Derived from Organic Residues.*. Anyi Jin (Universitat Politècnica de Catalunya)

P-31 - *Resinas de poliuretano sostenibles a partir de recursos naturales: síntesis y aplicaciones.* Dulce Muñoz (Fundación Tecnológica Advantx)

P-32 - *Exploring The Exceptional Vitrimeric Performance Of Poly(Dithiourethanes): An In-Depth Study Of Dynamic Characteristics.* FEDERICO GUERRERO RUIZ (Centro de Fisica de Materiales (CSIC, UPV/EHU)-Materials Physics Center (MPC))

P-33 - *4D Printable Electroactive And Biodegradable PEDOT:κ-Carrageenan Inks For (Bio)Electronics.* Rajat - Rai (POLYMAT, UPV/EHU)

P-34 - *Vegetable Oil-Based Inks For 3D Printing Using A Thiol—Michael—Epoxy Dual-Curing Strategy.* Oihane Varela Manrique (POLYMAT, UPV/EHU)

P-35 - *Rheological And Tribological Behaviour Of Green Lubricating Greases Based On Cellulose Acetate/Silica Nanocomposites.* Manuel Toro Gallego (Pro2TecS – Chemical Product and Process Technology Research Center, Department of Chemical Engineering and Materials Science, Universidad de Huelva, ETSI, Campus de "El Carmen", 21071)

P-36 - *Influence Of The Type Of Clay On The Oil Structuring Properties Of Electrospun Cellulose/Clay Nanocomposites.* Concepción Valencia (Universidad de Huelva)

P-37 - *Fabricación De Vitrímeros Con Propiedades Mecánicas Variables Y Evaluación De La Reprocesabilidad Mediante La Activación De Reacciones De Transesterificación.* Naroa Ayensa Serrano (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

Poster presentations Session 02 (September 17th)

P-01 - *Tire Filling: From Design To Advanced Characterization By Low-Field NMR.* Laura Diñeiro García (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-02 - *Diseño De Estructuras Poliméricas Biobasadas Con Capacidad Antimicrobiana Y Antioxidante.* Alejandro Funes López (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-03 - *Efficient Synthetic Route For Cyano-Based Polymers From The Bulk Thermal Polymerization Of Aminomalononitrile.* Carlos Hortelano de la Fuente (Instituto Nacional de Técnica Aeroespacial)

P-04 - *Síntesis Y Funcionalización De Biopoliésteres Hiperramificados Soportados En Celulosa Microcristalina.* Estefanía Sánchez Safont (Universitat Jaume I)

P-06 - *Study Of The Self-Healing Capacity Of A Modified PLA With A Coumarin Methacrylate.* Antoni Pagés Llobet (Universitat de Girona)

P-07 - *Aromatic polymers having high fractional free volume and large thermal and chemical stability for energy-saving applications.* Angel E (False)

P-08 - *Nanomechanical Properties Of Solid And Foamed PCL-Sepiolite Electrospun Fibers.*. Violeta Hurtado García (Universidad de Valldolid)

P-09 - *Caracterización Térmica Y Viscoelástica De Plásticos Comerciales Para Ortodoncia Invisible.* José Ignacio Delgado Castaño (IMDEA materiales)

P-10 - *Desarrollo De Fibras Poliméricas Basadas En Celulosa Y Poli(ácido Láctico) Mediante Electrohilado En Fundido Para Aplicaciones Biomédicas.*. Elena Navas Ortiz (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-11 - *Modulación De La Biodegradabilidad De Poliuretanos Para Aplicaciones Biomédicas.* Alejandra Rubio Hernandez-Sampelayo (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-12 - *Hidrogeles Conductores En Base A Colágeno Como Apósitos Para Heridas.* Alberto Romero (Universidad de Concepción)

P-13 - *Photocrosslinked Hydrogel Derived From An Unsaturated Poly(Ester Amide).* María José Lovato Vélez (Universidad Politécnica de Cataluña)

P-14 - *Amphiphilic Pseudo-Proteins Via Michael PEGylation And Their Application For Fabricating Core-Shell Particles.*. Davit Makharadze (Polytechnic University of Catalonia)

P-15 - *Estudios De La Formulación De Hidrogeles Aplicados A La Bioimpresión De Implantes.* David Patrocinio Caballero (CCMI Jesús Usón, Fundación de Cirugía de Mínima Invasión Jesús Usón)

P-16 - *Development Of Chemically Crosslinked Pectin And Hyaluronic Acid Hydrogels With High Stability And PH Response For 3D Extrusion Printing.* Jorge Mercado Rico (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-17 - *Michael Additions To Activated Alkynes For The Preparation Of PH-Responsive Hydrogels.* Milagros Piñol Lacambra (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))

P-18 - *Sistemas Piezoeléctricos Basados En Polilactida Con Estabilidad Térmica Mejorada Y Propiedades Mecánicas Ajustables.* Asier Panfilo Elechiguerra (UPV/EHU)

P-19 - *Linear Dendritic Block Copolymers As Thermoresponsive Nanocarriers In Aqueous Media.* Javier Martín Martín (Universidad de Zaragoza)

P-20 - *Nuevos Biomateriales Basados En Copolímeros De GelMa Para Regeneración ósea.* Jesus L. Pablos (Dpto Química en Ciencias Farmacéuticas, Facultad de Farmacia, Instituto de Investigación Sanitaria Hospital 12 de Octubre, imas12, Universidad Complutense de Madrid, UCM, 28040, Madrid, Spain)

P-21 - *Thermo-Responsive Nanovectors From Self-Assembled Amphiphilic Degradable Block Copolymers.* María Val-Carreres Castellote (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))"

P-22 - *Characterization Of The Isothermal Crystallization Of Poly(Vinylidene Fluoride) Blended With The Ionic Liquid [Emim]2[Co(SCN)4].* Isabel Tort-Ausina (Centro de Biomateriales e Ingeniería Tisular. Universitat POlitècnica de València.)

P-23 - *Elastomeric Protein-Based Bioactive Eutectogel For Drug Delivery On The Skin.* Pegah Pegah Sanjarnia (POLYMAT, UPV/EHU)

P-24 - *PLA Electrospun Fibers Reinforced With Yerba Mate Nanoparticles And Vegetable Oils As Plasticizers.* Víctor Oliver Cuenca (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-25 - *Hidrogeles Termosensibles Personalizados Para Aplicaciones En Biomedicina Y Medicina Regenerativa.* Ana García Crespo (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-26 - *Development Of Reabsorbable Basement Membrane Equivalent Based On Bioactive, Recombinant Elastin-Like Polymers For Wound Healing Applications.* Raúl Escribano Arranz (Universidad de Valladolid GIR Bioforge)

P-27 - *Study Of The Effect Of The Addition Of Inorganic Nanoparticles On Biodegradable-Polymeric Electrospun Nanofibers.* Laura Peponi (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-28 - *ELR-Based Hydrogel Loaded With Plasma-Treated PLA Microparticles As An Efficient System For Controlled Release Of Lactic Acid.* Julio Fernandez Fernandez (Universidad de Valladolid GIR Bioforge)

P-29 - *Biomineralization assisted by peptide self-assembly.* Jennifer (False)

P-30 - *Tuning the Underwater Adhesiveness of Antibacterial Polysaccharides Complex Coacervates.* Mehdi (False)

P-31 - *Chitosan-NLCs Lipo-hydrogels as carriers in wound healing..* Rubén Gil- Gonzalo (Instituto Pluridisciplinar UCM)

Poster presentations Session 03 (September 18th)

P-01 - *Valorization Of Forestry Derivatives Into Functional Acrylic Polymers For Specific Applications..* Alba Tirado Bermúdez (Universitat Rovira i Virgili)

P-02 - *RAFT-PhotoPISA Polymeric Nano-Objects For Functionalized Luminescent Copper Nanoclusters (CuNCs) And Its Application As Selective Hg2+ Sensors..* Olga García Ballesteros (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-03 - *On The Use Of Deep Eutectic Solvents To Improve The Mechanical Properties Of Electrospun Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate) Fiber Mats.* Ozan Basar (Instituto de Agroquímica y Tecnología de Alimentos (IATA) - CSIC)

P-04 - *Generation Of Polymer Blends Casted From Poly(Styrene-Co-Acrylonitrile) Core/ Acrylic Shell Latexes.* Jordi Solera Sendra (Departament d'Enginyeria Química, Universitat Politècnica de Catalunya)

P-05 - *Exploiting The Base-Triggered Thiol/Vinyl-Ether Addition To Prepare Well-Defined Nanophase Separated Thermo-Switchable Adhesives.* Aritz Lamas Nuñez (POLYMAT, UPV/EHU)

P-06 - *Enhanced Photocatalytic NOx Removal Using Cellulose Paper Filled With Zinc Oxide And Calcium Carbonate.* Felicia Tjus (LTH, Lunds Faculty of Engineering)

P-07 - *Rational Tailoring Of Stereocomplexed PLA-Based Nanocomposites For Potential Film Packaging Applications.* Mohammad Raef (Department of Mining-Metallurgy Engineering and Materials Science, POLYMAT, Faculty of Engineering in Bilbao, University of the Basque Country UPV/EHU, Plaza Torres Quevedo 1, 48013)

P-08 - *Innovative Mixed Matrix Membranes (MMMs) For Cost-Effective CO2 Separation In Biogas Upgrading.* Javier Laguna Humayor (Universidad de Valladolid)

P-10 - *The Effect Of PEDOT-DBSA Nanoparticles On Hydrogels For Vapor Generation By Solar Action.* David Alejandro Naranjo Tovar (Universitat Politècnica de Catalunya)

P-11 - *Influencia De La Radiación De Neutrones En La Microestructura De La Celulosa En Tejidos De Lino.* César Barta Gil (Universidad Carlos III)

P-12 - *Kinetics Of Emulsion Polymerization In Aqueous Phase Using Microfluidics.* Juan Felipe Hincapie Alvarez (POLYMAT, UPV/EHU)

P-13 - *Estudio Molecular Y Conformacional De Nuevos Biopolímeros Bacterianos.* Andrés Cardil Tornos (Instituto de Estructura de la Materia (CSIC))

P-14 - *Nanocellular Polymers As A Tool To Improve Energy Efficiency..* Félix Lizalde Arroyo (Cellular Materials Laboratory (CellMat), Universidad de Valladolid)

P-15 - *Poly(Methyl)Methacrylate-Based Polymer Optical Fibers: Correlation Between Processing-Property Relationship And Luminescent Solar Concentrator Uses.* Miriam Guadaño Sánchez (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-16 - *Development Of Fluorescent Nanoparticle Doped-Polymeric Preforms Toward Optical Fibers For Solar Concentrators.* Natalia Hernansanz Luque (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-17 - *Nanocellular Polystyrene As An Alternative For VIP Panel Cores.* Marcos Merillas Fernández (Cellular Materials Laboratory (CellMat), Universidad de Valladolid)

P-18 - *New Photoactive Redox Monomers And Polymers For Energy Applications.* Laura Pérez Vidal (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-19 - *New Method For Polymeric Cellular Material Production: Acetone Effects On PMMA Gel Precursors.* Mario Fernández dela Fuente (Cellular Materials Laboratory (CellMat), Universidad de Valladolid)

P-20 - *Optimizing Nanofiltration Membrane Layer-By-Layer Modification: A Chemometric And Morphological Analysis Of Positively Charged Membranes.* Tanaz Moghadamfar (UPC Barcelona East School of Engineering EEBE)

P-21 - *Four-Dimensional Printed Liquid Crystal Elastomer Photoactuators Reprogrammed By Means Of Light-Reversible Perylene Diimide Radicals.* Lorena Montesino Redondo (Instituto de Nanociencia y Materiales de Aragón (INMA-CSIC))

P-22 - *Optimisation Of Pickering Phase Change Emulsions Based On PEG400/D-Limonene/SiO2 Nanoparticles.* Adrián Tenorio-Alfonso (Pro2TecS Chemical Product and Process Technology Research Centre, University of Huelva)

P-23 - *Natural Polymer-Based Hydrogels As Injectable Semi-Solid Electrodes For Sustainable Batteries.* Sergio Peñas Núñez (POLYMAT, UPV/EHU)

P-24 - *Development Of Ester-Amide Copolymers For Applications As Electrolytes In Solid-State Batteries.* Anthony Alexander Vasquez Medina (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-25 - *Novel -CF3 Free Lithium Salt For SEI Improvement In Polymer Electrolytes.* Izaskun Serna Tamayo (Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA))

P-26 - *Formulation Of Water-Based Polymeric Electrolytes For CO2 Electrochemical Capture.* Daniel García Giménez (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-27 - *Single-Ion Conducting Polymer Nanoparticles For Solid-State Electrolytes..* Alejandro Herranz Berzosa (POLYMAT, UPV/EHU)

P-28 - *Ion Transport Properties In Sulfonated Polymer Membranes For Batteries.* Marta Santos Rodríguez (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-29 - *Novel Single-Ion Conducting Polymer Electrolytes With High Toughness And High Resistance Against Lithium Dendrites.* David Fraile Insagurbe (CIC-EnergiGUNE)

P-30 - *Lignin-Derived Carbon-Based Electrodes For Sustainable Supercapacitor Production.*. Nicolás Manuel Menéndez Stabile (Institut de Ciència dels Materials de la Universitat de València (ICMUV))

P-31 - *Nanofibers Obtained From Lignocelullosic Biomass Residue For Energy Applications.* Clara Maria Gómez Clari (Universidad de valencia)

P-32 - *Membranas De Matriz Mixta De Polisulfona Basadas En Truxeno Metilado Para Purificación De H2.* Mar López González (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-33 - *Reversible Colorimetric And Fluorescence Solid Sensors Based On Aryl Hydrazone Derivatives Of 1,8-Naphthalimides For Caustic Media And Biogenic Amine Vapors.* Teresa Corrales Viscasillas (Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC))

P-34 - *Exploring stimuli-responsive Single-Chain Nanoparticles: synthesis, characterization, and surface behavior.* Leyre Oria-Ledesma (Centro de Física de Materiales)

P-35 - *Desarrollo De Nuevos Sistemas De Liberación De Antineoplásicos Basados En Biopolímeros Para El Tratamiento De Glioblastoma.* Pedro Valentín Badía Hernandez (Universidad Miguel Hernández)

PLENARY LECTURES

CONTROLLED POLYMERIZATION AND CLICK CHEMISTRY APPROACHES TO SMART BLOCK COPOLYMERS

Luis Oriol [1,2]

1. *Liquid Crystals and Polymers Group (CLiP). Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza, España*
2. *Dpt. Química Orgánica, Facultad de Ciencias, Zaragoza, España*

Introduction

Smart block copolymers (BCs) with a precise control of the macromolecular structure are functional materials of high interest in nanoscience, able to segregate into periodic nanostructures and respond to a variety of stimuli, allowing for modulation of their physical and/or chemical properties. A large variety of applications have been described for these materials in optoelectronics, energy or nanomedicine among others. The access to these materials was highly boosted by the emergence of controlled polymerizations and the application of click chemistry principles to polymer science that opened up new possibilities in the efficient synthesis of block copolymers with a precise macromolecular structure and on-demand functionalization.

Methodology

In the CLiP labs, we have developed an intense research on the optimization of radical controlled polymerizations and ROPs in combination with click chemistries to prepare smart BCs either with linear-linear or linear-dendritic topologies. The efficient click connection of functional moieties to macromolecular chains was approached by covalent click connection but also by an efficient click supramolecular connection mediated by H-bonds. We first used radical controlled polymerizations and having azobenzenes as light responsive moieties confined into bulk nanodomains to develop a large variety of optical materials mainly addressed to optical data storage.[1] Encouraged by the good response of the confined azobenzenes, we developed reproducible amphiphilic linear-dendritic BCs with an exact number of azobenzenes and precisely prepared by coupling of preformed blocks using azide-alkyne click chemistry.[2] These BCs self-assembled into vesicles or micelles of controlled morphology, which were able to release encapsulated molecules using light as external stimulus.[3] To implement their use as nanocarriers for the release of bioactive molecules triggered by external irradiation, BCs having visible or NIR light responsive moieties were developed.[4] The appropriated chemical design of BCs also allows the easy preparation of metal-polymer hybrids with Pd-nanosheets directly synthesized in the core of BC micelles processed by microfluidics and with an excellent response to NIR for their application to photothermal therapy.[5]

Results and conclusions

Click chemistry approaches have been also applied to synthesize degradable BCs with a programmed thermoresponse close to physiological temperature, using non-ionic groups to mainly promote UCST-like response. Due to the versatility of click functionalization antimicrobial materials can be developed using the same platforms but using ionic groups. More recently, the synthesis of polymeric hydrogels is being investigated using spontaneous click reactions performed at room temperature in aqueous media (pH= 7.4) and cleavable (unclick) under slightly acidic conditions.

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RECREATING TENDON STRUCTURE AND BIOMECHANICAL ENVIRONMENT USING MAGNETIC 3D BIOPRINTING

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Introduction

Currently used therapies to treat tendon injuries and disease are quite limited, often resulting in poor outcomes for the patients, including a high reinjury rate. Tissue Engineering strategies might offer better solutions but the complex hierarchical structure, unique biomechanical properties, susceptibility to physical stimulus and overall low regenerative ability of tendon tissues results in very significant challenges for the development of effective therapies tendon-mimetic constructs for tissue regeneration. These include, the recreation of the complex hierarchical and fibrillar architecture of tendon extracellular matrix, the ability to remotely actuate mechanotransduction mechanisms and the provision of adequate biochemical cues that trigger regenerative responses.

Methodology

Our team has been exploring the development of cell-laden 3D magnetically responsive systems that recapitulate key features of the native tissue and that can be remotely actuated both during in vitro culture and/or upon in vivo implantation, through the application of external magnetic stimuli. We have been exploring conventional and innovative tools such as multimaterial 3D bioprinting to design magnetic responsive systems mimicking specific aspects of tendon tissue architecture, composition and biomechanical properties, which, combined with adequate stem cells, shall render appropriate behavioural instructions to stimulate the regeneration of tendon tissue. We have demonstrated that the magnetic stimulus of different intensities/frequencies can trigger tenonegic differentiation od hASCs and/or modulate inflammatory response of various cell types. Simultaneously, the 3D cell-laden magnetic system are also being as sophisticated 3D tissue models to unravel mechanisms behind tendon homeostasis and repair that shall support the base knowledge to establish rational design criteria for the biofabrication of living tendon substitutes offering the prospect of tendon regeneration as opposed to simple tissue repair.

POLYMER ELECTROLYTES, THE KEY TO SOLID-STATE BATTERIES.

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Introduction

Polymers were until forty years ago, only known to be insulators. The advent of poly(aniline), CH_x, then later PEDOT have shown them to be possible electronic conductors. At the same time, it was found that poly(ethylene oxide), PEO forms solid complexes with some metal salts (NaI, KSCN…) and that these complexes become ionically conductive at temperatures 50 – 100°C. Since, there have been increasing activity on polymer electrolytes, with in perspective their implementation in solid-state high energy density batteries, especially those harnessing the lithium metal. PEO remains the most studied polymer, with a strong solvating power for a variety of salts, from alkali metals to alkaline, but new host polymeric structures have recently emerged, poly(esters), like poly(caprolactone) — PCL and poly(carbonates), like poly(trimethylene carbonate), — PTMC and poly(propylene carbonate) — PPC.

In the case of PEO, which is a crystalline polymer, the complexes, also crystalline, are governed by phase diagrams, and the conductivity has been found to be the property of the amorphous phase resulting of eutectics between pure PEO and the complexes, either $P(EO)_3MX$ or $P(EO)_6MX$ depending on the anion X^-. The conductivity obeys a VTF law, governed by the free volume allowed by the polymer and by the glass transition T_g of the complex.

For a given cation, mostly Li^+, the anion plays de determining role for the attainment of the amorphous domain at the lowest possible temperature, and when reached, the value of the conductivity. This has led to the identification of new anions with highly delocalized negative change. In particular, the fluorinated sulfonimide family, like $(CF_3SO_2)_2N^-$ — TFSI and $(FSO_2)_2N^-$ — FSI give the most favorable phase diagrams and the highest conductivities, thanks to the flexibility of the S–N–S bond that contributes to lower the T_g of these electrolytes.

In a battery, only the cations (Li^+) are exchanged at the electrodes, but like in liquids, both the positive charge and the negative charge (X^-) are mobile in polymer electrolytes, which gives rise to overvoltages and concentration polarization during operation. In a recent trend, what is dubbed “single ion conductors”, i.e. polymers complexes in which the anions are attached to another polymer or a nanoparticle, thus immobile have gained momentum.

Polymers electrolytes are being used in the only solid-state battery commercial today.

CONDUCTING POLYMERS FOR BIOELECTRONIC MEDICINE

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Introduction

Bioelectronic medicine provides a new means of addressing disease via the electrical stimulation of tissues: Deep brain stimulation, for example, has shown exceptional promise in the treatment of neurological and neuropsychiatric disorders, while stimulation of peripheral nerves is being explored to treat autoimmune disorders. To bring these technologies to patients at scale, however, significant challenges remain to be addressed. Key among these is our ability to establish stable and efficient interfaces between electronics and the human body. I will show examples of how this can be achieved using conducting polymer devices engineered to communicate with the body and evolve with it.

FROM WASTE TO ADVANCED MATERIALS BASED ON MICROBIAL BIOTECHNOLOGY STRATEGIES

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Abstract

Bacteria are able to naturally synthesize a wide range of biopolymers such as polyamides, polysaccharides, polyesters and polyphosphates. From a circular economy perspective, these biopolymers are extremely important in the current context of decreasing petroleum-derived synthetic materials. This is mainly due to their suitability for production in sustainable bioprocesses and the fact that their properties can be tailored using of microbial biotechnology tools combined with materials science[1]. They have attracted much attention in many fields, such as biomedicine, cosmetics, textiles and packaging offering a sustainable alternative to petroleum-based plastics.

Biopolymers such as polyhydroxyalkanoates (PHAs) and bacterial cellulose (BC) are produced via fermentation by microorganisms such as *Pseudomonas putida*, *Cupriavidus necator*, *Rodospirillum rubrum* (PHAs) and *Komagataeibacter medellinensis* (BC). They are generated through the revalorization of agricultural and urban wastes and the large-scale production in bioreactors. Synthetic biology and metabolic engineering are applied to produce improved strains for bioprocessing and for the generation of tailored polymers in terms of monomer composition. Moreover, by incorporating bioactive agents such as living bacterial cells or anchoring antibiotic peptides or enzybiotics, their properties can be further diversified [2-4]. A living antibiotic such as *Bdellovibrio bacteriovorus* or a model bacterium in environmental biotechnology such as *Pseudomonas putida* have been included in biopolymer matrices by material colonization or encapsulation[5].

Finally, and in light of the current situation of environmental plastic pollution and climate change, it is evident that intrinsic biodegradability or compostability are not the only factor to be considered as an efficient solution; reduction, reuse and recycling strategies are necessary to maintain bioplastics and their derivatives in the circular value change[6]. In this context we are developing enzymes for the biodegradation of these materials and the production of monomeric intermediates. Employing enzymes as biocatalysts emerges as a more selective and environmentally friendly alternative to chemical recycling, allowing the production of new bioplastics and added value and high-quality products.

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KEYNOTES

NEW INSIGHTS INTO THE STRUCTURAL ORGANIZATION OF SEMICONDUCTING POLYMERS FOR PHOTOVOLTAICS

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Introduction

The precise determination of structural organization of semiconducting polymers is of paramount importance for the further development of organic electronic technologies, as their solid-state microstructure and optoelectronic properties are closely interlinked. In this presentation I will argue that the microstructure of these materials does not seem to fit neither in “common” structural models for polymers, i.e. the amorphous, semi-crystalline and paracrystalline models, nor with other stablished partial-order mesophases, such as condis crystals or liquid crystals. As such, we introduced in 2022 a new model: the semi-paracrystallinity. Although the semi-paracrystalline model enables a suitable framework that allows solving some previous conundrums, it is still far from fully capturing the complex molecular organization in semiconducting polymers for organic photovoltaics (OPV). The most-important open questions and the potential requirements of a successful structural model will be discussed in this talk. Moreover, I will present our most recent results on structural aspects of advanced polymers for OPV, such as D18, D18-Cl, PM6, and FTAZ. I will discuss the solid-state microstructure and the thermotropic phase behavior (including phase transitions) of these polymers and how these depend on the molecular weights. I will also show how to selectively control the “type of molecular packing” in the champion polymer D18 to achieve films displaying either a “liquid-crystalline-like” ordering or a “crystalline-like” ordering. Our study reveals, moreover, that these distinct structural organization yield markedly different mechanical behavior in D18 films.

MULTIRESPONSIVE NANOGELS FOR MUCOSAL DRUG DELIVERY

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Introduction

Thiol bearing materials recently gained increased interest due to their ability to overcome mucosal clearance and thus to deliver drugs to submucosal layers in sufficient concentrations.[1] To date, mostly free thiol bearing materials have been employed for submucosal delivery of drugs. However, in aqueous environment disulfides and thiols are in a dynamic equilibrium resulting in the occasionally presence of free thiols for disulfide containing materials as well. The stimuli-responsive nanogel (NG) technology is shaping up as a potential strategy to transport and deliver small molecule drugs as well as therapeutic biomacromolecules.[2] Key features such as NG size, polarity/lipophilicity, volume phase transition temperature, surface decoration, targeting ability, etc., have been correlated with the potential of responsive NGs to deliver and release bioactive molecules. In this context, we hereby present the development of disulfide-bearing NGs as redox-responsive nanocarriers for overcoming restrictive barriers in mucosal drug delivery of therapeutics.

Methodology

A series of disulfide-bearing crosslinkers suitable for free radical polymerization were employed. NGs were prepared by precipitation polymerization. By varying the crosslinker and monomer feed ratio, their hydrodynamic diameter was tuned to values of 100–200 nm. Characterization of the NGs and of their interaction with mucose were performed using dynamic light scattering, gel permeation chromatography, Raman spectroscopy, rheology, Franz cells, etc. Cytotoxicity and mucopenetration of pristine and protein-loaded NGs were assayed on Caco-2 cells, intestinal mucose, human-based models of the bronchial epithelium, and in C. elegans.

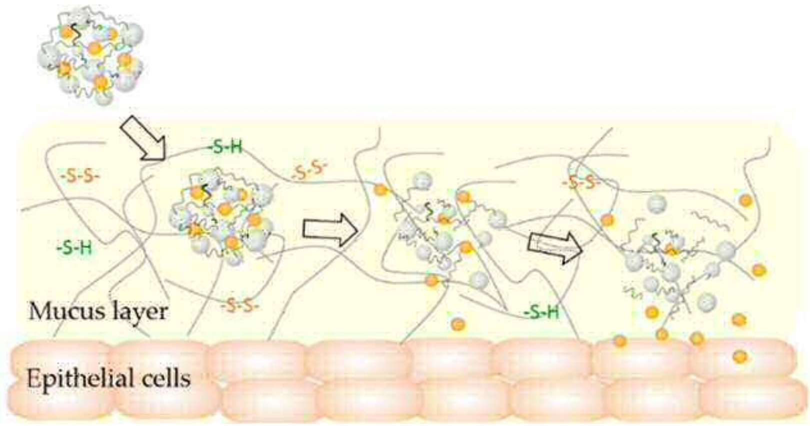

Fig 1. Submucosal delivery of therapeutic actives through interaction of disulfide-containing nanogels

Results and Discussion

A comprehensive screening of monomers and crosslinkers was realized to control the number and location of disulfide linkers within the NGs' structure. The main aim was to assess the degradability of the NGs in reductive conditions and its correlation with their mucoadhesive/mucopenetrating properties. NG interactions with the mucus and potential mucopenetrating properties were tested with mucin, in gastrointestinal mucus of freshly excised porcine small intestines, and in reconstructed human-based models of bronchial epithelium. The NGs were further loaded with proteins as model drugs and their mucosal penetration was demonstrated in three-dimensional human models and in C. elegans. In all cases, the nature and the amount of disulfide linkages showed to be of great relevance.

Conclusions

The results demonstrated that the incorporation of disulfide bonds provides the NGs not only with degradable points that later enable the cargo release, but also with a programmable capacity for mucoadhesion or mucopenetration. High loading efficiencies and transmembrane transport of highly challenging proteins was demonstrated. Further applications against cystic fibrosis, bovine mastitis, and Chagas disease are currently being explored.

Acknowledgments

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THIOL-MEDIATED DYNAMIC COVALENT HYDROGELS WITH TUNABLE VISCOELASTICITY FOR 3D CELL CULTURE

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In native tissues, the mechanical properties of the extracellular matrix (ECM) are essential for regulating cellular behavior. Different dynamic covalent chemistries (DCC) have been employed in the crosslinking of hydrogel networks to recapitulate some of the dynamic mechanical properties of native tissue, e.g., viscoelasticity. However, the currently available DCC toolkit remains limited to a few options, and often they come short to comply some of these requirements: (i) the chemical reaction must take place under mild physiological conditions (i.e., narrow operational pH and temperature), (ii) the overall chemical system should be selective, uncomplicated to implement, and inexpensive; and (iii) the resulting dynamic covalent network should be stable and support viability and functions of embedded living cells. Thus, developing novel DCC that comply these requirements is drawing considerable attention. In this work, inspired by the luciferin click ligation, we introduce for the first time a thiol-mediated bonding as a novel DCC for hydrogel crosslinking, enabling us to access poly(ethylene glycol) (PEG) hydrogels with dynamic crosslinks and modulable viscoelasticity. Dynamic bonding forms rapidly via a thiol-aryl nitrile chemical reaction under physiological conditions. The resulting dynamic hydrogels exhibit tunable viscoelastic properties, self-healing, self-recovery and fast stress relaxation behaviors, which in turn are tunable by pH, macromer molecular weight and concentration. By combining the mentioned dynamic bonding with complementary static bonding, the matrix stress relaxation can be finely controlled. When encapsulating human mesenchymal stem cells (hMSCs) to study the cell-material interactions in response to increased dynamicity in the hydrogel network, we found increased viability and larger cell volume in the hydrogels with higher dynamicity. The novel bonding shown here expands the existing toolbox of dynamic covalent crosslinking chemistry for soft matrices formation, with envisioned applications in the tissue engineering field. In combination with key engineering technologies, such as microfluidics and biofabrication, we have started to explore the applicability of these new matrices towards advanced tissue models.

CONJUGATED POROUS POLYMERS AND COVALENT ORGANIC FRAMEWORK AS WELL AS HYBRID THEREOF FOR SOLAR FUELS PRODUCTION

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Introduction

The fast depletion of fossil energy sources and quick global climate change force the development of key technologies to overcome these problems. Artificial photosynthesis (AP) systems are able to efficiently capture and convert solar energy and then, store it in the form of chemical bonds. Solar energy is therefore used to split water and produce hydrogen, transform carbon dioxide and water into a renewable source of energy-rich carbon-containing products or, even, N2 fixation though ammonia production. Conventionally, inorganic semiconductors such as metal oxides and chalcogenides have been the most widely studied materials for this purpose. However, we are witnessing a renaissance of organic-based semiconductors due to the description of more robust materials like graphitic carbon nitride (g-C3N4), conjugated porous polymers (CPPs), metal─organic frameworks (MOFs) and covalent organic frameworks (COFs) as photocatalysts. [1]

Methodology

In this sense, the development of new CPPs and COFs and their heterojunction with inorganic semiconductors has brought great attention to their use as photocatalysts for the production of renewable fuels.[2] These hybrids are expected to improve charge separation with respect to the inorganic phase by itself, and the presence of these polymeric frameworks provides chemical versatility.

Results and conclusions

Here, we will show the last results published by our research team in this topic.[3–5] We will descript not only the selection chromophores with redox properties to guarantee the light harvesting but also the synthetic strategies to achieve robust and more photoactive AP systems. On the other hand, we will show how the control of the CPPs nanoparticle size led to an improvement in the photocatalytic results but also open the door to the use of these materials as thin films in photoelectrocatalytic technologies.[5–7]

Acknowledgments

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REVALORIZACIÓN DE RESIDUOS AGROINDUSTRIALES PARA EL DESARROLLO DE NUEVOS MATERIALES BIODEGRADABLES

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Introduction

En el contexto de la economía circular y con el fin de sustituir los plásticos de un solo uso, entre otras posibles aplicaciones, los residuos generados tanto en agricultura como en la industria, constituyen fuentes altamente interesantes de compuestos que pueden utilizarse como aditivos o componentes de biomateriales.

Methodology

El análisis composicional y estructural de estos residuos es fundamental para extraer de ellos el mayor valor posible.

Results and conclusions

En los últimos años, desde el grupo de envases del IATA, se han explorado diferentes residuos y estrategias de valorización de los mismos intentando optimizar procesos, reduciendo costes, y entender el papel que tienen los diferentes componentes de los mismos en las propiedades finales de los materiales. En concreto, se ha puesto un especial énfasis en materiales obtenidos a partir de carbohidratos extraídos de distintas fuentes como residuos de algas, setas y diversas plantas y cultivos terrestres y marinos. Estos carbohidratos pueden utilizarse como aditivos en formulaciones de materiales más complejos, pero también pueden constituir nuevas estructuras biopoliméricas con aplicaciones tanto en alimentación (por ejemplo, como recubrimientos comestibles), como en otros sectores industriales mediante la estructuración de los mismos (aerogeles para diversas aplicaciones, incluyendo aislamiento o sorción/liberación). En esta ponencia, se mostrarán diversos ejemplos de aprovechamiento de residuos para la obtención de nuevos materiales biodegradables en el contexto de diversos proyectos de investigación.

Acknowledgments and References

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IMPROVING POLYMER CIRCULARITY THROUGH CHEMICAL RECYCLING STRATEGIES

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Introduction

Polymers play a crucial role in our daily lives due to a combination of properties such as durability, light weight, low cost or easy processability, but they also present serious drawbacks at the end of their life, as these materials are overwhelmingly disposed of in landfills or leaked into the environment.

Methodology

The solution must be to promote the effective polymer recycling. While reprocessing (primary recycling) and mechanical recycling processes (secondary recycling) are part of the solution, they have some drawbacks when applied to complex polymer waste streams: the need for sorting and washing, and polymer degradation that reduces the performance of recycled polymers. For these reasons, there is currently a growing interest in the capabilities and potential of chemical recycling (tertiary recycling) because of the affordability and efficiency of processes for converting polymers into chemical products (i.e., recovering their original chemical constituents) that can be reused as feedstocks for the chemical industry. According to these statements, polymer recycling can only go further by integrating chemical recycling processes that complement traditional mechanical recycling to increase the volumes of recycled polymer waste and upcycle their performance and properties. However, this is a complex unresolved challenge due to three main interrelated reasons: lack of recycling processes or difficulties in controlling the existing processes, deficiencies in the structural characterization of the recycled materials, and limitations in the reuse of these secondary raw materials in added-value products and applications.

Results and conclusions

In this work, three different chemical recycling strategies based on pyrolysis, chemolysis and devulcanization are described to demonstrate their potential application to treat complex polymer waste streams (from polymer mixtures and textile fibers discarded by the recycling industry to end-of-life tires) to increase the sustainability, quality, and the applicability of their recycled products.

In this respect, a pioneer chemical recycling method has been developed by our Group to convert polyester (e.g., PET) waste into a liquid polyol[1]. In this selective method, the reaction takes place under milder conditions than conventional methods, while its versatility allows to transform PET waste into different polyols (controlling the molecular weight and chemical composition) by varying the reaction conditions (temperature, reaction time, organo/catalyst). Finally, these recycled polyols have been used as secondary raw materials for the synthesis of high-performance polyurethanes for different applications, proving to be an attractive and sustainable PET waste recovery.

In the case of ground tyre rubber (GTR), the application of two complementary recycling approaches, such as pyrolysis and devulcanization, is mandatory to increase the sustainability, quality, and especially the applicability of their recycled products (recovered carbon black and devulcanized rubber, respectively) again in the tire industry[2].

This work provides fundamental insights into the structure of devulcanized rubber and reinforcement mechanisms of recovered carbon black at a molecular level to overcome the lack of understanding of its use in tire rubber compounds, redefining the current paradigm for these recycling approaches and providing a clear roadmap for the development of the next generation of these recycled materials.

Acknowledgments and References

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THIN NANOGEL DRESSING OF BIOMOLECULES TO APPROACH SMART APPLICATIONS

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Introduction

During my presentation, I will demonstrate how to merge functional biomolecules, such as enzymes, with artificial materials, like polymers, to create biohybrids that have targeted functions. The use of polymeric networks, which act as flexible and porous scaffolds, can enhance the stability and robustness of enzymes in conditions that would otherwise cause free enzyme systems to break down. These hybrids open new avenues of applications in chemical synthesis, the alimentary industry, and medicine, particularly in the development of sensors.

Methodology

Our strategy consists of wrapping individual enzymes within these polymeric networks, which are rationally designed to confer the biomolecule with additional features. Specifically, my focus for this presentation will be on the use of a molecular dressing strategy for the design of innovative multifunctional hybrid biomaterials. The composition of the polymer can be tailored to anchor functional units such as fluorescent reporters or metalorganic catalysts. The convenient allocation of these small molecules in the confined surroundings of the enzyme permits the design of efficient one-pot cascade reactions and efficient electron shuttling between enzymes and electrodes.

Results and conclusions

From the examples developed in the lab, I will deepen into the use of molecular dressing strategy for enzyme-mediated electrochemistry, which has garnered significant attention for its applications in the alimentary industry and medicine, particularly in the development of sensors. In this presentation, I introduce a novel approach involving the deposition of imprinted enzymes onto untreated carbon electrodes. As a proof of concept, we have demonstrated the deposition of glucose oxidase-loaded cobalt biohybrids onto flat carbon electrodes. The resulting bioelectrodes exhibit robustness over consecutive measurements. The thin functional nanogel coating on enzymes opens avenues for the fabrication of a distinct family of biohybrids, presenting exceptional features for enzyme-mediated electrochemistry. This innovative approach addresses key challenges, paving the way for broader applications in various fields.

Acknowledgments

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ADVANCING SOFT ROBOTIC FUNCTIONS THROUGH ADDITIVE MANUFACTURING OF LIQUID CRYSTAL ELASTOMERS

Carlos Sánchez Somolinos

INMA (CSIC-UZ), Zaragoza, España

Introduction

The ability to structure smart materials in three dimensions can provide soft robotic systems with sensing and actuation capabilities, as well as other advanced functionalities. In particular, digital fabrication techniques can achieve all of this with high reproducibility, scalability, and flexibility in design, making them a key enabling technology for the future development of soft robotic systems with potential impact in various technological areas, including microfluidics, photonics, and biomedicine. Liquid crystalline elastomers (LCEs) are particularly interesting materials in soft robotics as they have demonstrated great potential for implementing complex shape-morphing structures when exposed to stimuli such as heat, light, or humidity. Recent developments in LCE fabrication have enabled the creation of actuators and devices with digitally defined director patterns, enabling programmed shape morphing. [1-3] However, challenges remain, such as the limited availability of functionalities and the miniaturization of structures. This lecture presents recent efforts carried out at the Advanced Manufacturing Laboratory, with an emphasis on advancing new functionalities and achieving finer feature sizes. [4-6]

Acknowledgments

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3D BIOPRINTING BIOMIMETIC BREAST CANCER MODELS USING DECELLULARIZED EXTRACELLULAR MATRICES.

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Introduction

The extracellular matrix (ECM) is a critical component of the tumor microenvironment, playing a significant role in cancer progression and drug resistance. Composed of structural proteins like collagen, glycoproteins, and proteoglycans, the ECM is a dynamic and versatile network that influences cellular processes such as growth, proliferation, and migration. In cancer, the ECM becomes disorganized and dysregulated, contributing to abnormal cellular behavior through complex feedback mechanisms. This disarray is primarily driven by cancer-associated fibroblasts (CAFs) and immune cells, which alter ECM metabolism, further promoting tumor progression.

Methodology

In this study, we developed a novel bioink using decellularized and delipidated porcine breast tissue-derived matrices (TDM), which closely mimics the complexity of the tumor ECM. This TDM-based bioink is compatible with 3D bioprinting, achieving good printability, shape fidelity, and cell compatibility. To enhance the biomimetic properties of the bioink, gelatin methacrylamide and alginate were incorporated, allowing for successful bioprinting of the TDM. Additionally, the bioink composition was optimized by incorporating Collagen type I (Col1), which not only improved the printability but also increased the proliferation of breast cancer cells (BCCs).

Results and conclusions

Our results demonstrated that BCCs could proliferate within the TDM bioinks, forming cell clusters and spheroids, both with and without Col1. Notably, the presence of Col1 enhanced cellular proliferation but also increased sensitivity to doxorubicin, a commonly used chemotherapeutic agent. These findings suggest that our TDM-based bioink can be used to create artificial breast tumors that closely recreate the tumor ECM, offering a more biomimetic model for studying ECM-cell interactions, cancer progression, and drug screening.

This work highlights the potential of 3D bioprinting to develop advanced cancer models that better represent the in vivo tumor environment, providing valuable tools for cancer research and therapeutic development.

ANTIMICROBIAL CATIONIC POLYMERS BASED ON THIAZOLE RINGS, A COMPONENT OF VITAMIN B

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Introduction

Our research group, Macromolecular Engineering Group, has been at the forefront of developing antimicrobial polymers with potent effectiveness to circumvent bacterial resistance [1]. Our research goal is to develop cationic polymers that mimic the host-defense peptides which exert their activity by acting on bacterial membranes, and then, having low potential for building up antibiotic-resistance. Specially, we design amphiphilic polymers bearing triazolium and thiazolium groups (a derivative of Vitamin B) that display potent and selective antimicrobial activity against clinically relevant bacteria, with negligible toxicity to human cells. Certainly, enhancing their antimicrobial activity while minimizing toxicity to mammalian cells requires precise control over their structural parameters, including the hydrophobicity/hydrophilicity balance, cationic density, molecular weight, and functional groups, among others. Additionally, combining different biocidal functionalities to enhance effectiveness or even provide synergistic effects is considered a very promising approach in fighting bacterial infections [2,3]. Over the past few years, our group has designed a variety of polymeric systems with antimicrobial properties, starting from methacrylic polymers [4] to recently synthesizing bio-based and biodegradable polymers derived from itaconic acid and chitosan [5,6]. Research on biobased/biodegradable antimicrobial polymers is emerging as fruitful area that opens up new opportunities for a sustainable and safety development. Biodegradability is an important and desired property in many biomedical applications, including bioresorbable stents and prosthesis, food packaging and agricultural uses, whereas biobased polymers obtained from renewable resource might also contribute to sustainability reducing dependence of fossil derived plastics.

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ORAL PRESENTATIONS

WATER-SOLUBLE CYCLIC POLYMERS WITH POTENTIAL BIOMEDICAL APPLICATIONS

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Introduction

Cyclic polymers are currently at the forefront of macromolecular science. This is due to the intriguing physical and chemical properties presented by cyclic polymers, which arise from the absence of end groups and their circular architecture. The extensive research conducted on synthetic polymers has been crucial for understanding their property-structure relationships. This has only been possible through innovative advances in organic synthesis and catalysis, creating a variety of pathways to cyclization of preformed chains through ring-closure strategies and the ring-expansion polymerization (REP) of diverse monomers [1]. Cyclic polymers that are water-soluble hold promising applications in the biomedical field. Szoka et al. demonstrated that cyclic PEGylated polycaprolactone and cyclic PEGylated polyacrylic acid comb polymers with molecular weights above the renal filtration threshold exhibited longer circulation times than their linear analogues [2]. This property is attributed to the increased difficulty cyclic polymers face in crossing nanopores compared to linear polymers due to greater conformational constraints when diffuse across small spaces. These promising results offer a window of opportunity for utilizing cyclic polymers as drug carriers or imaging agents.

Methodology

Our methodology includes the synthesis of a diversity of cyclic polymers as illustrated in Fig. 1.

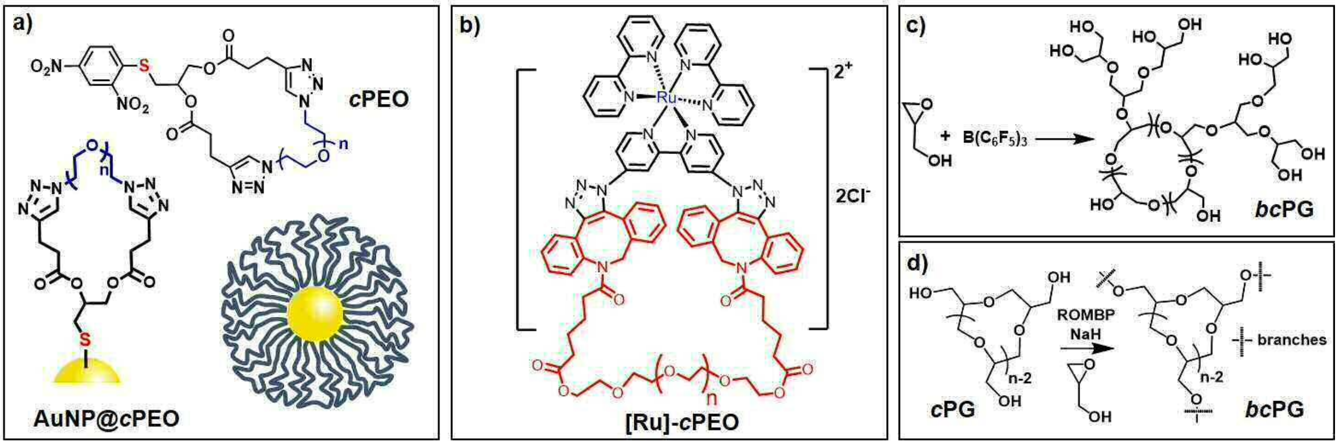

Fig. 1. Water-soluble cyclic polymers synthesized in our lab.

Results and conclusions

I will present our recent developments on the area of water-soluble cyclic polymers with potential applications in the biomedical field. This includes designing and developing synthetic strategies to produce materials based on cyclic polymers (Fig. 1.): (a) cyclic poly(ethylene oxide) (PEO) as surface ligand of gold nanoparticles [3], (b) luminescent cyclic PEO-polypyridyl ruthenium complex ([Ru]-cPEO), which efficiently accumulated into MCF7 cancer cells [4], (c) branched cyclic polyglycidol (bcPG), which is non-cytotoxic and able to cross a barrier of endothelial hCMEC/D3 cells in a blood-brain barrier model [5], and (d) bcPG by combining REP of cyclic poly(tert-butyl glycidyl ether) [6], and ring-opening multibranching polymerization of glycidol.

Acknowledgments

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ITACONIC ACID: A VERSATILE BIOBASED BUILDING BLOCK FOR THE REPLACEMENT OF (METH)ACRYLIC ACID IN PHOTOCURABLE FORMULATIONS FOR 3D PRINTING

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Introduction

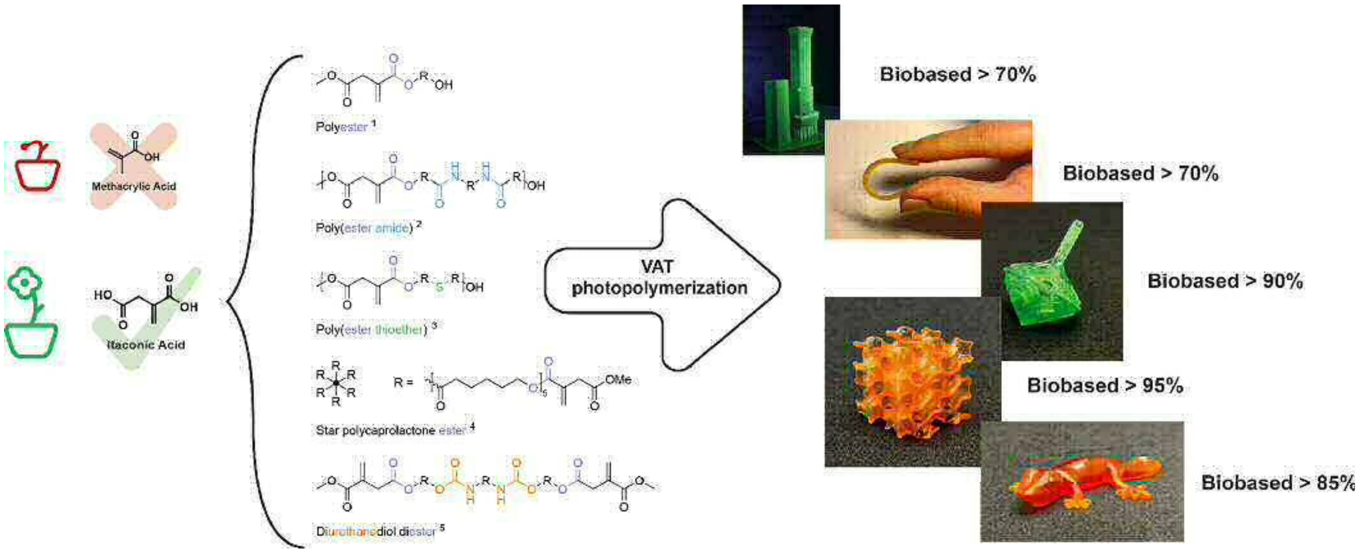
Recent studies have highlighted the risks of using fossil-derived materials in industries like additive manufacturing, especially in vat photopolymerization (VP). Toxic components like (meth)acrylic acid derivatives pose environmental and health risks. To address this pressing issue, researchers are now focusing on itaconic acid (IA), an emerging building block that can create liquid compounds that photopolymerize under photoradical conditions. Unlike traditional fossil-based formulations, IA is produced by fermentation of biomasses with engineered bacterial strains. It is one of the few fully biobased compounds that contain the acrylate moiety in their chemical structure, making it an ideal alternative to (meth)acrylic acid in photocurable formulations.

Methodology

IA, being a dicarboxylic acid, has been utilized to develop polyesters [1], poly(ester amide)s [2], and poly(ester thioether)s [3], but it was also used as a functionalizing moiety for non-photocurable biobased compounds such as branched polycaprolactone [4] and non-isocyanate diurethanes [5]. Polymers were prepared by tin-catalyzed polycondensation, while terminal IA moieties were introduced using the corresponding acyl chloride.

Results and conclusions

In our works, we have combined these macromers with small molecular weight IA-based reactive diluents to create fully biobased resins that photocure into solid 3D printed objects via VP. The resulting objects, which exhibit mechanical properties and thermal stabilities fully comparable to traditional fossil-based formulations, can be printed with great dimensional accuracy. They are characterized by elastic moduli ranging from a few MPa to 1 GPa, depending on the formulation. The proposed approach suggests how itaconic acid can be employed as a replacement for methacrylic acid in photocurable formulations, offering additional versatility given by its ability to for photocurable polymers.



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TRANSFORMING COMMODITY PLASTIC PVC INTO EFFICIENT CATALYTIC SINGLE-CHAIN NANOPARTICLES

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Introducción/Introduction

Recycling and waste valorization of polymeric materials, particularly polyvinyl chloride (PVC), are gaining attention to combat plastic pollution. PVC, the third most produced synthetic polymer globally, faces recycling challenges, especially in flexible forms due to banned plasticizers. Recent advancements include efficient PVC dechlorination and conversion into useful products like fuels and flash graphene. A novel approach transforms PVC into catalytic single-chain nanoparticles (SCNPs), which have applications in drug delivery, catalysis, and sensing [1-2]. This method uses functionalized polymer chains to create stable SCNPs, showcasing the potential to upcycle PVC waste into valuable, functional materials for various industries.

Metodología/Methodology

The process to create valorized PVC-SCNPs (vPVC-SCNPs) involved two main steps. Initially, PVC was partially azidated to obtain PVC-N3. The azidation was performed using sodium azide (NaN3) and N, N-dimethylformamide (DMF) as solvent at 80 °C. Then, intra-chain metal-free click chemistry was employed, using Sondheimer diyne [3] as an external crosslinker, to form the SCNPs. Finally, vPVC-SCNPs were loaded with Cu(II) ions using CuCl2 as salt. All reactions were carried out using green solvents.

Resultados y Conclusiones/Results and conclusions

PVC samples with approximately 40 kDa were sourced commercially as well as from flexible and rigid tubes. PVC-N3 was prepared through azidation of PVC, resulting in a 12.2 mol % substitution (determined by elemental analysis). PVC-N3 was subsequently characterized by 1H and 13C NMR, SEC, and IR spectroscopy. The strain-promoted double-click (SPDC) reaction using the Sondheimer diyne was employed to form SCNPs from PVC-N3. The formation of SCNPs was confirmed by Dynamic light scattering (DLS) measurements and SEC in THF, exhibiting a reduction in average hydrodynamic radius (Rh) from 10.1 nm (PVC-N3) to 6.5 nm (vPVC-SCNPs). The compact domains of SCNPs provide avenues for developing recyclable, enzyme-mimetic catalysts leveraging the folded/collapsed chain's beneficial outer coordination sphere effect. Additionally, vPVC-SCNPs loaded with Cu(II) ions (7.3 mol %, determined by ICP-MS) were explored as recyclable/enzyme-mimetic catalysts for various Cu(II)-catalyzed reactions. CONCLUSIONS We introduce an upcycling method for polyvinyl chloride (PVC), transforming it into "valorized" PVC-SCNPs (vPVC-SCNPs) using green solvents and metal-free click chemistry. These nanoparticles, loaded with Cu(II) ions, act as efficient recyclable catalysts for various organic reactions, demonstrating broad applicability for other azide-functionalizable plastics.

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CRISPR-MEDIATED TRANSCRIPTIONAL ACTIVATION TECHNOLOGY (CRISPRA) AS AN OPPORTUNITY FOR ENHANCING ELASTIN LIKE RECOMBINAMERS (ELRS) EXPRESSION IN BACTERIA

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Introducción/Introduction

ELRs are known for their thermoresponsive properties and biocompatibility. These properties and ability to alter ELRs structure through genetic engineering and chemical modifications gives potential for their applications in a variety of areas of Biomedical engineering[1]. CRISPRa is a technology, that leverages the CRISPR/Cas9 system to activate gene expression. For that, three plasmids are introduced into the bacterial cell: one carrying the gene of interest, another encoding the catalytically inactive Cas9 protein (dCas9) fused to the transcription activator, and a third plasmid bearing the guide RNA (gRNA), which is designed to be complementary to a specific site on the gene of interest-carrying plasmid to locate transcription activator just upstream the transcription start site[2]. Enhancing ELR expression in bacterial cells is crucial for ELR subsequent production, prompting this study on the use of CRISPRa technology to improve ELR expression.

Metodología/Methodology

The gene encoding a representative ELR (E50I60) was used as the target gene. T4 phage anti-sigma factor AsiA-m2.1 was employed as the transcriptional activator, and the gRNA was specific to the plasmid encoding the ELR gene. Co-transformation of these three plasmids into E. coli (BLR) resulted in efficient transformation, but no significant difference in ELR expression was observed compared to the established method without CRISPRa. Consequently, the promoter on the plasmid encoding the ELR gene was changed from T7 to J23110, and the bacterial strain was switched from BLR (E. coli) to BW25113 (E. coli). Total RNA was extracted, and 1 µg of RNA was converted to cDNA. qPCR was performed using TaqMan Universal Master Mix II. qPCR was optimised for finding most efficient concentrations of primers and Taq probe. Gene expression levels were calculated using the standard curve method. As a standards, we used a PCR product, derived from the plasmid, that contains target gene sequence.

Resultados y Conclusiones/Results and conclusions

Following the changes in bacterial strain and promoter, higher expression levels of the target gene (E50I60) were observed in samples utilizing the CRISPRa system compared to those without it. Ongoing research is essential to further optimize and enhance this technology to maximize CRISPRa's potential for improving ELR expression.

Agradecimientos y Referencias/Acknowledgments and References

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CONDUCTING POLYMERS EFFECT IN THE VOLUME PHASE TRANSITION OF THERMOSENSITIVE PNIPAAM-BASED HYDROGELS

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Introduction

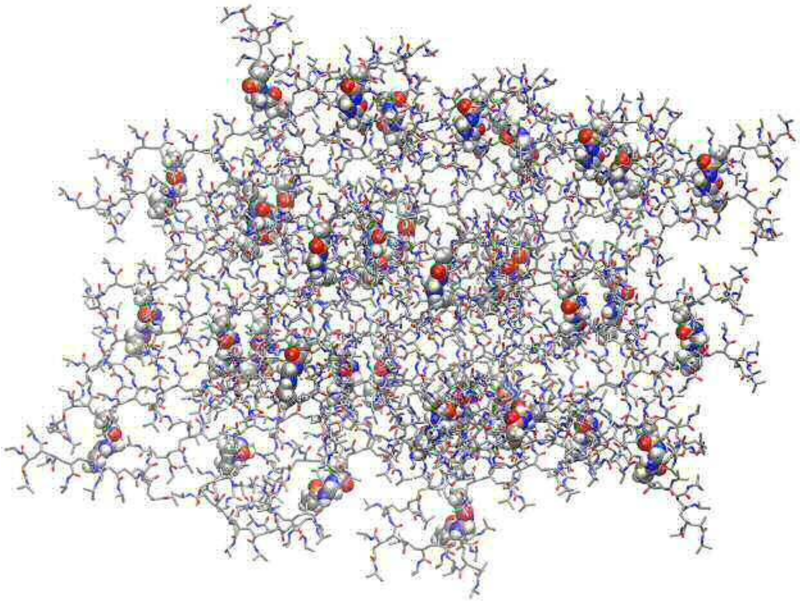
Thermosensitive conducting hydrogels (TCH) represent a fascinating class of composite materials with diverse applications, spanning from biomedical uses to addressing pressing issues like water scarcity [1-2]. At the heart of their functionality lie conducting polymers (CPs), pivotal in conferring electrochemical and photothermal properties to TCH. While the volume phase transition (VPT) phenomenon in thermosensitive polymers has been extensively explored, the precise role of CPs and their underlying chemical interactions remain largely uncharted territory [3].

Methodology

In this study, we synthesized a novel TCH leveraging poly(N-isopropylacrylamide) (PNIPAAm) as the thermosensitive polymer but enhanced with poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles. This served as an ideal model system to delve into the interplay between CPs and VPT through a multifaceted experimental and theoretical approach. By meticulously examining the hydrogel's response to temperature shifts using Raman spectroscopy, coupled with atomistic simulations employing advanced hybrid methodologies and artificial intelligence, we uncovered a significant shielding effect exerted by CPs.

Results and conclusions

This shielding effect stems from robust chemical interactions with NIPAAm, precipitating a selective dehydration of the hydrogel microenvironment. Remarkably, this phenomenon mirrors the behavior observed during VPT triggered by temperature elevation. Understanding these intricate interactions between conducting and thermosensitive polymers is paramount for the systematic advancement and fine-tuning of future CPHs' performance. This knowledge paves the way for a more nuanced adaptation of these materials to suit their intended applications with greater precision.



PNIPAAm-MBA hydrogel model of 3D Cross-linked system.

Acknowledgments

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A NOVEL AND SELF-CONSISTENT PHYSICAL FRAMEWORK TO CHARACTERIZE MOLECULAR STRUCTURE AND DYNAMICS OF REINFORCED RUBBERS BASED ON A COMBINATION OF EXPERIMENTAL TECHNIQUES

Fernando Martín Salamanca, Zenen Zepeda Rodríguez, Laura Diñeiro García, Marina Montero Escrivá, Rebeca Herrero , Alberto Fernández Torres, Rodrigo Navarro , Juan López Valentín

ICTP, Madrid, España

Introduction

Elasticity in rubber materials depends on molecular parameters that define the structure. Crosslink density is the most well-known, although it has been proven that the molecular weight of polymer chains (entanglements) or dangling chain ends (network defects) are also crucial to understand the structure-properties relationships on unfilled rubbers. Additional effects arise when reinforced rubbers are considered, such as hydrodinamic amplification, filler-filler interactions or filler-rubber interactions. The development of a self-consistent physical framework was required to quantify all the molecular parameters necessary to quantify the molecular structure of reinforced rubbers. In order to achieve this challenging goal, Multiple Quantum (MQ) NMR experiments and tensile tests were performed and their respective theoretical backgrounds were unified to accomplish the quantitative determination of all the molecular parameters that define the molecular structure.

Methodology

The methodology consisted in 4 separated phases: i) preparation of the samples, ii) tensile tests experiments, iii) MQ-NMR experiments and iv) data analysis. The preparation of the samples followed a standard method which can be found in the literature [1]. The tensile tests were performed at low-speed (10 mm/min) to minimize the viscous response of the material. MQ-NMR experiments provided structural information about the order parameter by the application of an advanced Baum-Pines pulse sequence. The data obtained were treated with a theoretical approach based on the order parameter and the tube model.

Results and conclusions

The real crosslink density, the entanglement density, the finite extensibility parameter, both stress and strain amplification factors, the fraction of network defects and the density of filler-rubber interactions were determined for the first time. Some experimental approaches provide inconsistencies in the determination of the network structure of rubber compounds and a combination of experimental techniques is needed to characterize every parameter. MQ-NMR provides information on the segmental order at a molecular level, network imperfections and the spatial distribution of the restrictions of movement, while tube model discerns between crosslinks and entanglements and is easy to work with and generalize it to filled samples.

Acknowledgments

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SELF-HEALING SUPRAMOLECULAR POLYURETHANES BASED ON MULTIPLE HYDROGEN BONDS

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Introduction

Supramolecular polymers are capable of ordering into higher order structures when activated by temperature. This requires non-covalent interactions such as hydrogen bonds. The introduction of 2-ureido-4-[1H]-pyrimidinone (UPy) moieties within the polymer matrix is a strategy for the design of thermally-responsive self-healing materials with advanced performance, due to the ability of these units to easily dimerise via quadruple hydrogen bonding. In the present work, two types of polyurethane with the same chemical composition were synthesised, but showing different behaviour. One was able to self-repair triggered by heat, while the other did not show this attractive property.

Methodology

Polyurethanes functionalised with UPy units were obtained according to the procedures described elsewhere [1]. Two polycaprolactone polyols of different molecular weights (512 and 2054) were used as soft segments. The chemical structure of the polymers was confirmed by liquid NMR (400 MHz), while the molecular structure and dynamics were analysed by low-field NMR (0.5 T). The self-healing capacity was determined by constant rate stress-strain tests, varying time and temperature.

Results and conclusions

The synthesis of the polyurethanes bearing UPy units was successful reaching high molecular weights. In addition, the content of UPy units and the chemical structure of the polyurethanes was confirmed by liquid NMR. The thermal properties of the polyurethanes, obtained by DSC, showed the presence of a single glass transition temperature. This situation is characteristic in polyurethanes with a lack of phase segregation between the hard and soft segments. However, by DMTA tests, two transitions were appreciated: at low temperature corresponding to the Tg of the material, while at high temperature it was assigned to the dissociation of the UPy dimers. The self-healing tests showed that only the polyurethane with a short soft segment (PCL531) showed a self-healing capacity at a temperature of 100°C, for 24h. However, its counterpart (longer chain PCL) barely showed self-healing capability under the same conditions. Using advanced low-field NMR sequences, it could be determined that 95% of the polyurethane derived from PCL531 showed high molecular mobility whereby self-healing took place, whereas for its partner the mobile phase content was only 60% at the same temperature.

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DETAILED MORPHOLOGY OF ABS LATEX NANOPARTICLES REVEALED BY MATHEMATICAL MODEL AND HAADF-STEM TOMOGRAPHY

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Introduction

ABS polymer is used in many applications, such as automotive, electronic devices, healthcare, among others, by customizing its characteristics to meet specific requirements of the products. These characteristics include polymer microstructure, grafting density and morphology of the ABS polymer, among others. ABS nanoparticles can be synthesised by seeded emulsion polymerization leading to structured polymer particles that are used as impact modifiers in ABS blends.One of the key characteristics of the ABS polymer is the grafting density of the SAN chains onto the PB backbone chains that controls the effective dispersion and compatibility of the ABS polymer in SAN matrixes commonly used in the main applications.

Methodology

Characterization of the microstructure and grafting properties can be obtained by analysing microscopically the morphology of the ABS polymer particle. However, in the literature, the morphological study of the ABS is mainly limited to the polymer blends and very rarely the morphology of ABS latexes has been analysed. The main limitation of conventional microscopy imaging techniques is a generation of 2D data for an object that is actually 3-dimensional, which creates an ambiguity in interpretation and statistical analysis. In addition to the experimental approaches, plenty of effort has been devoted to understand the mechanisms and driving forces, controlling the morphology of structured polymer particles by modelling approaches.1,2 In this work, the particle morphology of the ABS latex particles were determined by means of a mathematical model and high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) tomography of selectively stained latexes.

Results and conclusions

The characterization technique was used to analyse the internal SAN cluster distribution among the PBD matrix as well as the thickness and level of partial diffusion of the external clusters. A mathematical model for the development of dynamic evolution of the polymer-polymer structured latex nanoparticles was used to predict detail particle morphology of the ABS nanoparticles by means of the size distribution of internal and external clusters. The model prediction was assessed using the morphology of the particles revealed by HAADF-STEM tomography.

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EFECTO DE LA VELOCIDAD DE ENFRIAMIENTO EN LAS TRANSICIONES DE FASE DE SISTEMAS BASADOS EN ÁCIDO POLILÁCTICO CON NUCLEANTES POLIMÉRICOS

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Introducción

El PLA, polímero biobasado, ha recibido mucha atención debido a su biodegradabilidad, biocompatibilidad y aplicaciones [1] en sectores donde hasta ahora estaban cubiertas por productos procedentes de fuentes fósiles. Además, su monómero presenta un átomo de carbono asimétrico y, en consecuencia, la polimerización a partir de lactidas ópticamente activas puede conducir a un "conjunto" de polímeros con estereosecuencias en sus macrocadenas. Diversos estudios demuestran que los estereocomplejos de PLA pueden mostrar mejoras en las propiedades térmicas y mecánicas de los materiales finales [2]. Conjuntamente, el uso de plastificantes puede reducir la energía de plegado de la cadena y aumentar la movilidad de los segmentos mejorando la procesabilidad, flexibilidad y ductilidad, afectando su capacidad de cristalización y fomentando la formación de estereocomplejos [3]. El propósito del presente trabajo es analizar el efecto de dos agentes nucleantes basados en PLA sobre la formación de estereocomplejos, el grado de cristalización, la fase cristalina y las propiedades térmicas y mecánicas de dos matrices de PLA.

Metodología

Se prepararon y caracterizaron mezclas por extrusión en fundido de dos tipos de PLA (LM72304 (LM7) y LM62502 (LM6), ErcrosBio) con dos agentes nucleantes (LN300 y LD552, ErcrosBio) y se procesaron por compresión aplicándose dos tratamientos térmicos distintos.

Resultados y Conclusiones

Los resultados revelan que la familia de muestras LM6, comparada con la LM7, promueve en mayor medida la formación de cristales estereocomplejos, independientemente del tratamiento térmico. La velocidad de enfriamiento aplicada durante el procesado de los films es decisiva en la formación de las fases cristalinas, las características de los homocristales y los valores de microdureza. Las muestras enfriadas rápidamente, mostraron mayor formación de cristales estereocomplejos, mientras que las muestras enfriadas lentamente, presentaron una mezcla de cristales estereocomplejos y homocomplejos. Las medidas de microdureza revelaron que las muestras enfriadas lentamente tenían mayor rigidez superficial, debido a la mayor cristalinidad general. Ambos nucleantes demostraron ser efectivos en la promoción de la estereocomplejación del PLA.

Agradecimientos y Referencias

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STRUCTURAL AND CRYSTALLINE CHARACTERIZATION OF EVEN-ODD NYLONS OBTAINED FROM PIMELIC ACID

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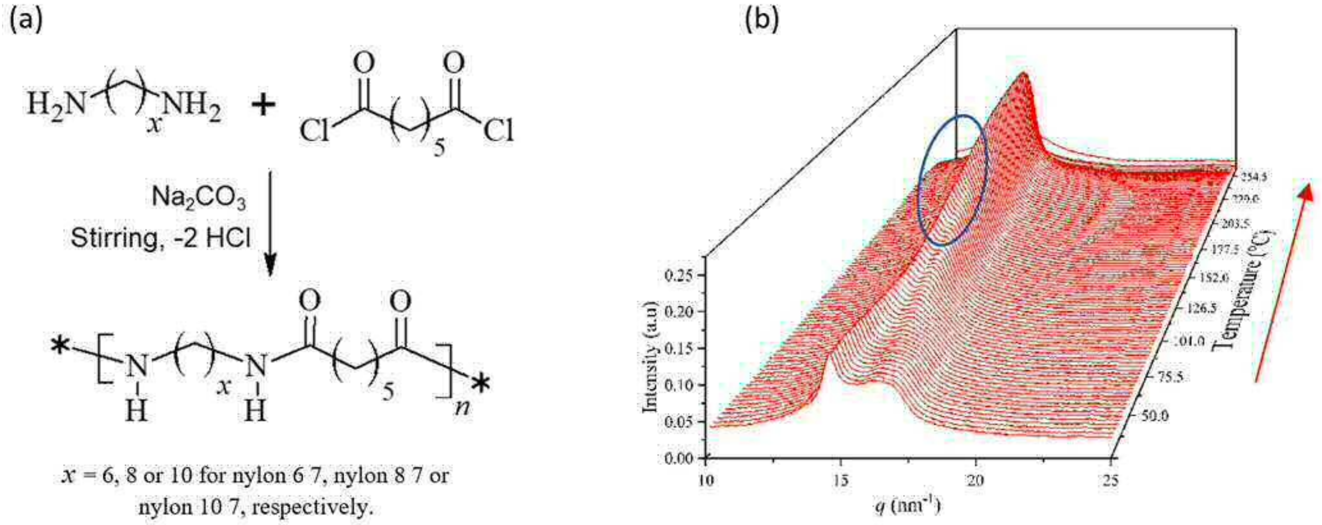
Introduction

Nylon is the commonly used name for aliphatic polyamides, a class of polymers known for their excellent mechanical and thermal resistance due to the amide group's ability to form strong hydrogen bonds[1]. These polymers can be produced either through the polymerization of bi-functionalized A-B monomers, such as lactams or ω-amino acids, or by the polycondensation of monomers with complementary A-A and B-B functional groups, as diamines and dicarboxylic acids. Commercial nylons typically consist of monomers with an even number of carbons, including nylons 6, 66, 612, and 12. The structure of these nylons can be categorized into the well-known α/β and γ crystalline forms. However, nylons with odd-numbered units present intriguing unresolved questions. For instance, thermally induced phase transitions at lower temperatures of the Brill transition observed in conventional nylons[2]. In this work, we report the study of nylons of the type *x*-7 with five methylene groups between adjacent C=O groups for each nylon, while the number of methylene groups between adjacent NH groups increases by two for each successive member of the series.

Methodology

The obtained polymers, named nylon 6-7, nylon 8-7, and nylon 10-7, were synthetized by interfacial polymerization and characterized by FT-IR, NMR and GPC. Crystallization kinetic was studied using DSC and polarized-light optical microscopy under iso and non-isothermal conditions. Avrami theory was used to determine the main kinetic parameters and Lauritzen-Hoffmann theory was applied in order to study the regimes of the crystallization in the spherulitic morphology. Crystalline structures of the selected nylons were studied using synchrotron light based WAXS.



(a): Reaction scheme for the interfacial polymerization of pimelic acid derived nylons. (b): Representative WAXS profiles variation with temperature during heating of a nylon 6 7 sample, in which it is possible to observe intermediate thermal transitions, indicated in a blue ellipsoid.

Results and conclusions

Synchrotron experiments performed using an temperature plate, were conducted during heating and cooling ramps, when the samples underwent melting and crystallization phenomena. By using SAXS, lamellae information was acquired, specifically during crystallization from melt state and from quenched amorphous samples. Crystallization processes became more difficult and slower while increasing the length of the diamine units in the polymers. Results allow to better understand how the different crystallization parameters influenced the final crystalline structure of this nylons.

Acknowledgments

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MODELOS ATOMÍSTICOS Y DE GRANO-GRUESO PARA LA MODELIZACIÓN DE DISOLUCIONES DE POLISACÁRIDOS DE ORIGEN BACTERIANO.

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Introducción

Los polisacáridos basados en glucosa producidos por bacterias tienen una rica variedad en su estructura química que depende del tipo de bacteria y de las condiciones de cultivo [1]. El conocimiento de las relaciones entre las propiedades y estructura de estos polisacáridos es esencial para desarrollar nuevos materiales con mejoras en su funcionalidad.

Los polisacáridos aquí estudiados son la celulosa bacteriana, curdlan y MLG (mixed-linkage β-glucan). Estos polisacáridos se diferencian en la forma de enlazar las unidades de glucosa. Por ejemplo, el MLG producido por la bacteria *Sinorhizobium meliloti 8530* es de especial interés debido a que es un material único que presenta enlaces β(1,4) y β(1,3) perfectamente alternantes[2]. Este tipo de polisacáridos suelen ser insolubles en agua lo cual dificulta su aplicación, por lo que se suelen modificar de diferentes formar para aumentar su solubilidad.

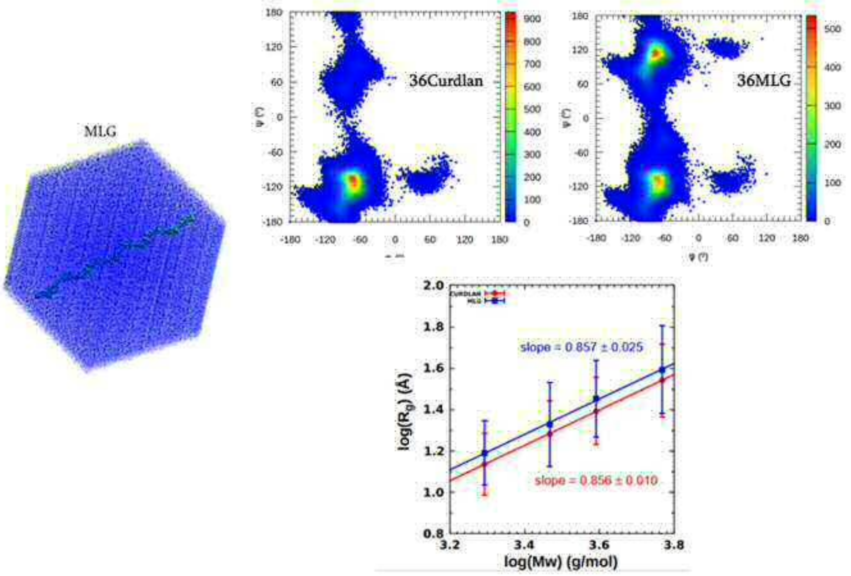
La modelización computacional permite construir modelos con un control preciso de la estructura y mediante simulación calcular sus propiedades.

Metodología

i) Simulación mediante dinámica molecular (MD) de disoluciones acuosas de diferentes modelos atomísticos (AA, all-atom) usando distintas concentraciones de CMC, curdlan y MLG.

ii) Desarrollo de modelos de grano-grueso (CG) mediante la aplicación de la técnica conocida como IBI[3].

iii) Creación y simulación de modelos CG de alto peso molecular.



Características conformacionales del Curdlan y MLG

Resultados y Conclusiones

Se han evaluado las diferencias conformacionales entre CMC, Curdlan y MLG con dos grados de sustitución diferentes. Las simulaciones atomísticas han permitido desarrollar un modelo CG que permite estudiar tiempos y pesos moleculares más altos. Se han calculado los radios de giro y mapas conformaciones en función de la concentración y del peso molecular. Los radios de giro comparan bien con las evidencias experimentales. Estos modelos nos sirven para en un futuro hacer un estudio de las propiedades reológicas que podemos comparar directamente con experimentos.

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RELATIONSHIP BETWEEN PLA STRUCTURE AND WETTABILITY PROPERTIES

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Introduction

In 1997, a bio-inspired micro-nano rough topography, based on the lotus leaf, was described. This topography is capable of retaining an air layer between the substrate and the water, causing droplets to minimize their contact area and promoting droplet sliding. Since then, water repellent surfaces have gained great importance due to their specific properties such as self-cleaning, anti-corrosion, anti-icing, and anti-biofouling.

The large-scale production of surfaces with water repellency, requires creating roughness using simple techniques that do not involve high energy waste, to fulfil environmental requirements. In this sense, HEMPOL group developed some years ago an industrially viable method to produce all-polymer hydrophobic surfaces [1] with PMMA/PVDF blends, which was also successful in producing superhydrophobic PET [2]. More recently, the method has been applied to polylactic acid (PLA) surfaces [3], where a strong impact of the PLA structure on the surface topography and hence on the wetting behaviour, has been detected.

For a better understanding of the relationship between polymer structure and surface topography, in this work, several PLAs varying in molecular weight and tacticity have been studied for the obtention of superhydrophobic surfaces. In this way, the structural parameters triggering the topographical structure will be defined.

Metodología/Methodology

Several PLA samples from different suppliers varying molecular weight and microstructure, were hot compressed to prepare thin films. Then, to develop the topography required, a simple treatment consisting on the immersion of the material in different solvents was performed. This procedure leads to the induction of polymer crystallization thus varying the surface morphology. The influence of the different molecular weights and tacticities on the crystallization have been studied by using differential scanning calorimetry (DSC) and infrared spectroscopy (FTIR). Also, the obtained topographies have been studied by combining scanning electron microscopy (SEM) and optical profilometry. Finally, the wettability behaviour of the resulting surfaces was evaluated using a conventional drop shape tensiometer.

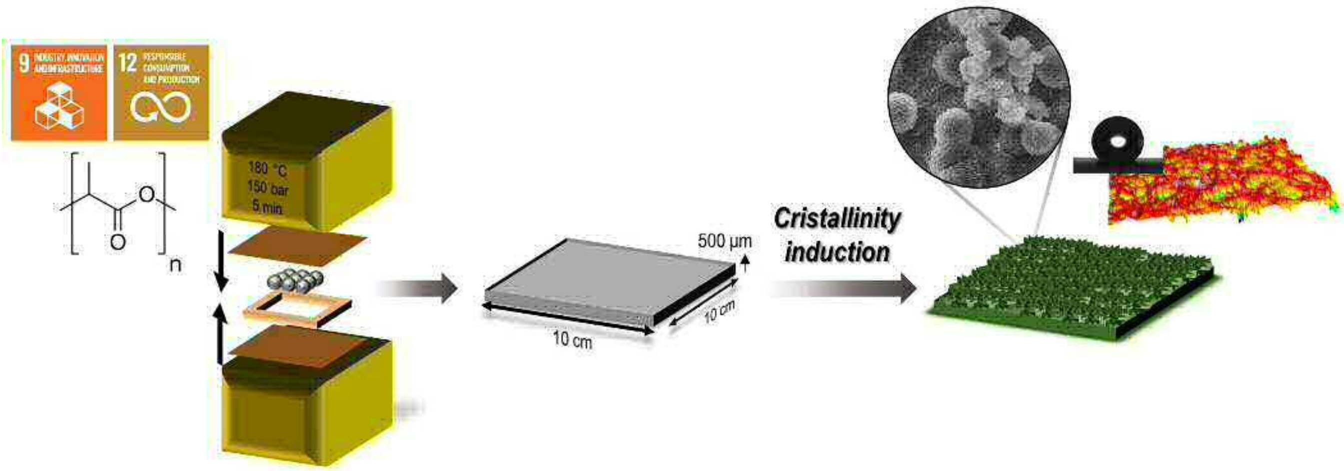

Figure 1. Schematic representation of the methodology followed in this work

Results and conclusions

In conclusion, the relationship between the molecular weights and the tacticity of the polymer and its ability to crystallize could be determined, successfully structuring all types of PLA surfaces.

Acknowledgments

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GRAFTING OF A PHOTOCROSSLINKABLE COUMARIN-BASED METHACRYLATE TO PLA FOR 3D PRINTING PURPOSES

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Introduction

Poly(lactic acid) (PLA) is a biopolymer which can potentially resemble in mechanical properties to oil-based commodities. However, in manufacturing techniques such as Fused Deposition Modelling (FDM), due to the intrinsic properties of the technique, PLA-based pieces present a poor interlayer adhesion reducing the mechanical properties of the manufactured piece (1). To improve the material performance, one proposed strategy can be photocrosslinking PLA chains through PLA functionalization (2). Functionalization of PLA requires grafting a molecule capable of reacting between them and ultimately crosslinking the polymeric chains. Coumarins can be considered precursors of crosslinking due to they undergo a reactive process based on a photodimerization reaction under UV radiation (350nm). This photodimerization is produced by a [2π+2π] cycloaddition of two coumarin units forming a cyclobutane ring.

Methodology

In this research, a methacrylic derivative of coumarin has been synthesised through the reaction between umbelliferone (7-hydroxycoumarin) with methacryloyl chloride, using tritethylamine as base-assistant. Later, the already synthesised coumarin derivative was grafted onto PLA via reactive extrusion free-radical grafting. The monomer was characterised by FT-IR, 1H-NMR, 13C-NMR and different 2D NMR experiments, confirming its structure.

Results and conclusions

Once grafted in bulk onto PLA, the highest grafting degree value was 0.7% calculated by q-1H-NMR. To reach such grafting, 10 wt% of the monomer was added to the polymer using 5 wt% dicumylperoxide as initiator. Based on GPC characterisation, the initial addition of the coumarin methacrylic derivative favours the grafting process hindering the side chemical crosslinking reaction between PLA· macroradicals. DSC measurements showed an increment in crystallinity possibly due to the peroxide-induced crosslinking/branching structures that act as nucleating agents. Finally, samples are UV irradiated and photocrosslinking is confirmed by UV/Vis spectroscopy, obtaining the greatest decrease in intensity of the lactone band by irradiating for 48 hours (Figure 1).

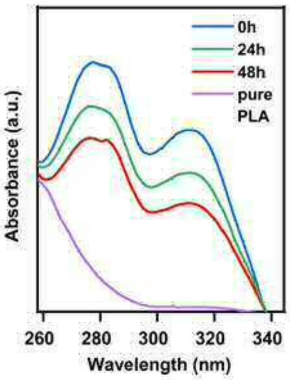

Figure 1. UV patterns of modified PLA samples irradiated during specific periods of time.

Acknowledgments

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ENGINEERING AN IMMUNOCOMPETENT GUT ON A CHIP MODEL WITH CONTROLLED PERMEABILITY USING SYNTHETIC POLYMERS

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Introduction

Intestinal bowel disease (IBD) is a chronic immune-mediated disorder characterized by chronic inflammation of the gastrointestinal tract, comprising Crohn’s disease and ulcerative colitis. The unknown etiology of IBD, along with its heterogeneous and multifactorial nature, make essential the development of relevant and functional model platforms that enable the fundamental understanding of the disorder [1]. Human intestinal organoids (HIOs) have enormous potential for IBD modeling, but their derivation in static three-dimensional matrices without perfusion can restrict their development and functionality. Currently, the fabrication of perfusable gut-on-a-chip platforms that include hydrogel matrices for HIOs culture, involve painstaking, time-consuming, and specific laser-based methodologies limited to natural matrices [2]. Here, we engineered a rapid and facile methodology to generate perfusable microchannels on poly(ethylene glycol) norbornene (PEG-NB) hydrogels [3] to develop gut-on-a-chip models for IBD diagnostic, modeling, and drug screening applications.

Methodology

Patterns on PEG-4NB hydrogels were created using a photomask and an OmniCure UV Curing System. Polymer solutions consisting of 10 wt% of PEG-4NB crosslinked with DTT were covered with the photomask and exposed during 1 second to UV light at 85 mW/cm^2. Characterization in terms of hydrogel swelling and shape fidelity of the generated patterns were analyzed by gravimetric technique and optical microscopy, respectively. The open lumen created in the hydrogels was then used for cell seeding and media perfusion, culturing single cells obtained after disassociation of mature HIOs. The gut compartment was evaluated through immunostaining and single-cell RNA sequencing. The gut-on-a-chip model was exposed to inflammatory stimuli (i.e., IFN-γ, TNF-α cytokines, or *E. coli* lysate) through the perfusable lumen to assess intestinal barrier functionality. The production of inflammatory cytokines was analyzed by LEGENDplex and flow cytometry.

Results and conclusions

The gut compartment revealed diverse intestinal cell populations on the chip. We observed that the inflammatory stimuli resulted in increased permeability of the epithelial barrier and upregulation of inflammatory cytokines (e.g., IL-8, IL-6, IL-10). Furthermore, the perfusable lumen exhibited a significant loss of epithelial structures and reduced lateral protein intensity (i.e., EpCAM, Zo-1) after inflammation. These results demonstrate the efficacy of our system in recreating responses to inflammatory processes *in vitro*, using both human-derived lymphoid and gut organoids in a fully synthetic and perfusable hydrogel platform. This gut-on-a-chip platform can be used to study inflammatory syndromes and mechanisms.

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NEW GENERATION OF IODINATED EMBOLIC LIQUID: A SUCCESS CASE IN THE LABORATORY-TO-CLINIC TRANSLATION OF POLYMERIC MEDICAL DEVICES.

Raquel Palao Suay[1,2], Silvia Alujas [3], Sofia Valle [3], Alex Gómez Castel[3], María Molina Crisol[3], Luis Duocastella Codina[3], María Rosa Aguilar De Armas[1,2]

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Introduction

Endovascular embolization is a minimally invasive surgical procedure for the treatment of vascular malformations and hypervascular tumors. Liquid embolic materials that solidify *in situ* are increasingly being explored due to their ability to deeply penetrate vasculature. Currently used precipitating liquids embolic agents, such as Onyx^{TM} and PHIL$^{®}$, have some limitations (visualization, artefacts, microcatheter entrapment…) [1]. This work aims the customization of a new liquid polymeric formulation for clinic applications, focusing on the improvement of imaging properties, efficacy, safety and compatibility with microcatheters.

Methodology

Methacrylic derivatives of 2,3,5-triiodobenzoic acid were synthesized by its conjugation with 2-hydroxylethyl methacrylate (M3I), mono-2-(methacryloyloxy) ethyl succinate (M3I$_{ext}$) and poly(ethylene glycol) methacrylate (P3I) using *N,N'-Dicyclohexylcarbodiimide* as coupling agent . These iodinated monomers were polymerized with other hydrophilic monomers (R$_1$ or/and R$_2$, such as HEMA) by radical polymerization (*figure 1 [A]*). The properties of these polymers (molecular weight, T$_g$, logP…) were compared to analyze the influence of the length chain of the iodinated monomers and to achieve the greatest embolization potential. Finally, these polymeric formulations were evaluated in the rete mirabile and kidney porcine serving as an endovascular embolization model [2].

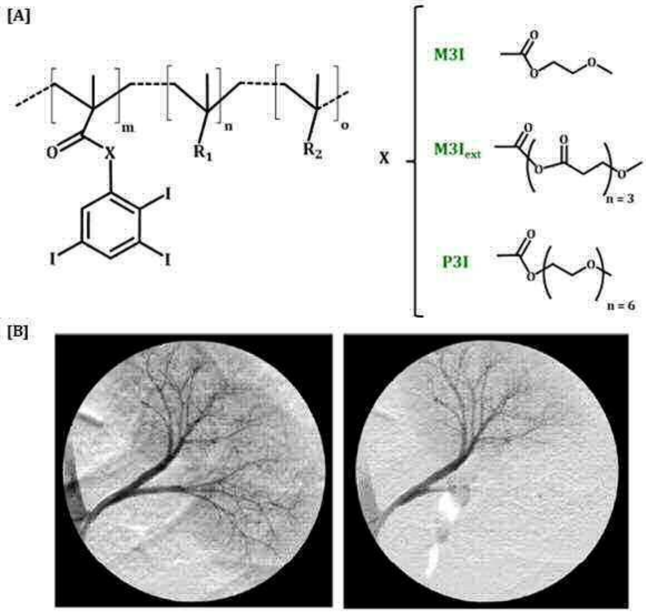

Figure 1. [A] Chemical structure of polymers based on iodinated monomers with different chain length. [B] Angiographic images of the kidney of a porcine embolization model before (left) and after (right) embolization with iodinated polymeric formulation dissolved in DMSO. The tinted areas correspond to non-embolized territories.

Results and conclusions

Different iodinated polymers were successfully synthesized and characterized. In particular, as the chain length of iodinated monomer increased, polymers more hydrophilic and with lower T_g were obtained, giving rise to more flexible coagulated products. However, the increase of chain length of these iodinated monomers significantly comprised the *in vivo* visualization.

Preclinical embolization model allowed to compare the technical characteristics of the different polymeric formulations, optimizing conditions to successfully achieve the complete vascularization of the porcine organs with total control of the injection, minimal reflux and without microcatheter entrapment (*figure 1 [B]*). The endovascular embolization model demonstrated the effectiveness of the iodinated polymer formulations in DMSO, overcoming the limitations of ONYX and PHIL. This research has laid the foundation for the development of new embolic iodinate liquid that has currently involved in clinical trials to evaluate its safety and efficacy [2].

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MULTIFUNCTIONAL CURCUMIN-BASED POLYMER COATING: A PROMISING PLATFORM AGAINST BACTERIA, INFLAMMATION AND COAGULATION

Julia Sánchez Bodón, Isabel Moreno Benítez, Leyre Pérez Álvarez, Antonio Veloso Fernández, Leire Ruiz Rubio, José Luis Vilas Vilela

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Introduction

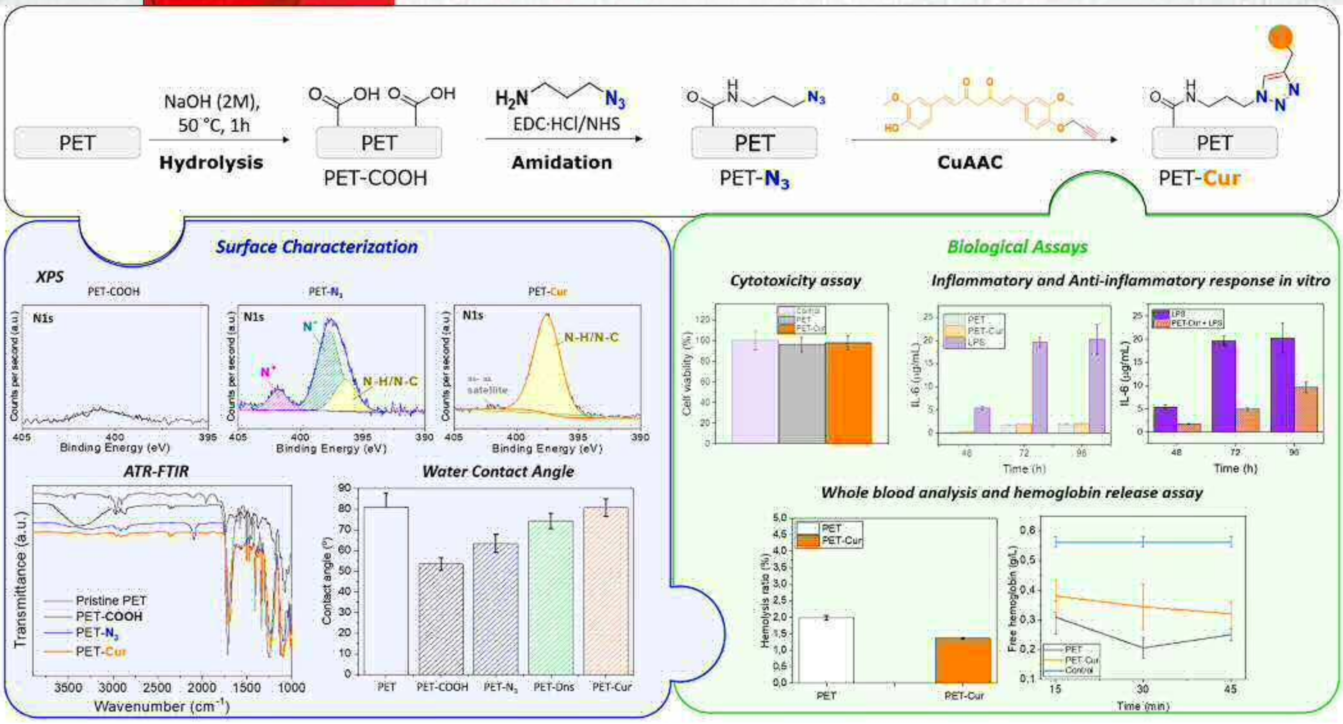
Polymers have advanced medical devices and implants, improving patient outcomes with their biocompatibility, flexibility, and durability.1 However, implant-associated infections (IAIs) remain a challenge, requiring innovative strategies to combat bacterial contamination and inflammation for long-term implant success.2 Among the vast array of methodologies to avoid these risks, Click Chemistry, particularly the Copper (I)-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) reaction, enables precise surface functionalization while preserving the bulk properties of materials. This versatile method enhances polymer antimicrobial and anti-inflammatory properties.3,4 This study focuses on the immobilization of a curcumin derivative, a natural polyphenol, onto polyethylene terephthalate (PET) surfaces, aiming to combat bacterial adhesion, inflammation, and coagulation commonly associated with medical.

Methodology

PET surfaces were treated with NaOH (2M) and reacted with 3-azidopropan-1-amine (2 mmol) under ED·HCl/NHS (0.13 mmol) conditions for 24 h at room temperature. After, previously synthesized curcumin derivative (1 mmol) was reacted with the alkyne groups on PET surfaces under $\mathrm{CuSO4\cdot 5H2O}$/sodium ascorbate (0.13 mmol) for 24 h at room temperature.

Results and conclusions

Surface chemical modifications were meticulously characterized using various techniques. UV-Vis confirmed 64% amidation with propargylamine. XPS detected different nitrogen species before and after click reaction, ATR-FTIR showed R-N=N+=N- new bands, and SEM with contact angle measurements indicated changes in wettability and roughness, verifying curcumin derivative conjugation. Biological assays demonstrated biocompatibility and therapeutic efficacy. Cytotoxicity assessments showed no adverse effects on cell viability, while inflammation tests revealed a significant reduction in IL-6 levels, indicating reduced inflammatory responses. Antibacterial assays confirmed strong inhibitory effects against Gram-positive and Gram-negative bacteria, showcasing the antimicrobial properties of curcumin-immobilized PET surfaces. Hemocompatibility assessments, including hemolysis rate analysis and whole blood clotting assays, confirmed the antithrombogenic nature of PET-Cur surfaces. Overall, this study uses click chemistry to bioconjugate curcumin onto PET, enhancing its biomedical applications and overcoming curcumin poor bioavailability. The integration of curcumin derivatives onto polymer surfaces represents a promising strategy to enhance the biocompatibility and therapeutic functionality of medical implants, offering new avenues for combating implant-associated infections and promoting patient well-being



PET surface preactivation and curcumin bioconjugation scheme. Nitrogen high resolution XPS spectra, ATR-FTIR spectra and Water Contact Angle value of functionalized PET surfaces. Biological assays perfomed on obtained PET-Curcumin surfaces.

Acknowledgments and

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SUSTAINABLE POLYLACTIC ACID (PLA)/SARGASSUM BIOPLASTICS PREPARED USING SBS. EFFECT OF SARGASSUM CONTENT ON MORPHOLOGY AND MECHANICAL PROPERTIES

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Introduction

Bioplastics are already a sustainable alternative to traditional plastics. Among them, polylactic acid (PLA) is one of the most promising biodegradable polymers. Many researchers are exploring new possibilities to develop sustainable and innovative bioplastics to meet the growing demand for more sustainable products [1, 2]. In this sense, the modification of bioplastics with natural materials, such as those derived from algae, is of special interest. An example can be the incorporation of *sargassum*, a type of seaweed, into bioplastics such as PLA to create composite materials with improved properties and performance such as the slow release of fertilizers, thus addressing multiple environmental and functional objectives. [3]. This study focuses on the preparation of commercial PLA fibrillar polymeric materials, filled with sargassum particles, using *Solution Blow Spinning.* Over the past years, the Group of Polymer Composite Materials and Interphases (GMCPI) of the UC3M has been investigating on the production of fibrillar polymers and polymer nanocomposite materials using Solution Blow Spinning (SBS) [4].

Methodology

PLA-based composite materials filled with sargassum particles were prepared using SBS. The effect of the concentration of sargassum on the final material was studied, preparing materials with concentrations of 0.0, 0.5, 1.0, 2.0, 3.0 and 5.0 % (% by weight), with the concentration of the PLA solution in dichloromethane of 10 % (%, g/mL)

Results and conclusions

Morphological and structural characterization was carried out as preliminary studies to finally understand the performance of materials in terms of active components release. Figure 1 shows an example of the fibrillar materials obtained for the PLA-based system filled with 1% *Sargassum* (%wt). Mechanical characterization of the materials was carried out by means of uniaxial tensile tests, and the properties obtained were discussed in terms of the structural, morphological and thermal analyses.

Figure 1. SEM image of the PLA - 1% Sargassum solution blow spun sample

Acknowledgments and

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A HIGHLY OXYGENATED BIOMIMETIC HYDROGEL WITH A PREDICTIVE OXYGEN DURABILITY MODEL TO ENHANCE POST-TRANSPLANTION CELLULAR SURVIVAL

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Introduction

Pancreatic islet transplantation aims to reverse type 1 diabetes by restoring the production of insulin. Post-transplantation islet survival is inherently limited by the lack of suitable support extracellular matrix (ECM) and hypoxia, which is aggravated when using macroencapsulation devices. Graft failure can be overcome by cell encapsulation in highly oxygenated biomaterials, like Oxygel, able to provide oxygen and ECM-support. For its optimal performance, oxygen payload, release kinetics and their interaction with cells need to be characterized. Prediction of the oxygen durability after cell encapsulation would be critical for the design of oxygenated hydrogel-loaded macroencapsulation devices for cell transplantation.

Methodology

Oxygel was formulated by the shear mixing of Hyaluronic acid hydrogel with a Perfluorodecalin/lipoid nanoemulsion and oxygenated by flushing oxygen simultaneously to gel infusion using a customized set-up. Mechanical properties were characterized by Rheometry. Post-oxygenation oxygen levels of Oxygel were monitored by needle-type oxygen microsensors. Oxygen diffusion coefficient (Dv) was estimated by the experimental fitting of oxygen release profiles to a Fickian diffusion model. An oxygen durability model was developed, considering gel formulation and cell metabolism features, and used with different cell lines using experimentally recorded (Seahorse analyzer) or bibliographic OCR-values. For model validation INS-1E cells were encapsulated in oxygenated-oxygel within macroencapsulation devices and oxygen was monitored, comparing experimental oxygen-stabilization with modelled oxygen-durability times. Cell viability after encapsulation was determined by Live/Dead staining

Results and conclusions

Oxygel was developed as an ECM-based injectable hydrogel with high oxygen-loading capacity aimed to enhance cell survival in macroencapsulation devices (Viability >75% after encapsulation in Oxygel). High post-oxygenation oxygen tension was achieved in Oxygel and PFD emulsion (65-85 % oxygen-saturation). Acellular Oxygel released oxygen for 90 h until stabilization at atmospheric levels, presenting a 14.5-times smaller Dv than PBS, explained by the multiple diffusional barriers present in Oxygel. These release kinetics are beneficial as high oxygen payloads will be readily available for cell consumption prolongedly. The effect of cell consumption in the oxygen levels after encapsulation of INS-1E was demonstrated, showing lower oxygen stabilization times upon cell density increase. Correlations between the predicted oxygen durability and the experimental oxygen stabilization times were found, demonstating the accuracy of the model. This model demonstrates the potential impact of oxygen levels, cell density and OCR for the graft success, and could be applied to any oxygenated biomaterial used as a cell scaffold, with a particular focus on those intended for cell transplantation applications.

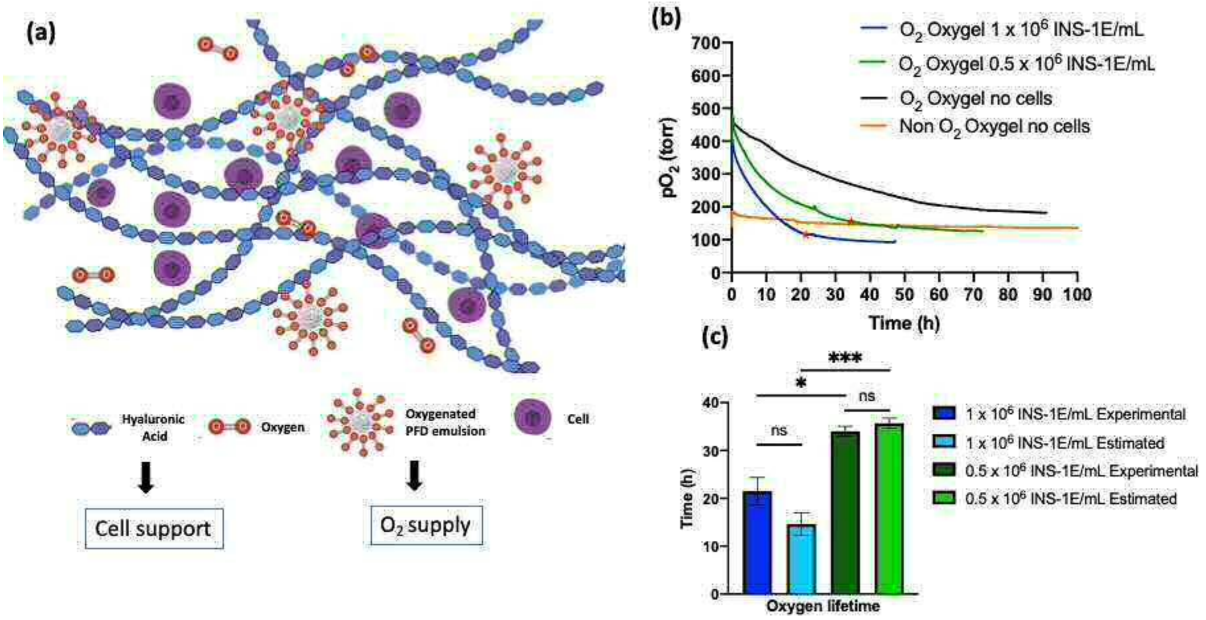

Figure 1. (a) Schematic representing Oxygel, a biomaterial based on physically crosslinked hyaluronic acid hydrogels and Perfluorocarbon/lipoid nanoemulsions, design to provide cell suport and oxygen supply, respectively. (b) Oxygen profiles of oxygenated Oxygel containing 1 million INS-1E/mL, 0.5 million INS-1E/mL, no cells, and non-oxygenated gel (n = 4). (c) Comparison of model predicted oxygen durability and experimentally stabilization times of cell containing Oxygel (n=4); ns ($p > 0.05$), *$p < 0.05$, ***$p < 0.001$.

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DEGRADABLE HYDROGEL ANTIFOULING COATINGS DERIVED FROM LACTIC ACID-BASED SOLVENT

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Introduction

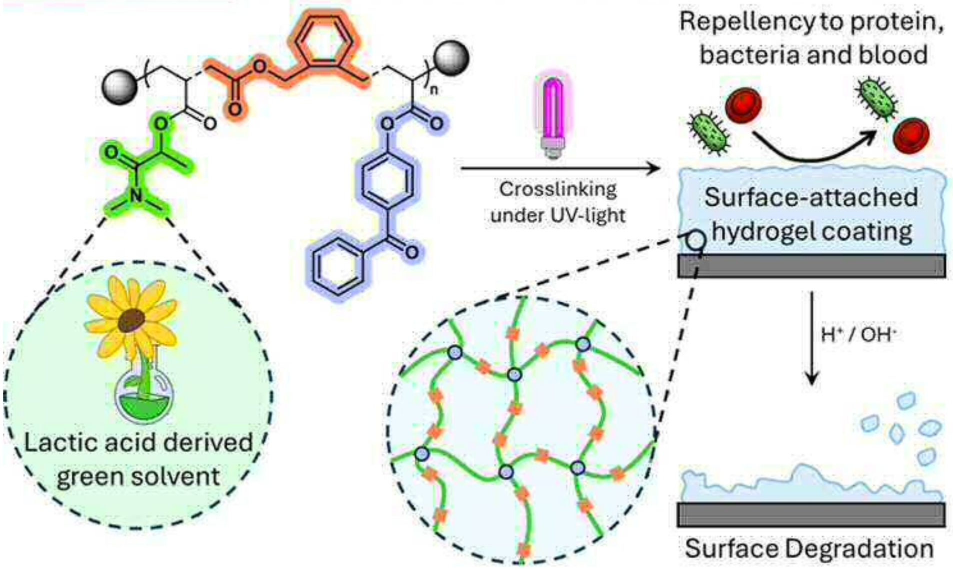
N,N-Dimethyl lactamide (DML) is a green solvent derived from lactic acid, known for its excellent sustainability profile and being free of hazard labels. Our group has proposed its chemical transformation into an acrylic monomer, N,N-dimethyl lactamide acrylate (DMLA), for radical polymerization to explore value-added applications of polymer structures incorporating poly(DMLA) building block. Poly(DMLA) properties, such as water solubility and non-toxicity, encouraged us to investigate coating technologies for medical devices. Recently, we demonstrated that poly(DMLA) brushes effectively block protein adsorption, bacterial colonization, and blood clot formation, matching the performance of well-established fossil-based polymer brushes. In this communication, we report on the synthesis, characterization, and device application of ultra-thin hydrogel antifouling coatings with improved sustainability consisting of up to 95% poly(DMLA). The remaining portion comprises functional monomers such as benzophenone acrylate (BP), to allow cross-linking, and a cyclic ketene acetal (CKA) monomer. The latter enables the coatings to be endowed with degradability by introducing hydrolysable ester bonds along the acrylic backbone.

Methodology

CKA was terpolymerized with DMLA and BP in a controlled manner by RAFT polymerization. Surface-attached hydrogel coatings were prepared by in situ cross-linking of polymers deposited from aqueous solutions. These coatings were characterized using ellipsometry, XPS, and AFM. Their protein fouling and blood clotting properties were analyzed by SPR and FESEM, respectively.

Results and conclusions

CKA was successfully terpolymerized with DMLA and BPA to deliver hydrophilic polymers with Mn up to 20,000 g mol–1 and $Đ < 1.75$, despite its low reactivity ratio compared to the acrylic monomers. Polymers with variable CKA content, ranging from 0 to 24%, exhibited thermoresponsive behavior in aqueous solution, with cloud point temperatures (Tcp) from 100 to 24.2 ºC, respectively. Moreover, they degraded faster in acidic or basic conditions compared to poly(DMLA), while were stable under physiological conditions. Surface-attached hydrogels coatings applied to hernia meshes, central venous catheters, and extracorporeal membrane oxygenators exhibited remarkable antifouling behavior, prevention of bacterial attachment, protection against thrombus and fast degradability under acidic and basic environments.



Surface-attached hydrogels coating were prepared by crosslinking terpolymers containing lactic acid derived DMLA monomer and applied to medical devices to explore its repellency to proteins, bacteria and blood.

Acknowledgments

This work was supported by MICIU/AEI/10.13039/501100011033 and ESF+ through project PID2020-114098RB-I00 (to G.L. and M.G.), a FPI grant PRE2021-100387 (to M.P.) and the Serra Hunter Programme of the Government of Catalonia (to G.L.).

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FIBRAS ELECTROHILADAS AVANZADAS DOPADAS CON NANOPARTÍCULAS DE COBRE PARA LA ELIMINACIÓN DE PESTICIDAS EN AGUA

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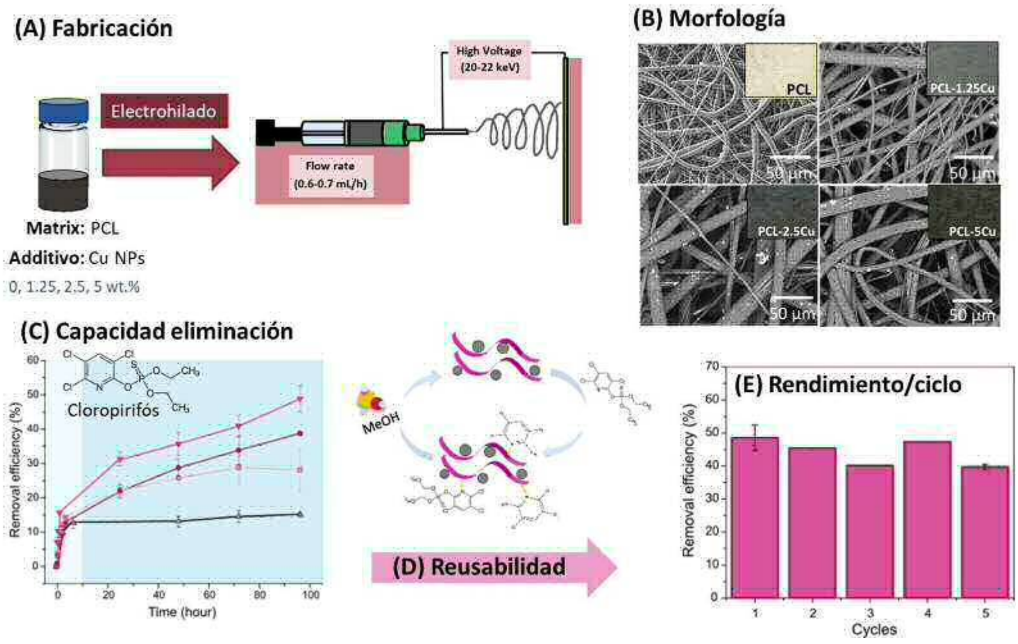
Introducción

La falta de restricciones y control de la regulación de pesticidas ha dado lugar importantes desastres ecológicos y efectos nocivos en la salud de las personas. En 2020, la Unión Europea prohibió el "Cloropirifós", el agroquímico más empleado en España desde hace 50 años debido a su gran toxicidad y estabilidad. Su exposición en pequeñas concentraciones (0.1-0.5 µg/L) puede generar importantes problemas de salud en el sistema nervioso, respiratorio y cardiovascular. Por tanto, es necesario encontrar métodos eficaces para eliminar este pesticida que se encuentra actualmente acumulado en el ambiente. Algunas nanopartículas metálicas, como las de cobre, han demostrado una gran capacidad de degradar este pesticida. Sin embargo, la aplicabilidad del cobre está altamente limitada por su baja estabilidad, ya que se oxida rápidamente perdiendo eficacia, y su liberación en el ambiente puede generar efectos nocivos y deben ser regulados. La introducción de estas nanopartículas en una matriz polimérica podría ser una potencial solución a este problema.

Metodología

Los materiales se han fabricado mediante el electrohilado de una disolución con PCL y nanopartículas de cobre. Las características morfológicas y químicas de las fibras se han analizado con SEM-EDS, XPS, Raman e infrarrojo. La capacidad y proceso de degradación del pesticida se ha analizado utilizando UV-Vis y UPLC-MS-TOF



Resultados y Conclusiones

Las fibras electrohiladas compuestas de PCL dopado con nanopartículas de cobre uniformemente distribuidas y unidas a la superficie fabricadas han mostrado una excelente capacidad de reducir la concentración del pesticida en agua en alrededor 50 % después de un ciclo de 96 horas. Cabe destacar que la actividad catalítica del material es independiente de las condiciones ambientales de luz, lo que asegura su efectividad en aguas en aguas subterráneas. Además, este material presenta una gran reusabilidad, manteniendo el mismo rendimiento del proceso, al menos, 5 ciclos después de un proceso de lavado con metanol, alcanzando una eliminación de 100 mg/mL de pesticida. Estas características se han atribuido a la capacidad del PCL de proteger a las nanopartículas de cobre frente a la oxidación y a su liberación. Por tanto, este trabajo presenta un material compuesto polimérico con un gran valor para el tratamiento y remediación de aguas contaminadas.

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ADVANCEMENTS IN NOX ABATEMENT TECHNIQUES USING IMPREGNATED POROUS BIOPOLYMERIC AEROGEL

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Introduction

NOx is a hazardous gas need to avoid. One way to minimize the exposition is to use air filters. The cost for air filters is due to the production of the filters but also to produce filter equipment and for the needed electricity. To minimize the energy consumption, it is very important to minimize the pressure drop over the filter. For the filter it's important to have sustainable raw material and that the reactivity is high so that the filter will hold for a long period, and after use that the filter can be either reused or disposed of in a good way

Methodology

The trials at IVL used the equipment with gas tubes and sensors as described in figure includes gas tube, filter holder, measurement system of water and NOx content, measuring NO2 and NO. For tests a cellulose aerogel impregnated with amines and hemoglobin, Ca-ion Crosslinked Aerogels (Ca-AG) were created by mixing carboxymethylated cellulose nanofiber gel with $CaCl_2$, freezing, solvent exchange in acetone, and drying. Hemoglobin-Containing MOF Functionalized Aerogels involved immersing aerogels in zinc acetate, adding hemoglobin to HMIM solution, stirring, washing, soaking in ethanol, and drying. Additionally, a gluten-based polymer impregnated with polyethyleneimine was tested.

Results and conclusions

A gas mixture of 8 ppm NO2 was prepared by mixing 3.0 ml/min of a 2000 ppm NO2 gas stream with 750 ml/min of dry room air. The NOx adsorption for aerogel samples of 0.24 g (5.0 cm^3) aerogel doped with ZIF and hemoglobin, 0.32 g (5.6 cm^3) aerogel doped with ZIF, and 0.26 g (9.7 cm^3) undoped aerogel were now tested. Results are presented in attachment. The results show a clear advantage for the Aerogel doped with hemoglobin and ZIF giving a doubled uptake compared with ZIF only. Also, initial test on a gluten polymer impregnated with amines shows promising results, se figure.

Acknowledgments

This work was performed in the Swedish Mistra program Terraclean focusing on developing novel adsorbents

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POLYMER-INORGANIC NANOPARTICLE HYBRID TANDEMS AS SELECTIVE METAL SENSORS

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Introduction

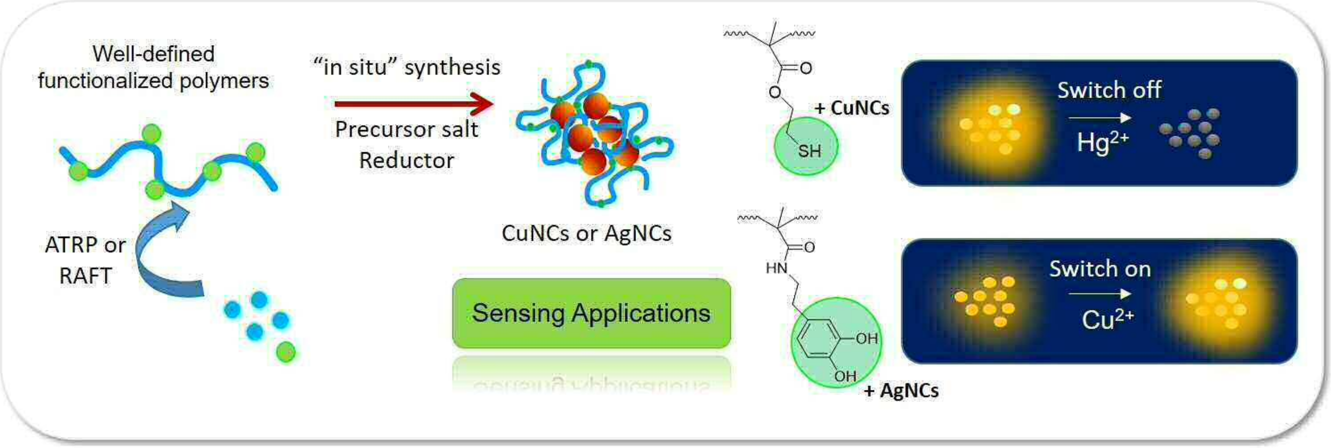
In recent years, significant progress has been made in developing new nanostructured and multifunctional materials by combining polymers with inorganic nanoparticles. This research is crucial due to its potential to address pressing challenges in fields such as healthcare, energy, sustainability, and environmental protection. Among inorganic nanoparticles, luminescent nanoparticles like copper and silver nanoclusters (NCs) stand out for their ability, when combined with polymers, to create a diverse range of nanohybrids with intriguing properties. These metallic nanoclusters offer distinct advantages over other luminescent nanoparticles due to their cost-effectiveness, biocompatibility, and exceptional photophysical properties when confined to sub-nanometer scales. In addition to their antimicrobial properties, they hold promise for novel therapeutic and sensing applications. Polymers with functional groups capable of binding to inorganic nanoparticles allow for the formation of unique hybrids. Controlled living radical polymerization (CLRP) allows the synthesis of macromolecules with precisely defined functionalities and architectures, opening the way to obtaining new hybrid nanostructures [1].

Methodology

We have synthesized polymers containing protected thiol and catechol functionalities using CLRP techniques such as Atom Transfer Radical Polymerization (ATRP) [2] and Reversible Addition-Fragmentation Chain Transfer (RAFT). Furthermore, we have applied the Polymerization-Induced Self-Assembly (PISA) technique to fabricate polymer nano-objects adorned with functional groups [3]. These versatile polymers have been used as anchor points, reducing agents, and protectors, facilitating the nanostructured assembly of in-situ-generated nanohybrids.

Results and conclusions

The luminescent properties of nanohybrids synthesized using block copolymer nano-objects obtained via Polymerization-Induced Self-Assembly (PISA) exhibit significant differences compared to those synthesized with statistical copolymers. Our research has also delved into the influence of these polymers on the photoluminescence of copper and silver NCs synthesized in aqueous media. Furthermore, we have explored their potential for detecting metal ions such as mercury (Hg^{2+}) and copper (Cu^{2+}) in aqueous environments. This detection is facilitated by fluorescence quenching ("switch-off") or the opposite effect ("switch-on") when NCs are in the presence of specific metals. These findings highlight their significant relevance in environmental sensing applications.



Acknowledgments

The Ministerio de Ciencia, Innovación y Universidades (MCIU), Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, UE) through the Project PGC2022-137762NB-I00 are acknowledged.

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EPOXIDIZED SOYBEAN OIL BASED THERMOSET AS MATRIX FOR FUNCTIONAL MATERIALS

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Introduction

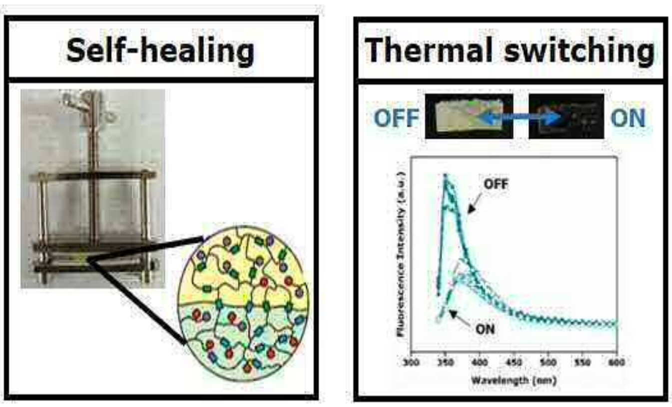
Nowadays, the replacing fossil based materials is still emergency subject since their biobased analogous, in general, have similar properties and processing conditions, however the biobased-derived building blocks are chemically different from fossil derivative ones leading to materials with different final properties.

Methodology

Curing process conditions were chosen following DSC. Chemical reaction between oxirane group of ESO resin and carboxylic acid group of CA was confirmed using FTIR. Thermal properties of investigated thermosets were studied using DSC and TGA. Moreover, DMA was employed in the case of nanocomposites. Morphology of investigated thermosets was studied by AFM. Thermo-responsive properties were analyzed using a spectrophotometer and self-healing properties by OM. UV-vis was used to study optical properties.

Results and conclusions

This investigation work deals with the design of thermoset materials based on epoxidized soybean oil (ESO) cured with citric acid (CA). Two different ESO/CA thermoset based materials were prepared and characterized. On the one hand, ESO/CA thermosetting system was modified with different content of low molecular weight 4′-(hexyloxy)-4-biphenyl-carbonitrile (HOBC) nematic liquid crystal. This modification allows to design thermoset materials with thermo-responsive properties of HOBC liquid crystals able to switch from highly opaque (OFF state) to highly transparent state (ON state) by applying temperature. It was proved that the thermo-responsive properties depend strongly on HOBC nematic liquid crystal content. Moreover, this switching behavior is reversible even after five heating/curing cycles and can be repeated without any sample deterioration. Additionally, it was also showed that the addition of a small amount of poly(ε-caprolactone-b-lactide) block copolymer (CLLA) shorter switching time and sharper switching temperature range. This behaviour offered thermosetting systems with faster recovery rate if compared with HOBC-EPE/CA thermosetting system. On the other hand, investigated thermoset materials maintained the heat driven self-healing properties of the ESO/CA matrix. On the other hand, the same ESO/CA thermoset was used as matrix for dispersion of sol-gel synthesized TiO2 nanoparticles. Obtained TiO2-ESO/CA nanocomposites maintained final properties of the ESO/CA matrix and showed UV-shielding properties of TiO2 nanoparticles.



Self-healing and thermo-responsive properties of ESO/CA thermoset based materials.

Acknowledgments and

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POLYMER BASED THERMOELECTRIC MATERIALS

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Introduction

Thermoelectric generators are able to convert temperature gradients into electric power due to the Seebeck effect. The efficiency themormoelectric materials is given the dimensionless figure of merit ZT ($ZT=S2\sigma T/\kappa$ where S, σ and κ are the Seebeck coefficient, the electrical and thermal conductivities, respectively). Traditionally, Inorganic materials based on bismuth telluride have dominated thermoelectric applications. However, during last decade organic based materials such as: conducting polymers and carbon based nanoscoposites have become very promising in terms of efficiency reaching ZT values comparable to classic thermometric materials at room temperature. Double wall carbon nanotubes (DWCNTs) combined with conducting polymers are widely used for producing thermoelectric nanocomposties due to their good electric properties. Layer-by-layer (LbL) method showed excellent results for the preparation of carbon nanocoposites with a remarkable thermoelectric efficiency. Additionally, the discovery of electrolytes with significantly larger ionic Seebeck coefficients has sparked interest in ionic thermoelectric systems, potentially revolutionizing thermoelectric material production from sustainable sources. While conventional thermoelectric applications rely on electron or hole thermodiffusion, ionic materials induce thermoelectric effects through ion thermodiffusion. Recently, ionic thermoelectric platforms based on hydrogels have emerged as promising candidates for high-efficiency materials.

Methodology

Preparation of the carbon based nanocoposites. The PEDOT:NPs and Polypyrrole:NPS /DWNT-PEDOT:PSS thin films were fabricated by using a programmable dip-coater robot. The substrate was immersed in the positively charged NPs solution (0.1 wt%) and then into the DWNT-PEDOT:PSS solution followed by rinsing stesp to complete one bilayer (BL) of conductive polymer NPs/DWNT-PEDOT:PSS. Subsequent cycles were repeated. Preparation of the lignin based hydroles. Lignin was initially dissolved in a NaOH solution. The solutions were used to prepare several formulations using different crosslinkiers such as: PEGDGE and Epichlorohydrin. Finally, the misture was poured into dishes until completion the crosslinking (24 h).

Results and conclusions

The samples were characterised from the structural, morphological and the thermoelectric point of view. A 20 bilayer PEDOT:NPs/DWNT-PEDOT:PSS (~2.1 μm thick) exhibited an electrical conductivity of 744 S cm−1 and Seebeck coefficient of 83 μV K−1 achieving a PF of 512 μW m−1 K−2 at room temperature. For the case of the polypyrrole based films the electrical conductivity (183.2 S/cm) and Seebeck coefficient (115 μV/K), resulting in a remarkable power factor of 242.2 μW/m·K2. The ionic thermoelectric materials based on lignin hydrogels showed a very high value of Sebeck coefficient in the range of 10-30 mV K−1 that are translated in iZT values higher than 3.5.

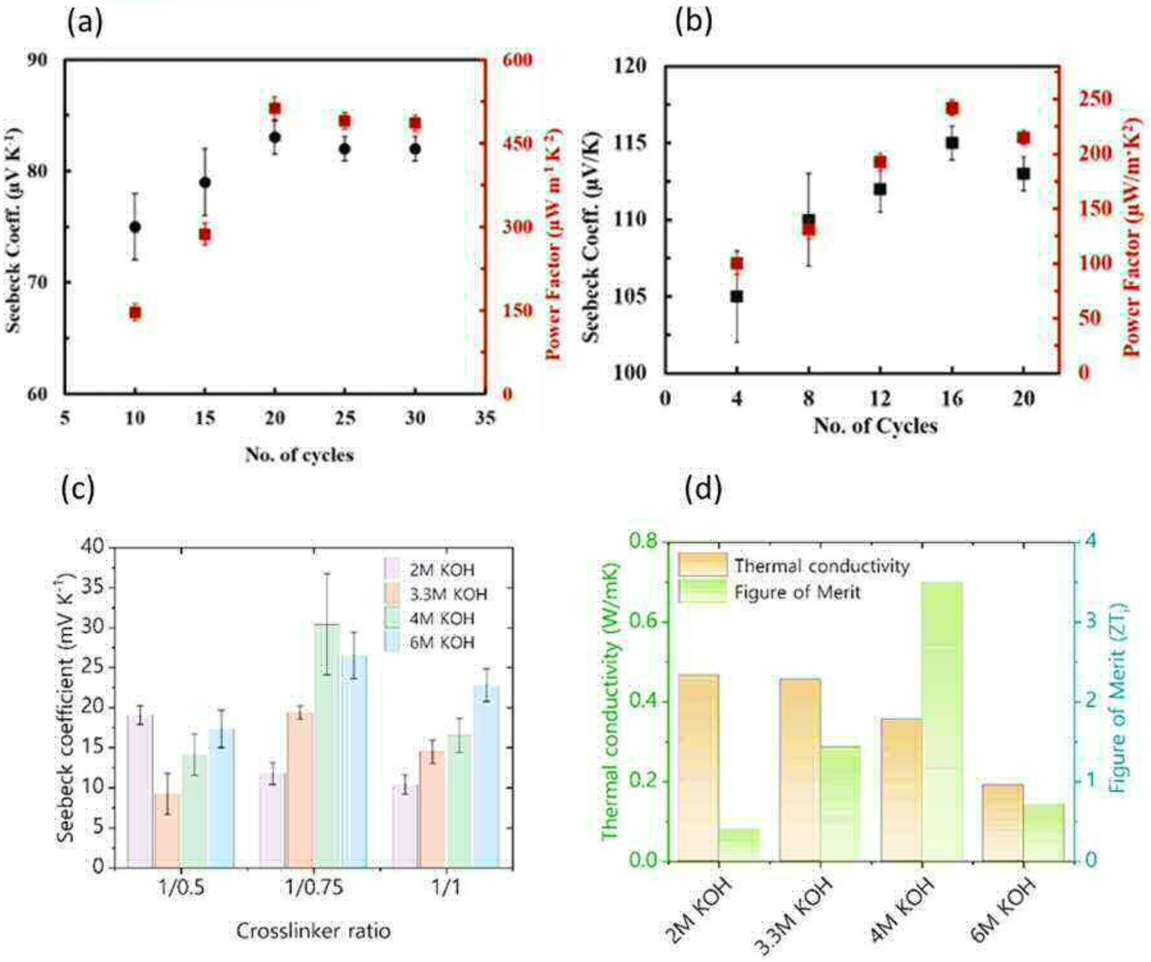

Figure 1 (a) Power factor of PEDOT/DWCNTs composites, (b) Power factor of Polypyrrole/DWCNTs composite, (c) and (d) themoelectric properites of lignin based hydrogels

Acknowledgments

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SUSTAINABLE LIGNIN-BASED HYDROGELS: SYNTHESIS AND FUNCTIONALIZATION OF IONIC THERMOELECTRIC MATERIALS

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Introduction

Fossil fuel depletion and climate disasters have sparked interest in capturing low-grade heat and converting it into electricity to address the energy crisis. Ionic thermoelectric materials (i-TEs) have garnered significant attention due to their unique properties such as excellent Seebeck coefficients, low thermal conductivity, and high electrical conductivity. Unlike conventional thermoelectric materials that rely on electron/holes transport, i-TEs utilize ions as charge carriers, enabling the conversion of heat into electricity. Research has focused on hydrogels for developing eco-friendly i-TE materials. Hydrogels are three-dimensional, highly versatile materials with tunable mechanical properties. They are capable of holding large amounts of water and allowing the movement of ions within the material. Recently, lignin presents a promising sustainable alternative for the development of i-TE materials. Lignin has a highly branched aromatic structure and functional groups that boast high reactivity. This unique combination makes lignin an ideal candidate for designing high performance lignin-based hydrogels. [1]

Methodology

This study focuses on the synthesis of lignin-based hydrogels through chemical crosslinking [1] and then functionalization with amine group. For the functionalization, this research utilizes a green synthesis method composed of NaOH-water, eliminating the need for organic solvents [2] as illustrated in Figure 1. The amination of crosslinked hydrogel with 2-Chloroethylamine hydrochloride (CEH) was greatly affected by the concentration of CEH and reaction condition.

Results and conclusions

The synthesized crosslinked hydrogels exhibit lower value of Seebeck coefficient (1.614 mVK-1), ionic conductivity (4.04 mScm-1) and thermal conductivity (0.22 Wm-1. K), that give rise to small value of ionic figure of merit (0.0013). However, functionalized hydrogels result in high negative Seebeck coefficient (-7.873 mVK-1), superior ionic conductivity (6.09 mScm-1) and thermal conductivity (0.184 Wm-1. K) that leads to enhance ionic figure of merit 0.056 as compared to crosslinked hydrogel, making them suitable candidates for various applications such as energy harvesting, waste heat recovery and thermal management systems.

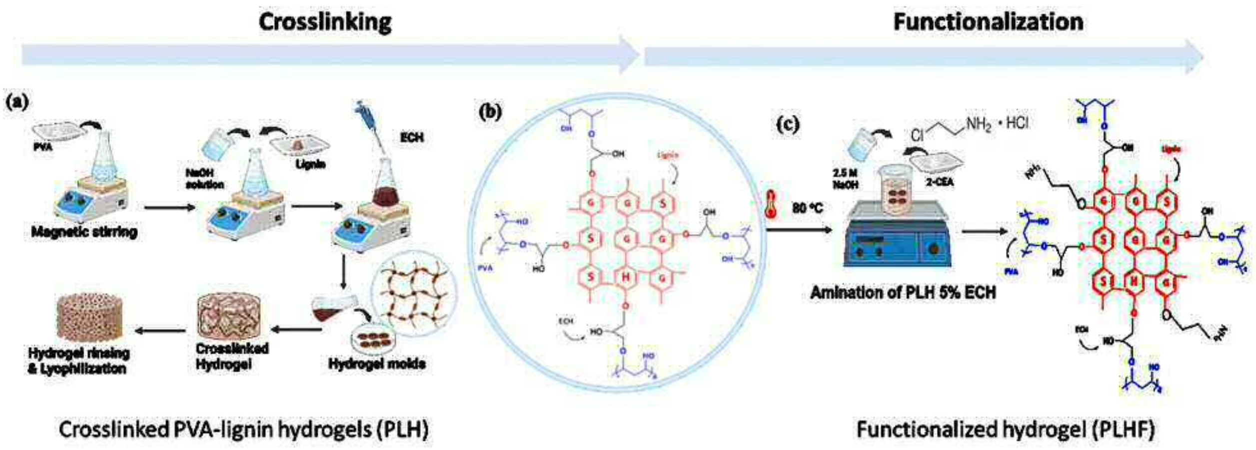

Fig 1: Schematic representation for synthesis of hydrogels

Acknowledgments

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NANOENCAPSULATION OF ALKANES FOR THERMALLY ACTIVE POLYMER COATINGS

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Introduction

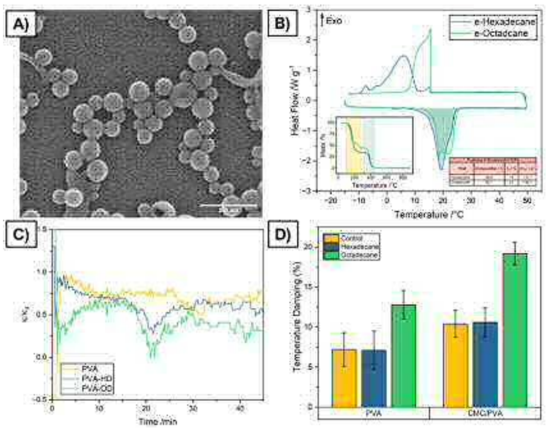
The intermittence of heat as a renewable energy source has been approached by their storage using the so-called phase change materials (PCMs). New technologies for reducing the energetic demand of buildings can be developed by incorporating PCMs in construction elements [1, 2]. However, this requires the encapsulation of the PCM to prevent its leakage and undesired interactions with the environment [2]. Here, we present different strategies to encapsulate organic PCMs, namely alkanes, within polymer nanocapsules and their application in thermally active polymer coatings.

Methodology

Miniemulsion-based strategies were conducted, following either a chemical or a physical method, by mixing the alkane and the shell precursor for its subsequent dispersion in an aqueous phase. Miniemulsions were obtained after a high-shear homogenization for the later formation of capsules under appropriate conditions. First, polyaniline and polystyrene capsules were synthesized via free-radical polymerization. Polyurethane nanoparticles were obtained by the polycondensation of an isocyanate and poly(ethylene glycol). Lignin shells were formed through emulsion-solvent evaporation. The nanocapsules were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Finally, the alkanes encapsulated in polystyrene were incorporated into polymer coatings in a home-made setup under controlled heating conditions.

Results and conclusions

The appropriate formation of nanocapsules was confirmed by SEM (figure 1.A). The thermal events observed in the DSC thermograms (figure 1.B) were associated with the phase transitions of the alkanes. The differences in the stored thermal energy between the different systems were correlated with the different loads of PCM determined by TGA. The thermoregulation capacity was assessed by comparing the relative heat conduction (figure 1.C) and the temperature damping (figure 1.D) of coated glasses placed as a rigid frontier between two compartments. The thermal conductivity of the films was enhanced after the addition of PCMs due to the heat consumption in the phase transition. As a result, their temperature damping increased proving the potential use of these materials as thermally active coatings for glass-based construction elements.



Morphologic (A) and thermal characterization (B) of nanoencapsulated alkanes. Temperature damping (C) and relative heat conductivity (D) of thermally active polymer coatings prepared with nanoencapsulated alkanes.

Acknowledgments

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DEVELOPMENT OF LIGNOSULFONATE BLENDS FOR CARBON PRECURSORS

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Introduction

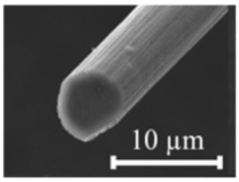
Carbon materials are mostly derived from poly(acrilonitrile) (PAN) due to its high carbon yield. The processability of PAN is limited to wet spinning, where the polymer is dissolved in an organic solvent before being injected in a coagulation bath and stretched into a fibre shape. This process is detrimental to the environment, due to the use of organic solvents (DMF, DMAc) and the fossil-based monomer. Lignosulfonate (LS) is a suitable replacement for PAN as a carbon precursor. It is a by-product from the pulp industry, with production rates close to one million tonnes per year. LS has an aromatic structure and sulfonate groups, which allow for high solubility in water. This work investigates the wet-spinnability of LS using poly(vinyl alcohol), PVA as a water soluble polymer binder.

Methodology

Ammonium LS was supplied by Borregard (Norway). All materials were purchased from Sigma Aldrich. The dope solution was prepared by dissolving PVA in deionised water under stirring at 90oC before adding LS. Various LS/PVA compositions and dope concentrations were prepared. The dope was injected into a coagulation bath using a custom-made set up. The fibres produced were winded on a spool before being prepared for heat treatment (10oC per min to 1000oC, in nitrogen). All material was characterised using FTIR, XRD, Raman and TGA.

Results and conclusions

Precursor material could be wet spun between 50 to 90% LS content. The influence of the dope solution and coagulation bath on the quality of the fibres obtained was investigated. Miscibility theory was used to evaluate the quality of the LS/PVA polymeric blends.



Acknowledgments and References

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CORRELATION BETWEEN THERMAL INSULATION PROPERTIES AND STRUCTURE IN PLA AEROGELS.

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Introduction

Approximately 40 % of global CO2 emissions come from buildings, mainly due to insufficient thermal insulation causing significant energy losses. The development of new super-insulating materials, such as aerogels, which are low-density porous materials with high thermal insulation capacity [1], is crucial. In recent years, there has been increasing interest in aerogels made from biopolymers owing to meeting the environmental demands. Among biopolymers, polylactic acid (PLA) is one of the most widely used globally; however, the insulating capacity of PLA aerogels remains underexplored.

Methodology

PLA aerogels were prepared by the TIPS (Thermal Induced Phase Separation) method, employing different contents of a semi-crystalline PLLA in a 1,4-dioxane/ethanol mixture as solvent. To obtain the final aerogels, the resulting gels were dried with supercritical CO2.

Results and conclusions

The obtained aerogels present low densities (36-167 kg/m3) with an internal structure composed of nanofibers with sizes around 100 nm. Large crystallinity degrees (63-70 %) were achieved, observing the coexistence of two crystalline structures of PLA, α and α'. Mechanical properties were investigated, yielding elastic moduli ranging from 0.15 to 12.82 MPa, exceeding values obtained for other common aerogels. The most insulating PLA aerogel reported in the literature has been produced, with a thermal conductivity of 27.11 mW/m·K. Moreover, a study of the thermal conductivity contributions has been carried out, being the conduction through the gaseous phase the main mechanism of heat transfer, accounting for around 60 % of the total thermal conductivity. The conduction through the solid phase ranges from 2 to 25 % of the total thermal conductivity, having greater weight than the radiative term in higher density samples. The optimum PLA content to achieve the required structure for maximum insulation has been identified. Hence, PLA aerogels became an interesting candidate for new bio-based insulation materials.

Acknowledgments

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ION CONDUCTING POLYMERS OF INTRINSIC MICROPOROSITY (PIMS) AS SELECTIVE MEMBRANES FOR REDOX FLOW BATTERIES

Juan Carlos Martínez López[1], Marta Santos Rodríguez[1], Víctor Oliver Cuenca[1], Giu Silva Testa[2], Ernst Van Eck [2], Evan Wenbo Zhao[2], Ángel Emilio Lozano[1], Cristina Álvarez [1], Javier Carretero González[1]

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Introduction

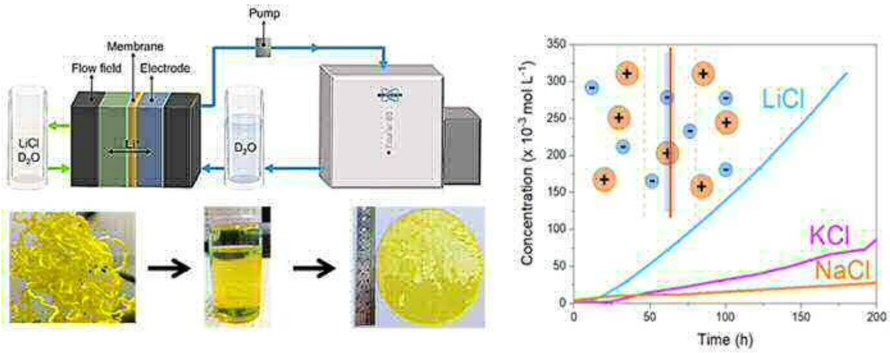
In this communication we are going to show a new family of Polymers of intrinsic microporosity (PIMs) that we have synthesized and characterized. [1,2] Besides, they have been modified to adapt its hydrophilicity and microporosity to be used as selective membranes in redox flow batteries.

Methodology

Different reaction conditions have been used to study how the insertion of COOH groups into the polymer affects to the ion transport in aqueous media. FTIR, 1H/13C-NMR, ICP-MS, gas permeability, N2/CO2 adsorption, ion permeation have been done. Moreover, in-line crossover and 7Li/35Cl diffusion NMR experiments have been done in those membranes exhibting optimun properties, followed by flow half-cell studies to know the cyclability and capacity reached using Li3/4Fe(CN)6 as redox species and the PIM membrane in aqueous media.

Results and conclusions

Comparable SBET areas have been founded for the new PIMs compared to the PIM-1 (benchmark polymer) (400-700 cm2 g-1).[3] A 65% modification of CN into COOH groups have been found to be the one with enhanced ion permeability and preference for Li ion (LiCl 2M, 6·10-9 cm2 s-1 vs NaCl 2M, 7.38·10-10 cm2 s-1 or KCl 2M, 1.05·10-9 cm2 s-1). Moreover, the electrochemical tests showed low polarization, high-rate capability and capacity retention values of 99 % when cycled at 10 mA cm-2 for more than 50 cycles in a symmetric redox flow-cell. These materials can be potentially used as highly selective and conducting membranes in redox flow batteries but also in separation processes and as a protective interlayer in metal-ion batteries.



Acknowledgments

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TRIMETALLIC LIGNIN-BASED CARBON NANOFIBERS AS HIGH-PERFORMANCE ELECTRODES FOR SUPERCAPACITORS

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Introduction

Lignin, the second most abundant natural polymer, is a sustainable feedstock for advanced materials. Lignin-based carbon nanofibers (CNFs) have shown promise in high-performance energy storage applications due to their high surface area and electroconductivity. Supercapacitors benefit from these properties, which enable rapid charge-discharge cycles and high power densities. Incorporating various metal elements (nickel, copper, and cobalt) into electrospun lignin-based CNFs can potentially enhance their electrochemical performance, leading to improved electrochemical performance.

Methodology

In this study, the first step involved dissolving 0.50 g of PVP in 4 mL of ethanol. Separately, a solution of 2 g of lignin and 0.2 g of nickel acetylacetonate in 4 mL of DMF was prepared. The solutions were then mixed and was stirred for 24 h. The resulting solution was then electrospun under controlled parameters (voltage, flow rate, …). Afterwards, the nanofibers underwent a two-stage process consisting of stabilization and carbonization, resulting in the formation of CNFs/Ni. A solution containing copper, cobalt precursors, and urea in deionized water was prepared and transferred to a hydrothermal autoclave for subsequent processing. The prepared CNFs/Ni was immersed in the solution and sonicated. The autoclave was then heated at 160°C in an oven for 6 h. After cooling to room temperature, the resulting CNFs/Ni@CuCo composites were obtained and then were washed with DI and dried. The trimetallic CNFs were characterized using different techniques. Electrochemical properties were measured using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), etc.

Results and conclusions

Results The ongoing research aims to focuses on producing and identifying optimal combinations of Ni, Cu, and Co doped in lignin-based CNFs to maximize supercapacitor performance. Promising pseudocapacitive behaviour is observed in the CNFs/Ni@CuCo composites during initial electrochemical testing, paving the way for in-depth investigation. Conclusions This research highlights the potential for tailored lignin-based CNFs with different ratios of lignin, PVP, and metal content, providing opportunities for superior supercapacitor performance. This research holds great potential to optimize formulations for sustainable and efficient energy storage applications.

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DIAMINOMALEONITRILE-BASED POLYMERS AS EMERGING MULTIFUNCTIONAL MATERIALS

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Introduction

In the last years, our research focused on using DAMN as a monomer for creating C=N-based conjugated polymers, aiming to develop efficient and green processes to reach multifunctional materials. The DAMN-based polymers have emerged as a subject of investigation, encapsulating their synthesis, optical and electromagnetic characteristic, and multifaceted applications that span the realms of chemistry, physics, and biology.

Methodology

Several DAMN-based polymers were synthesised in bulk (solid state [1] or melt [2]), and via solvothermal polymerization, using water [3,4] or n-alcohols, under conventional or microwave radiation heating. These samples were characterised by elemental analysis, FT-IR, UV-Vis, diffuse reflectance and NMR spectroscopies, thermal analysis, and SEM. Particle size distribution was measured by DLS. Their electrochemical and paramagnetic activity was determined by cyclic voltammetry, and ESR, respectively [3-6]. Catalytic potential for perchlorate decomposition was studied using DSC [7], and lindane photodegradation was monitored by GC-MS.

Results and conclusions

Synthesis: All DAMN polymerizations achieved high yields 75-98%, and those conducted in bulk, between 160 to 200 ºC and being air-stable [8] processes are really rapid [6]. This can also be extrapolated to the hydrothermal syntheses under microwave radiation, though under aqueous conditions the conversions are significantly decreased [4]. To address this, n-alcohols have recently been tested as solvents, attaining practically quantitative yields. Characterisation: DAMN polymers exhibit similar spectroscopic properties, found in all cases unresolved signals, indicating a complex and heterogeneous macrostructure. By the contrary their morphological, size and shape and thermal properties depend on markedly of the synthesis conditions. Potential Applications: Due to their notable semiconducting properties (band gap energies 0.6-2.5 eV) [4-7] making them potential metal-free additives for the design of high-performance composite energy materials [7], and as photocatalyst for efficient degradation of organics in water environments. Additionally, they have shown promise for the development of biosensors [5]. As a result, DAMN polymers can be obtained by different synthetic strategies of tuning the properties of their 2D macrostructures constituted by different N-heterocycles being a valuable alternative to the carbon nitrides.

Acknowledgments

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STRUCTURAL CONTROL OF SEMICONDUCTOR POLYMER D18 USED IN ORGANIC PHOTOVOLTAICS.

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Introduction

Organic photovoltaic devices typically include an electron donating semiconducting polymer and an electron accepting small molecule in their active layer. Among the champion polymers is the so-called D18, which stands out from their counterparts, as it develops high-degrees of structural order (in comparison with other OPV polymers, which are more disordered).

Methodology

In order to gain more insights into the special structural characteristics of D18, we performed a deep and comprehensive investigation of structural aspects of D18 combining GIWAXS, fast scanning calorimetry, TEM and polarized microscopy. Furthermore, we performed DMA tests to understand the link between the structure and the properties.

Results and conclusions

First, we resolve the actual solid-state microstructure and morphology of D18 when processed similarly as in devices and we understand its thermotropic phase behavior. But more interestingly, we discover that we are able to readily select the “type” of structural organization in D18, by playing with processing conditions. Specifically, we are able to promote either a “liquid-crystalline-like” ordering, featuring exceptionally intense (100) reflection in XRD while almost null π-π reflection or “crystal-like” order, characterized by an intense π-π reflection. Moreover, our study reveals markedly different mechanical behavior for D18 showing distinct structural organization.

Acknowledgments and References

Special thanks to professor Christian Müller to give us the possibility to carry out DMA measurements at Chalmers University of Technology.

ORDERING OF POLYMERIC NANOPARTICLES IN PEO-BASED SOLID POLYMERIC ELECTROLYTES

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Introduction

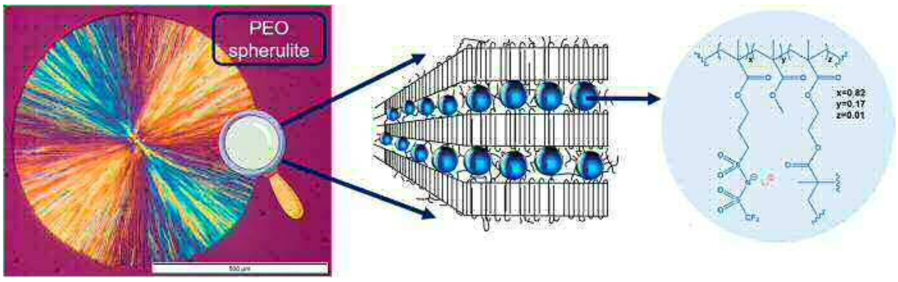
Controlling the crystallization rate of the polymer matrix can achieve the ordering of nanoparticles in semicrystalline polymers. When the spherulitic growth rate is slow relative to the diffusive transport of nanoparticles, the NPs can be preferentially moved into the interlamellar amorphous regions of the semicrystalline morphology [1]. This NP organization can improve some properties of the polymeric materials, such as mechanical properties and thermal and electrical conductivity [2]. In this work, a poly(ethylene oxide) (PEO)/single-ion lithium nanoparticles (LiNPs) system was used to order the LiNPs inside the PEO spherulites. In addition, the ionic conductivity of the electrolytes with the ordered nanoparticles and in the disordered state was compared.

Methodology

LiNPs were synthesized using the methodology proposal by Gallastegui et al, [3]. Blends of PEO 15wt% LiNPs were prepared, and DSC was used to order the LiNPs within the PEO matrix during isothermal crystallization at high crystallization temperatures. The samples were characterized by TEM and SAXS, and the ionic conductivity was measured in different conditions and temperatures.

Results and conclusions

Spherulitic growth was measured for the PEO 15 wt% LiNPs sample to determine the temperature range in which PEO crystallizes more slowly, i.e., between 52 and 58 ºC. Then, the isothermal crystallization of the samples was carried out in the DSC; each sample was crystallized at the chosen crystallization temperature during 24h. SAXS was measured on the samples with ordered and disordered particles and a peak shift to lower q number was observed, indicating that the long period between the PEO lamellae increases due to the presence of the LiNPs within the interlamellar amorphous regions. TEM observations also indicated that NPs were successfully ordered. PEO crystallization achieved the ordering of lithium single-ion polymer nanoparticles, which was verified by TEM and SAXS. The ionic conductivity decreased when the LiNPs were ordered.



Ordering of polymer nanoparticles into the interlamellar amorphous regions of the semicrystalline morphology

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EXPLORING OXYGEN REDUCTION REACTION ELECTROCATALYSIS USING COVALENT ORGANIC FRAMEWORKS

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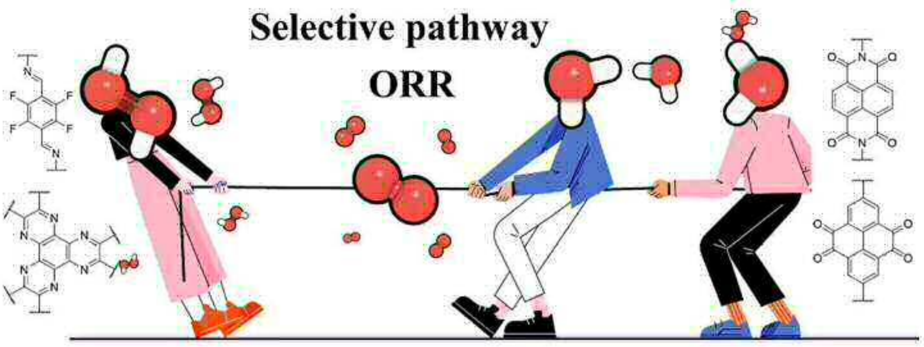
Introduction

Covalent organic frameworks (COFs) are a class of crystalline, porous, and organic polymers connected by strong covalent bonds. These materials display a hierarchically organized structures with predictable control over the structural features at the nanoscale.1 J. L. Segura's research group is dealing with the synthesis of COFs for the obtainment of ad-hoc materials. One of the main research outlines is the obtainment of metal-free and non-pyrolyzed electrocatalysts, specially for oxygen reduction reaction (ORR) electrocatalysis.2-5 This reaction is the art of selectively breaking the O=O bond to produce water peroxide or water through a two- or four-electron pathway respectively, which has emerged as a powerful tool for H2O2 in situ production or the assembly of fuel-cells. In this communication we will highlight our recent results concerning the dependence of the electrocatalytic response with the active site employed or the porosity of the material, modulating the electronic pathway or the performance (Figure 1).



Methodology

The methodology of this project is based on obtaining and characterizing COFs for their application as electrocatalysts. Firstly, crystalline polymers are obtained by solvothermal polymerizations or at room temperature. In addition, post-synthetic modifications have also been carried out to tailor properties of these materials. Solid state characterization is then carried out by techniques such as PXRD, adsorption isotherms, solid state 13C, FTIR, electron microscopy... The polymers are processed by liquid phase exfoliation to obtain covalent organic nanosheets (CONs) as colloids which are also characterized by electron microscopy, DLS or UV-visible spectroscopy. Finally, the CONs are deposited on glassy carbon electrodes that allow the electrocatalytic properties to be analyzed by techniques such as cyclic and linear voltammetry, chronoamperometry or electrochemical impedance spectroscopy.

Results and conclusions

The research carried out in our laboratory has resulted in ten COFs evaluated for ORR electrocatalysis. From this work it has been possible to obtain structure-selectivity and accessibility-performance relationships thanks to the crystalline and defined nature of the COF platform. Currently, work continues in the laboratory to obtain more competitive materials and to develop hydrogen fuel cells.

Acknowledgments

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HETERO-FUNCTIONALIZATION OF POLYITACONATES FOR DEVELOPING IMPROVED POLYMER DIELECTRICS: MERGING SULFONES WITH BULKY/RIGID CYCLES.

Sebastian Bonardd [1], Jon Maiz [1,2], Ángel Alegría [1,3], José A. Pomposo [1,2,3], Ester Verde [1,2], Galder Kortaberria [3], David Díaz Díaz[4,5]

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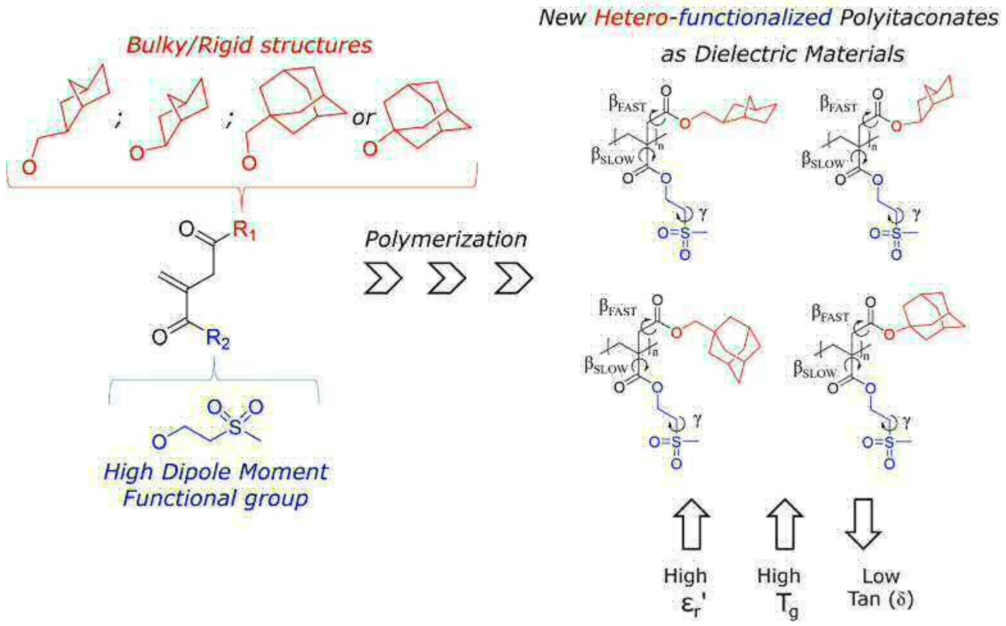
Introduction

In the last decade, all-polymer dielectrics have garnered increasing attention from the scientific community, resulting in an abrupt increase research interest [1]. As a consequence, the amount and diversity of new polymer materials with enhanced dielectric properties have shown a remarkable increase. This allows not only the development of new materials but also enriches our understanding of the topic from a theoretical perspective, which, in any case, reinforces the former. Arguably, the sudden interest in the field can be attributed to the energy situation our current society is facing. Without changing our consumption habits and the sources from which we obtain energy, an upcoming energy shortage is inevitable. Therefore, it is imperative to grasp that the development of efficient and sustainable energy acquisition processes from clean and renewable sources would be in vain if, once obtained, we are unable to utilize it effectively. To ensure this, one approach involves creating and/or reinforcing technologies that focus on efficient storage, conversion and distribution of obtained energy. This is where polymer dielectrics emerge as attractive candidates to achieve and promote a more efficient and effective energy storage process, particularly through the fabrication of improved capacitor devices.

Methodology

The obtained materials were characterized structurally, thermally, and dielectrically using infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermogravimetry (TGA), differential scanning calorimetry (DSC), and broad dielectric spectroscopy (BDS).



Results and conclusions

Four new polyitaconates were synthesized bearing sulfones as high dipole moment entities and norbornane or adamantane structures responsible for increasing the glass transition temperature (Tg) and thus the range of temperatures where they can work without degrading or showing high energy dissipation. As a result, all obtained polymers exhibited dielectric constants ($\varepsilon r'$) between 5.1 and 6.2 while presenting low loss factors ($Tan(\delta) < 0.01$), reaching the status of high-dielectric polymers with a low dissipative behavior. In addition, it was demonstrated that including bulky structures into their polymer backbone allows for an increase of up to 80 °C in their working temperature ranges, expanding the temperature range where they behave as Dipolar Glass Polymers in an outstanding manner. Overall, these materials seem to fulfill the basic requirements to be considered good candidates for dielectric applications such as energy storage, confirming the versatility of polyitaconate-based materials. [2]

Acknowledgments

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THERMAL AND DIELECTRIC STABILITY OF SELF-CROSSLINKABLE POLYPROPYLENE FUNCTIONALIZED WITH THERMO- OR PHOTO-ACTIVE GROUPS

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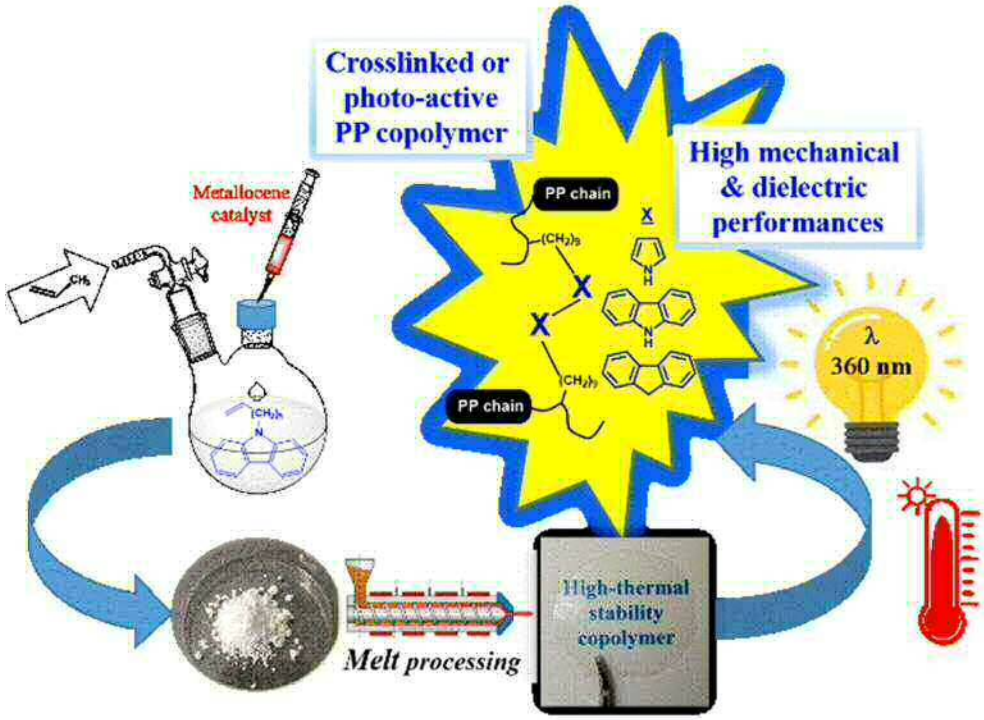
Introduction

Polypropylene (PP) is a polyolefin widely used in electrical and electronic applications, due to its nonpolar character and insulating properties. The ability of this material to tune flexibility makes it an ideal candidate for hosting molecules or functions, which can improve the performance of electric and electronic components in energy storage devices such as batteries, capacitors and supercapacitors. The work carried out by Chung et al. [1] has demonstrated the potential of functionalization to obtain high-performance PP. Furthermore, our research group has developed PP with high thermal stability and excellent dielectric response with diverse lab-synthesized olefins carrying polar groups [2-3].

Methodology

This work focuses on the synthesis of functionalized polypropylene through metallocene catalysis, specifically through copolymerization with a functionalized α-olefin containing a pyrrole, carbazole or fluorene group. The development of this study involves the synthesis of the functionalized olefins and their copolymerization with propylene. This is followed by the characterization of the molecular microstructure and semicrystalline morphology and the analysis of the thermal stability, as well as of the dielectric, mechano-dynamic and photo-physical properties.



Complete process to obtain new thermo- or photo-active PP copolymers, to explore their potential as high-performance dielectrics

Results and conclusions

The materials, prepared following the steps illustrated in the figure, show higher dielectric constant values than PP (ca. 3) and significant improvements in degradation resistance, due both to the strong interactions between the polar groups in the amorphous phase and to its self-crosslinking capacity, easily activated after processing. Moreover, the dielectric losses remain at the PP level (ca. <0.005). Consequently, the results confirm that these polar copolymers could be used as high performance materials in electrical and electronic components.

Acknowledgments

The authors gratefully acknowledge the financial support of the CSIC through Project PIE202060E215 and Spanish Ministry of Science and Innovation (MCIN) through Project PID2020-114930GB-I00.

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IMPACT OF MOLECULAR WEIGHT ON THE SOLID STATE STRUCTURE IN SEMICONDUCTING POLYMERS FOR PHOTOVOLTAICS

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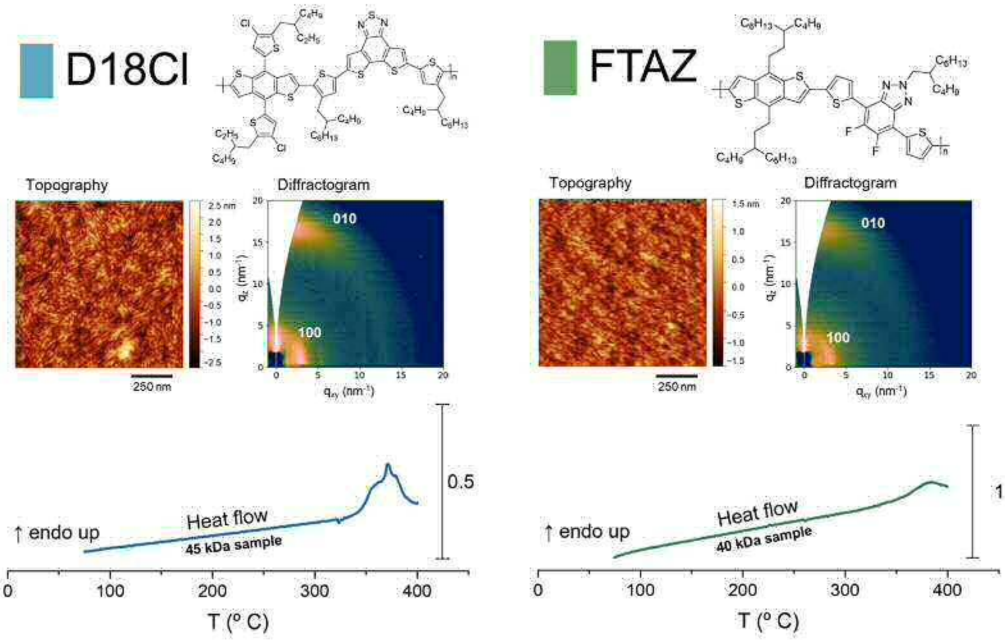
Introduction

Semiconducting conjugated polymers garnered through the years considerable scientific impact owing to their remarkable electronic properties, stability, and processability[1]. Nevertheless, their functional properties are strongly related to the internal structure, which is of no trivial interpretation, showing in some cases complex configurations such as paracrystallinity or semi-paracrystallinity[2]. Consequently, ensuring certain standards out of these materials necessitates a fundamental comprehension of the structural arrangement of their complex phases, which are also dependent on molecular weight[3]. In this study, we analyse two semiconducting polymers at different molecular weights, PBnDT-FTAZ and D18(Cl), which respectively exhibit lower and higher degrees of order in their chain packing (see Figure). This work aims to investigate and understand the impact of molecular weight on the solid state microstructure of semiconducting polymer thin films for photovoltaics.

Methodology

The investigation of the intrinsic configurational order was carried out with the help of GIWAXS (also by in-situ temperature ramp experiments) and AFM techniques, while fast scanning calorimetry allowed the investigation of all those processes involving phase transitions or internal dynamics. The X-ray scattering experiments were performed in ALBA synchrotron, using a beam of 50 microns in width, energy of 12.4 keV and 1 nm wavelength. AFM was employed to analyze the surface topography of the samples. The images were acquired in tapping mode using cantilevers with resonance frequency of about 150 kHz. The calorimetric characterization was carried out by Flash-DSC by means of annealing experiments aiming to detect the thermal process occurring in the material at specific annealing temperatures and times.



Molecular structure, AFM topography images, GIWAXS diffractograms, and DSC thermograms (in mW) of D18Cl and PBnDT-FTAZ.

Results and conclusions

The results obtained reveals different thermal processes which are directly linked to the inherent structure of the polymers themselves. Furthermore, the in-depth characterization of melting and crystallization phenomena provides insights into how molecular weight influences these phase transitions and their kinetics. By linking such results with in-situ GIWAXS studies, we were able to observe and describe several trends of the solid state dependency with molecular weight and type of polymer. This research contributes to the essential comprehension of semiconducting polymers, offering valuable insights into their complex structures and thermal behaviours, thereby creating opportunities for improved design and application of these materials in present and future technologies.

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UNDERSTANDING LI6.24LA3ZR2AL0.24O11.98 EFFECT ON POLY(IONIC LIQUID)-BASED HYBRID ELECTROLYTES FOR HIGH VOLTAGE SOLID-STATE LITHIUM BATTERIES

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Introduction

Solid-state lithium metal batteries (SSLMBs) are a promising solution for energy storage due to their high energy density, increased safety and durability. However, the development of SSLMBs faces the challenge of finding solid polymer electrolytes with electrooxidative stability compatible with high-voltage cathodes, such as Ni-rich NMCs. A viable alternative is the use of hybrid electrolytes composed of poly(ionic liquids), ionic liquids (ILs), lithium salt (LiFSI) and fillers to achieve flexible membranes with high ionic conductivity (>10-4 S cm-1) at room temperature.[1] However, a major knowledge gap in the field of hybrid electrolytes based on PILs lies in understanding the effect of fillers on the processability, physical-chemical properties and electrochemical performance of hybrid electrolytes.

Methodology

Hybrid electrolytes were prepared using poly(diallyldimethylammonium) bis(fluorosulfonyl)imide (PDDAFSI), N-methyl-N-propyl-pyrrolidinium-bis(Fluorosulfonyl)Imide (PYR13FSI), and lithium bis(fluorosulfonyl)imide LiFSI in a molar ratio of 1:1:1 in anhydrous acetonitrile, after different weight percentages (from 0 wt.% to 50 wt.%) of Li-ion conductive Li6.24La3Zr2Al0.24O11.98 (Al-LLZO) filler were added to the solution and each solution was stirred and then cast by a doctor blade. The prepared electrolytes were tested in Li/Li and Li/NMC622 coin cells at 25 ºC.

Results and conclusions

We have investigated the effect of Al-LLZO particles content on structural, thermal, mechanical and electrochemical properties of the hybrid electrolytes. Both TGA and microcalorimeter measurements show that the presence of Al-LLZO particles improves the thermal stability of the hybrid electrolytes. The addition of Al-LLZO led to a decrease in the transport properties (such as ionic conductivity, lithium transference number, etc.), but surprisingly the best battery performance in Li/Li symmetric coin cells (cycling 2000 h, 0.1/0.1 mA h cm-2) and Li/NMC622 coin cells (0.1C/1C, 200 cycles, 84% capacity retention) was obtained for the hybrid electrolyte with 2.6 vol.% (10 wt.%) of Al-LLZO particles. The result of this study indicates that the charge passed (C/cm2) throughout of full cells correlates well with the yield stress of the hybrid electrolytes. In turn, the yield stress of the hybrid electrolytes is dependent of the volume fraction of Al-LLZO in the polymer matrix.

Acknowledgments

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ANISOTROPIC COMPOSITES OF CONJUGATED POLYMERS AND POLYMER-WRAPPED CARBON NANOTUBES FOR THERMOELECTRIC APPLICATIONS

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Introduction

Polymer-wrapping allows precise selection of semiconducting single-walled carbon nanotube (SWCNTs) species, a quasi-one-dimensional carbon allotrope with promising properties and applications in electronics, biosensing and energy applications. When wrapped by a polymer in solution, SWCNTs form stable dispersions that can be readily casted via classical processing methods (e.g., spin coating, blade coating) to form thin films. Doping proceeds in these films following analogue methodologies as in conjugated polymers (e.g., charge-transfer) thus unlocking their superior thermoelectric performance. These processability properties render polymer-wrapped SWCNTs attractive to form thermoelectric composites in combination with workhorse conjugated polymers such as the poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT) family.

Methodology

In this regard, the alignment of conjugated polymers through high-temperature rubbing has been shown to skyrocket the thermoelectric power factor compared to isotropic samples, thus similar improvements could also be realized in composite form factors with the added benefits (improved Seebeck coefficient and electrical conductivity) of polymer-wrapped SWCNTs.

Results and conclusions

In this work we first study the thermoelectric properties of solution-processed, polymer-wrapped SWCNT films in isotropic and aligned form factors. Dip coating is used to prepare aligned self-assembled arrays of SWCNTs showing anisotropic properties. These are, however, found to underperform with respect to the isotropic controls likely due to a poor interconnection of the SWCNTs over areas of several mm2, as required by practical thermoelectric applications. Conversely, high-temperature rubbed PBTTT films in either variant (PBTTT-C14 and PBTTT-C12) show comparatively higher performance along the rubbing direction than orthogonally to it or the isotropic baseline. Through a simple layer overcoating, bilayered composites of SWCNTs and PBTTT are formed. Rather than keeping the SWCNTs unaffected, rubbing applied on said bilayers is found to (re)orient both the SWCNTs and the PBTTT as probed by polarized Raman mapping. In this new conceptual anisotropic composite, power factors exceeding 200 uW m-1 K-2 are accordingly demonstrated along the rubbing direction after 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) doping.

Acknowledgments

We acknowledge the Alexander von Humboldt Foundation for funding.

RECYCLABLE THERMALLY CONDUCTIVE VITRIMERS USING SEQUENTIAL STRESS-RELAXATION PROFILES

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Introduction

Poly(thiourethane)-poly(thiol-epoxy) hybrid materials were prepared using ternary thiol-isocyanate-epoxy formulations. Trimethylolpropane tris(3-mercaptopropionate) (S3) served as the crosslinking agent in a stoichiometric ratio with 4,4′-Diisocyanato-methylenedicyclohexane (HMDI) and an epoxy (bisphenol A diglycidyl ether, DG). A tetraphenylborate salt (BG) derived from 1,5,7 triazabicyclo[4,4,0]dec-5-ene (TBD) employed as a latent base to catalyze both curing and bond exchange reactions at moderately high temperatures, while 1-methylimidazole (MI) initiated the curing reactions, following a dual-curing sequence where the thiol-isocyanate reaction occurred first. Stoichiometric formulations were prepared with different ratios of isocyanate and epoxy groups.

Methodology

A series of techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) a long with a thermoconductometer and a hot-pressing mold were used in order to fully characterize the curing reactions and also thermal and mechanical behavior of the fully cured samples.

Results and conclusions

The glass transition temperature (Tg) of the materials ranged from 43°C for epoxy-rich samples to about 95°C for isocyanate-rich samples. Boron nitride (BN) fillers were added in different proportion to the formulations, up to 50 wt.% with respect to the resin mass, producing no change in the Tg of the cured materials. The thermal conductivity measurements revealed more than 10 times increase for the sample filled with 50 wt.% (2.13 W/mK) compared to one without filler (0.2 W/mK). All materials exhibited vitrimer-like behavior. Experiments showed that higher epoxy content slow down stress relaxation. It was observed that at 140°C the sample containing epoxy ratio of 50% is the threshold limit of complete stress relaxation. The presence of BN did not impede complete stress relaxation in samples with epoxy ratio of 50%.

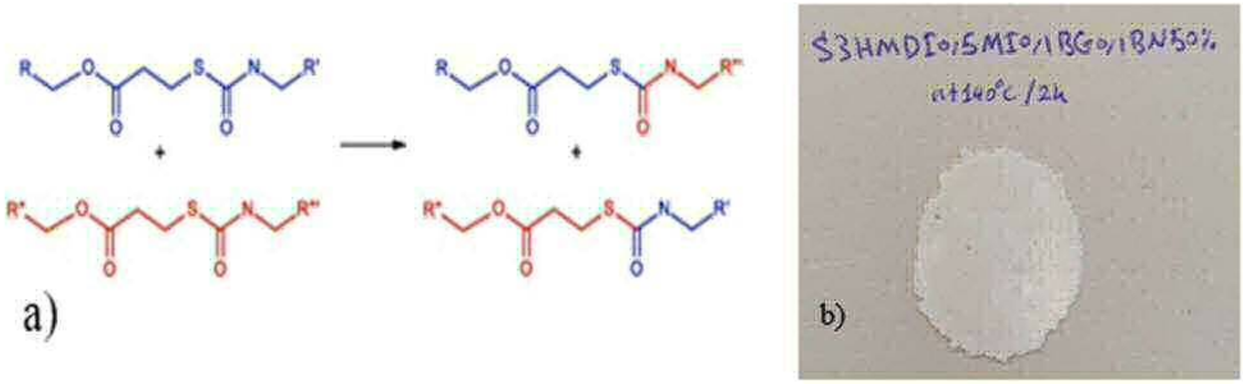

Fig1. a) Trans-thiocarbamoylation in the isocyanate-thiol networks. b) Recycling of S3HMDI0.50 at 10MPa within 2 hours using hot-press molding at 140ºC.

Exceeding the epoxy ratio of 50% was associated with more residual stress and as a result incomplete stress relaxation [1,2]. At lower temperatures, trans-thiocarbamoylation [fig1.a] was the dominant bond exchange mechanism. High temperatures (T>140°C) activated transesterification [2], enabling complete stress relaxation in epoxy-rich samples. Materials with epoxy ratio up to 50% and different BN filler content were successfully recycled by hot pressing of ground samples at 140°C within 2 hours under 10 MPa pressure [fig1.b].

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SYNTHESIS AND CHARACTERIZATION OF SUSTAINABLE THERMOPLASTIC POLYURETHANE CONTAINING RECYCLED BIS(2-HYDROXYETHYL) TEREPHTHALATE FOR ADVANCED APPLICATIONS

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Introduction

Polyethylene terephthalate (PET) is widely used in food packaging applications, generating a vast increase in post-consumer plastic waste. This type of waste has very high mechanically recycling rates especially the transparent PET. However, the PET bottles, trays and films are not due to the complex composition, therefore ending up in landfill or incinerated [1]. Chemical recycling of complex PET waste is a promising technology, which allows to obtain the bis(2-hydroxyethyl) terephthalate (BHET) monomer [1]. The recycled BHET could be used again to produce PET or other polymers such as polyester, epoxy or polyurethane resins [2]. In the present study, thermoplastic polyurethanes (TPUs) with different hard segments (HS) contents (40, 50 and 60 %wt) were prepared from chemically recycled BHET via a green route. TPUs with commercial butanediol were also synthesized for comparative purposes. The BHET monomer and the synthesized TPUs were extensively characterized. Moreover, their potential use of synthesised TPUs as membranes was addressed.

Methodology

Recycled BHET was obtained by chemical recycling of PET waste. Different grades of TPUs were synthesized varying the hard segment (HS) contents: 40, 50 and 60%wt. Moreover, two types of chain extenders were employed for their synthesis: bunanediol and recycled BHET. TPUs were synthesized by two-step prepolymer method in the absence of solvent. The TPUs obtained were herein characterized by infrared spectroscopy (FTIR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Additionally, membranes from synthesized TPUs were prepared by casting method and their gas permeation capability was evaluated.

Results and conclusions

New series of TPU materials were obtained using a sustainable synthesis without solvents. Moreover, the recycled BHET was upgraded by inclusion in the TPU production. The effect of recycled BHET was evaluated on the polymerization process, as well as on thermal properties. The synthesized polymers showed an interest combination of composition and thermal properties. Finally, membranes from the novel sustainable TPUs were prepared and characterized, showing promising results. In this investigation, the synthesis and properties of novel sustainable TPUs from chemically recycled BHET were studied as a strategy for promoting the circular economy of complex PET waste. Moreover, the use of synthesized TPUs in high-value applications such as gas separation membranes was valued.

Acknowledgments and References

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USING INDENTATION TO STUDY THE CREEP BEHAVIOUR OF SUSTAINABLE POLYURETHANE ADHESIVES

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Introduction

Creep can be generally understood as the viscoelastic and/or viscoplastic response of a material under application of a constant load and it is fundamental to a full understanding of material performance. Indentation testing is a convenient method for investigating creep processes as it is a robust technique with high reproducibility and requires a relatively small amount of sample. Traditional indenters, based on optical imaging of residual indentations, analyse creep in terms of viscoplastic deformation. The advent of modern instrumented indenters has allowed the additional study of viscoelastic creep.

Methodology

More recently, we have developed novel adhesives as binders for multilayer packaging to facilitate the separation of these components after use. This strategy incorporates Diels-Alder (DA) covalent bonds into a polyurethane (PUR) network. Heating above about 90 ºC causes the DA bonds to dissociate, breaking down the PUR structure. As a result, the adhesive properties are lost, allowing for delamination. Different adhesive formulations have been used, which are expected to influence the molecular architecture and in particular, the crosslinking density of the PUR network.

Results and conclusions

This presentation will provide an in-depth study of the relationship between indentation creep resistance and the molecular and structural characteristics of PUR-DA adhesives. We will show that increasing adduct content promotes viscoelastic flow. Parallel-plate shear rheometry results support this finding and suggest that it is related to changes in the network crosslinking density. Finally, it is shown that the incorporation of radiation-absorbing graphene not only aids in the bond dissociation process but also affects the overall mechanical performance under creep conditions.

Acknowledgments and References

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REVALORIZACIÓN DE RESIDUOS POST-CONSUMO DE RPET-O: EFECTO DE LA COMPATIBILIZACIÓN REACTIVA EN LA INTEGRIDAD MECÁNICA ESTRUCTURAL DE MEZCLAS PP/RPET-O.

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Introducción

Una problemática que se está presentando en el reciclaje y revalorización de residuos post-consumo de botellas de Poli(Etilén Tereftaláto) (rPET) es la aparición de formulaciones "opacas" con un contenido de entre 10 a 20% en peso de dióxido de titanio (TiO_2) (rPET-O).

Entre las alternativas planteadas para la revalorización de este residuo se ha planteado su incorporarlo como reforzante microfibrilar en el polipropileno (PP), inducido durante el proceamiento final. En este caso empleando rPET-O modificado mediante extrusión reactiva (REX-rPET-O). En trabajos previos se demostró que la adición de hasta 1% en peso de un agente multiepoxidado promueve la generación de estructuras ramificadas mejorando su comportamiento reológico extensional [1], lo que permitiría controlar la morfología resultante de la mezcla.

No obstante, este sistema se enfrenta a la inmiscibilidad inherente entre ambas fases y sus consecuencias negativas en el posterior desempeño mecánico. Se ha propuesto como agentes compatibilizantes potencialmente reactivos dos PP modificados: con glicidil metacrilato (PPgGMA) y con anhídrido maleico (PPgAM). La existencia de grupos epoxi remanentes en el REX-rPET-O podría favorecer la generación de una interfase adecuada que promueva una mejor compatibilización mecánica.

Metodología

Mediante extrusión doble-husillo se prepararon mezclas PP/REX-rPETO-O: 80/20 p/p, con y sin agente compatibilizante. Este último en una proporción de 10 % p/p respecto a la fase PP. Se realizó un estudio comparativo morfológico y fractográfico (SEM), mecánico y de propagación de grieta en muestras moldeadas por inyección. Para la cuantificación de los parámetros de fractura se aplicó el análisis del "Trabajo Esencial de Fractura" sobre probetas con entalla y ensayadas a flexión por tres puntos (SENB).

Resultados y Conclusiones

Ambos modficaciones del PP, en la proporción añadida, ejercen un efecto emulsificante sobre el rPET-O, siendo notorio para PPgAM.

El mejor balance entre propiedades mecánicas y a fractura se observa con el PPgGMA. Esto último gracias a la generación de una interfase con mayor efectividad en la transmisión de tensiones y deformaciones entre fases atribuible, en principio, al tipo de enlace químico generado (éter) durante el mezclado reactivo.

Agradecimientos

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THE DEVELOPMENT OF REMOTELY-TRIGGERED REVERSIBLE POLYURETHANE ADHESIVES BY ADDITION OF RADIATION ABSORBING NANOPARTICLES

Marian Gómez-Fatou , Araceli Flores , Gary Ellis , Peter Shuttleworth , **Horacio Salavagione**

ICTP, Madrid, España

Introduction

Plastic films used in food packaging are multi-layered materials with each layer serving a specific function. However, these materials are extremely difficult to recycle, and as a result typically end up in landfill or incineration plants. The main reason for this is that the current laminating adhesives present strong, irreversible adhesion, which limits the produced packaging systems to single-use applications. From a sustainability perspective, the recovery of individual polymers after use is of paramount importance. A crucial step in this process is to make the adhesion between the polymers reversible, which can be achieved by breaking down the adhesive structure. Therefore, innovative solutions are required to resolve this issue and a promising approach will be presented in this communication.

Methodology

This presentation will describe the development of a new, reusable polyurethane adhesive containing dynamic covalent Diels-Alder bonds that can be reversibly opened and closed via temperature control.

Results and conclusions

In our case, we demonstrate that this thermoreversible bond breaking/formation cycle in the adhesive can be repeated up to ~20 times. A further innovation is the incorporation of radiation-absorbing nanoparticles into the adhesive. This enables remote triggering of bond breaking in just tens of seconds using NIR radiation. In particular, a promising strategy based on the incorporation of graphene into thermoreversible adhesive resin formulations to trigger the rupture of the adhesive network will be described. Graphene is a thermal absorber that heats up rapidly under irradiation, efficiently dissipating this heat to the surrounding environment. This causes the adhesive network to collapse, resulting in remarkable changes in its mechanical properties. The effect of irradiation on the cyclability, fluidity and mechanical properties of the graphene-containing adhesives will be discussed.

The introduction of this novel adhesive concept as a drop-in substitute for conventional PU adhesives in the lamination process will facilitate the separation into clean waste streams and recycling of the individual polymer layers, thereby paving the way to a circular economy solution towards sustainable packaging.

Agradecimientos y Referencias/Acknowledgments and References

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DESARROLLO DE TERMOESTABLES EPOXÍDICOS CON ENLACES DINÁMICOS COVALENTES DE IMINA PARA COMPUESTOS SOSTENIBLES DE FIBRA DE CARBONO

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Introducción

La aparición de las resinas vitrímeras en los últimos años ha supuesto un avance en la reciclabilidad y sostenibilidad de los materiales compuestos. Sin embargo, las prestaciones actuales de la mayoría de ellas no son adecuadas para su uso en compuestos de altas prestaciones. El desarrollo de un compuesto vitrímero reforzado con fibra de carbono (FC) más ecológico, con propiedades térmicas y mecánicas similares a las de los compuestos fabricados con resinas convencionales, pero con capacidad de reciclaje, continua siendo un reto a solventar. Partiendo de investigaciones previas donde se desarrolló una resina vitrímera altamente biobasada y reciclable [1], este trabajo se centra en la mejora de las propiedades térmicas y mecánicas de dicha resina, manteniendo su reciclabilidad, y en su empleo para el desarrollo de compuestos de fibra de carbono

Metodología

Para el desarrollo del vitrímero, se empleó como endurecedor una base de Schiff obtenida a partir de una diamina aormática y vanilina (VSB). Como componente epoxídico, se combinan un aceite de soja epoxidado de base biológica (ESO) y una resina epoxídica aromática (TGDDM) que se incluirá en la red para ajustar la temperatura de transición vítrea (Tg) y las propiedades mecánicas de los compuestos finales. Se han empleado varias proporciones ESO:TGDDM y se han preparado composites de FC mediante moldeo por presión a 190ºC durante 2 h

Resultados y Conclusiones

La Tg del sistema VSB:ESO aumenta con el incremento del contenido de TGDDM en la matriz epoxídica debido a la mayor rigidez en la estructura aromática del TGDDM. Las propiedades térmicas y mecánicas observadas mediante DSC, TGA y DMA, son aceptables para aplicaciones de ingeniería ligera. Su resistencia a los disolventes muestra una eliminación del vitrímero sobre la FC en condiciones ácidas, debido a la hidrólisis de la base de Schiff. Ésta disminuye al aumentar el contenido de TGDDM en el sistema, dando lugar a un compromiso entre propiedades mecánicas y térmicas y su reciclabilidad. Este trabajo aporta nuevos conocimientos para diseñar vitrímeros con propiedades térmicas y mecánicas ajustadas y buena resistencia a los disolventes, que pueden reciclarse y degradarse en condiciones suaves, dando lugar a materiales compuestos de fibra de carbono más ecológicos.

Agradecimientos

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PRE-CLINICAL EVALUATION OF A NEW CLASS III BIODEGRADABLE STENT FOR THE TREATMENT OF URETHRAL STRICTURE

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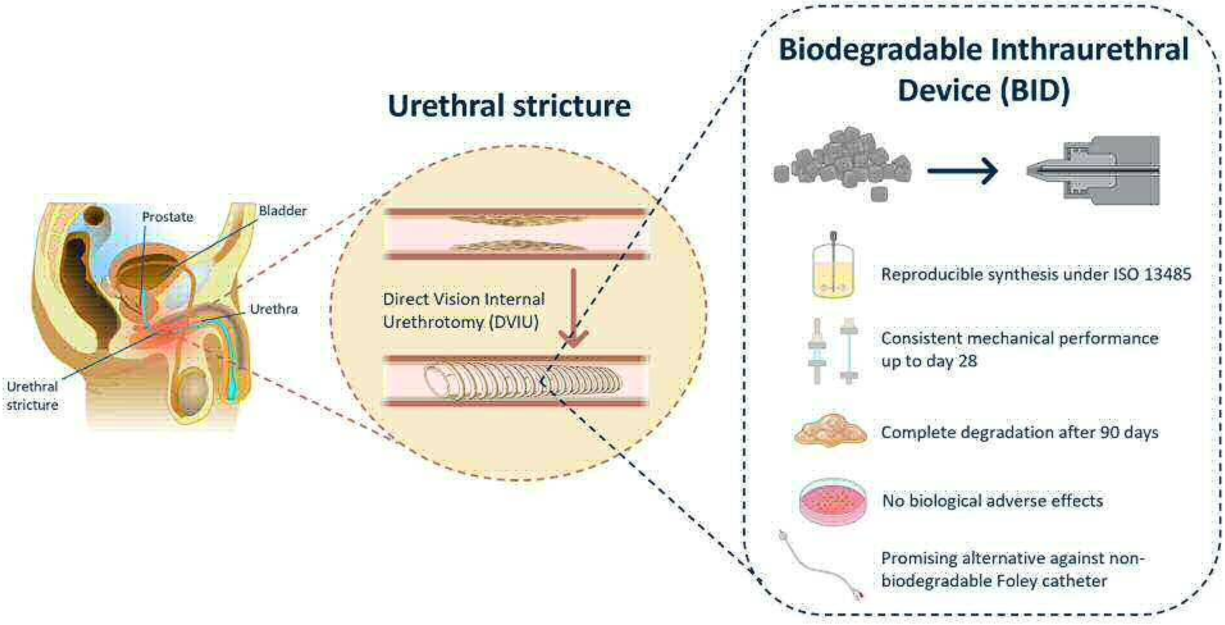
Introduction

Urethral stricture is a narrowing of the urethra, caused by the growth of aberrant tissue after an injury to the urethral mucosa or the surrounding tissues (1). Nowadays, after surgery to remove the abnormal fibrous scar, the postoperative treatment requires a Foley catheter for external urinary drainage for 3-7 days (2). However, they aggravate urinary tract infections (UTIs) and require a second intervention to remove them (3). Thus, we developed a completely biodegradable inthraurethral device (BID) as an alternative to the current postoperative practice.

Methodology

BID is composed of poly(D,L-lactide-co-ε-caprolactone) (PDLLCL) copolymer, synthesized by ring-opening polymerization (ROP) in bulk, manufactured by injection molding and sterilized by e-beam, according to ISO 13845. All characterization techniques were performed following the standards of the International Organization for Standardization (ISO). Physicochemical characterization was evaluated determining copolymer composition (1H NMR), molecular weight (GPC), thermal properties (DSC, TGA), and impurities (ICP, SEM). Additionally, hydrolytic degradation studies were carried out statically, and dynamically in a urethral simulator, in order to obtain a closer performance to that of the real application of the device. Mechanical characterization was performed including tensile strength, flow rate and kink stability measurements. Finally, biological evaluation was conducted, in which in vitro cytotoxicity, skin sensitization, dermal irritation and genotoxicity were evaluated. In vivo, acute/subacute and subchronic toxicity, including local effects after implantation were assessed in rodents urinary tract.



Results and conclusions

Our results showed a scalable synthetic procedure, obtaining high molecular weights, reproducible compositions, yields around 90% and absence of contaminants. Besides, BID showed consistent mechanical performance up to day 28, and a complete degradation of the device after 90 days. In vitro biological evaluation revealed no cytotoxicity, skin sensitization, dermal irritation or genotoxicity. Moreover, in vivo evaluation of acute/subacute toxicity at 1, 14 and 28 days, and subchronic at 12 weeks, demonstrated no relevant changes in clinical analyses or histological study after BID implantation, compared with non-biodegradable Foley catheter. Thus, it was concluded that BID is safe and could be a promising alternative to actual Foley catheters.

Acknowledgments

SGIker technical and human support (UPV/EHU, MICINN, GV/EJ, ESF) is gratefully acknowledged.

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CHEMORESPONSIVE BEHAVIOR IN DYNAMIC POLYMER NETWORKS

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Introduction

Stimuli-responsive, or "smart," materials are ubiquitous in modern technologies such as energy storage devices, wastewater treatment and lighting. These technologies exploit a wide variety of materials that can be triggere by voltage, light, temperature and magnetic fields. Living systems, in comparison to artificial stimuli-responsive materials, are regulated most frequently by specific chemical signals. After perhaps the first discovery [1], a number of publications have reported on the chemo-regulated mechanical behavior of smart materials [2]. The recent and rapid development of supramolecular systems and dynamic covalent chemistry have opened up a number of possibilities for designing chemoresponsive materials. In the future, such materials may be used in applications such as soft robotics and self-regulated drug-delivery devices. This contribution delineates our synthetic strategies to implement selective binding sites to suitable polymer networks leading to stimuli-responsive materials including chemoresponsive hydrogels and microstructured liquid crystal elastomers, LCEs [3].

Methodology

Our recent research has been focused on building fundamental knowledge on the preparation of chemoreponsive dynamic polymeric materials including LCEs and hydrogels. The latter will receive a special attention in this communication. Hydrogels were prepared by mixing appropriate amounts of functional star polymers (macromers, see Figure 1) in aqueous media. Almost immediate gelation was observed at neutral pH, a process that is associated with the end linking of reactive macromers. With the appropriate chemistry, such as boron-assisted aminal formation in our case, the thermodynamics and kinetics of bond formation, cleavage, and reformation enable stress relaxation and self-healing behavior. Additionally, equipping the functional star polymers with molecular receptors allows for chemoresponsive behavior in aqueous media at neutral pH. Indeed, the viscoelasticity of polymer networks can be modulated by the presence of biological species such as glucose and cysteine in biologically relevant environments.

Results and conclusions

Our results contribute to the fundamental understanding of the formation of dynamic polymer networks and the role of specific end-linking chemistries in well-defined polymer networks unveiling new opportunities for the preparation of stimuli-responsive materials.

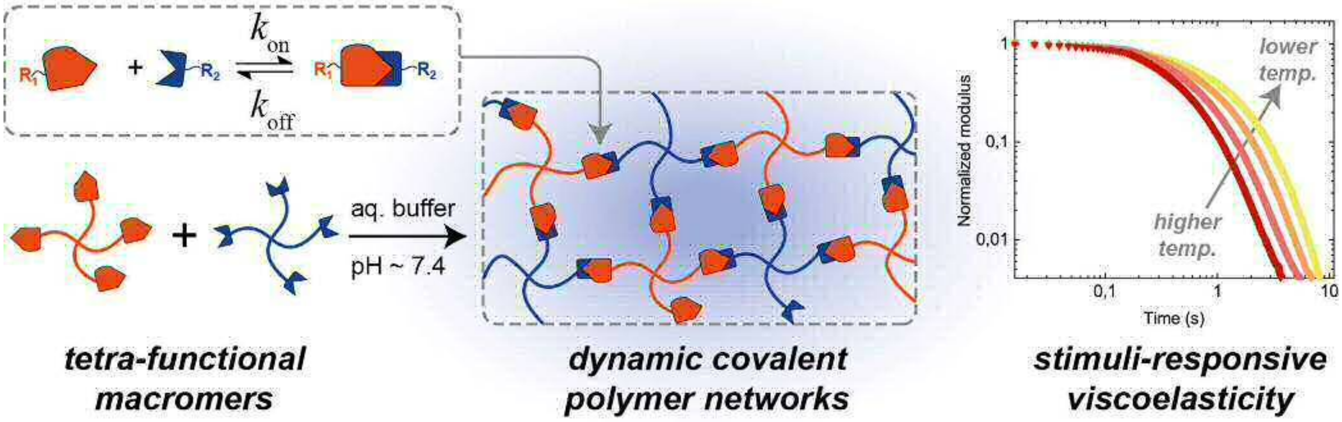

Figure 1. Overview for the design of stimuli-responsive dynamic covalent hydrogels.

Acknowledgments

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STIMULI-RESPONSIVE DENDRITIC HYDROGELS: TUNING THE MACROSCOPIC PROPERTIES FROM THE NANOSCALE

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Introduction

Dendritic hydrogels based on carbosilane crosslinkers are promising drug delivery systems, as their amphiphilic nature improves the compatibility with poorly water-soluble drugs.

Methodology

Using the highly efficient UV-initiated thiol–ene click chemistry, we generated different materials ranging from non-swelling networks to high-swelling hydrogels with stimuli-responsive properties [1-3].

Results and conclusions

We have demonstrated the impact of the nanosized dendritic crosslinker (nature, topology, generation) as well as the complementary polymer (like PEG or Pluronics) on the amphiphilic properties of the dendritic network, and thus on their swelling ability and drug release. The hydrogels are thermo- and/or pH-responsive, and exhibit an intriguing drug release pattern due to internal nanostructuring. The outstanding versatility of the dendritic crosslinkers enabled the design of functional hydrogels as well as degradable and nondegradable networks. Carbosilane-based dendritic hydrogels enable good control of the material macroscopic properties at a molecular level, and thus they can be fine-tuned for the desired purpose.

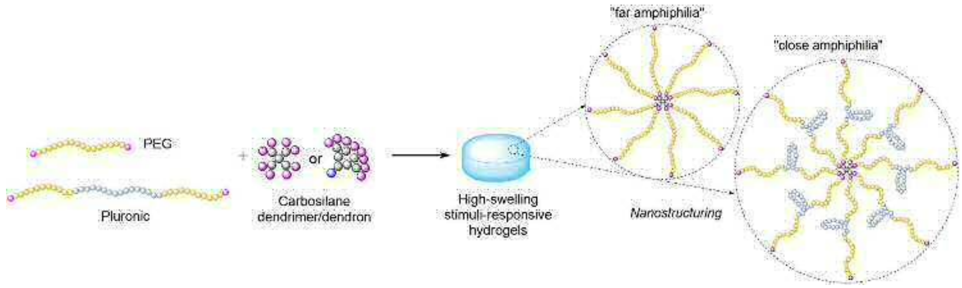

Figure 1. Design of amphiphilic hydrogels based on carbosilane dendritic crosslinkers.

Acknowledgments

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PREPARATION OF SILVER NANOPARTICLES (AGNPS) USING BETA CHITOSAN SUSPENSIONS

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Introduction

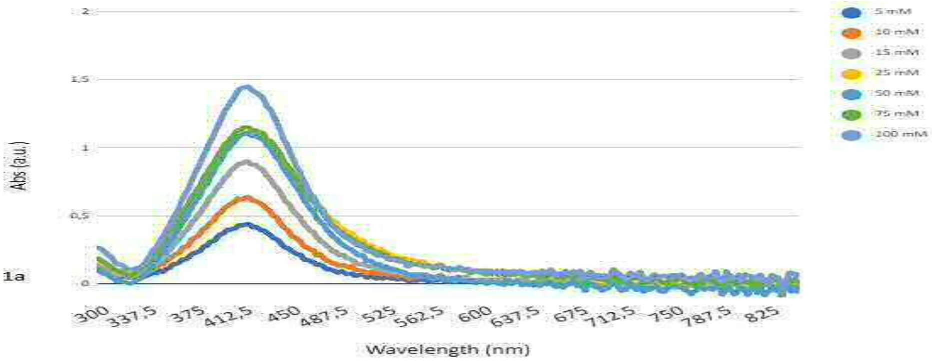
Chitosan produced by deacetylation of α-chitin has been widely used in the green synthesis of silver nanoparticles (AgNps) using the polymer as both stabilizing and/or reducing agent [1]. Squid pens are a novel, renewable source of β-chitin and chitosan. β-chitin has a parallel structure, which differs from α-chitin antiparallel structure. β-chitin conformation is more prone to intra-crystalline swelling than α-chitin conformation. Differences are also observed in the chitosan produced by both type of chitin structures such as less crystallinity and higher molecular weight, swelling and reactivity in chitosan samples from β-chitin [2,3].

Methodology

The synthesis was carried out by adding 200 µl of different concentrations of silver precursor $AgNO_3$ (5, 10, 15, 25,50, 75 and 100 mM) to 1 ml of chitosan solution in acetic acid (0.1 M) and the final solution was magnetically stirred at 90 C, then allowed to react for additional hours. The color of the solution progressed from colorless to yellow after the reaction was completed.

Results and conclusions

Isolated chitosan showed an acetylation degree over 0.90 and a molecular weight around 1500 KDa as determined by GPC.The formation of the colloidal AgNps was confirmed by the presence of a symmetric typical SPR band of metallic silver nanoparticles centered around 400 nm (Fig 1 a). Pseudospherical AgNPs were observed under TEM with a size smaller than 25 nm and low polidispersity. Interestingly, at 100 mM of AgNPs the formation of a gel-like structure (Fig 1b) occurred. ATR-FTIR analysis were conducted to determine the mechanism for silver reduction and AgNps stabilization. AgNPs were stable in dark conditions at 4ºC for at least one month, maintaining the intensity and symmetry of SPR band. These findings indicate that this source of chitosan could be an excellent source for producing nanocomposite materials that can be used in various industrial and biomedical or pharmaceutical applications not only as colloidal AgNPs but also in hydrogels and scaffolds.



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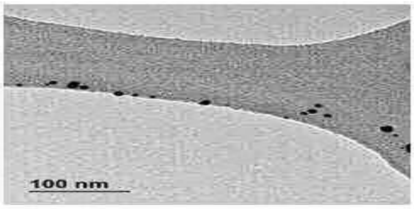

1b

Acknowledgments

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DEGRADABLE AMINO-YNE HYDROGELS: STUDY OF Β-AMINOACRYLATE CROSSLINK CLEAVAGE

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Introduction

Degradable hydrogels can be designed to provide tunability of degradation rates under physiological conditions, finding variety of applications in biomaterial field [1]. Amino-yne click chemistry, which takes place spontaneously in aqueous media by simply mixing amines and electron-withdrawing alkynes, provides an accessible pathway for a fast preparation of hydrogels [2,3]. Furthermore, the resultant β-aminoacrylate bond is cleavable under acidic conditions, allowing for the recovery of the initially conjugated amine. However, there is a lack of literature addressing the chemistry underlying this unclick reaction and the rest of products generated. Herein, we developed a study on the cleavage of β-aminoacrylate bond using model molecules and preparing degradable hydrogels.

Methodology

PEGalk was synthetized following reported protocol [3]. Degradation kinetics were performed by NMR experiments on Bruker AV-300/500 spectrometers. FESEM analysis was accomplished for morphology characterization. Rheological measurements were performed on a HAAKE™ MARS™ 40 rheometer. Internal structure of hydrogels was examined by HR-MAS NMR spectra on a Bruker Avance NEO400 spectrometer. Equilibrium water content and hydrogel’s degradation were studied through gravimetric analysis.

Results and conclusions

Amino-yne click chemistry was used for the synthesis of a β-aminoacrylate-based model molecule (Figure 1i). Acid pH induces the breakage of the bonds provoking the release of the amine, which was observed by NMR studies, as well as a complex mixture of other products that depend on the acidity of media. Hydrogels were prepared using a PEGalk and different polyamines (Figure 1ii), presenting high-water uptake capacity. The characterization of their properties and degradation by rheology, HR-MAS NMR spectroscopy and gravimetrical analysis led to the understanding of the dependence of cleavage rate of β-aminoacrylate crosslinks on the pH and temperature, mimicking model molecule results.

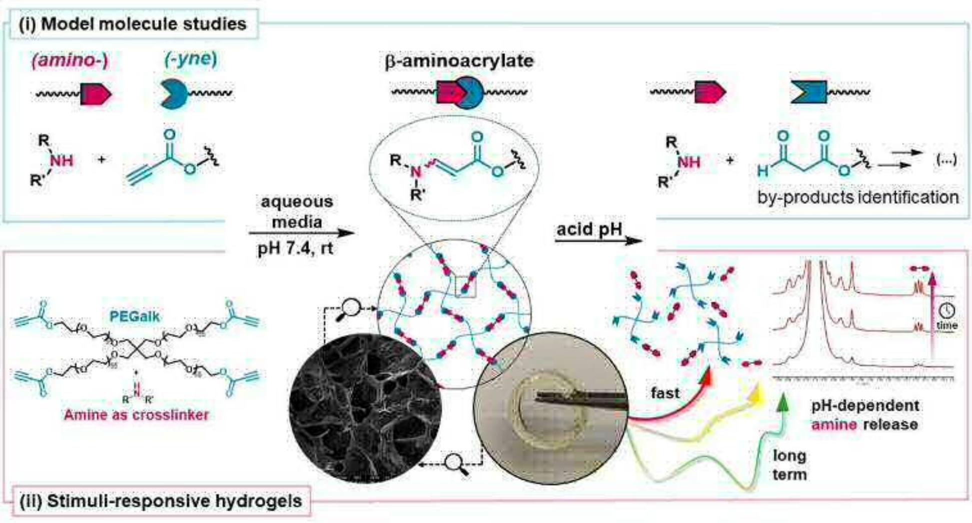

Figure 1. Scheme of (i) model molecule studies and (ii) synthesis and degradation of hydrogels.

Their labile nature is even detected at physiological conditions (days scale) but it is accelerated by decreasing the pH or increasing temperature (hours scale). Therefore, degradation kinetics can be controlled on-demand by modifying both stimuli, together with crosslink density. More importantly, in all cases degradation concludes with the recovery of the amine. This work paves the way to use of amino-yne click reaction for conjugation and release of amino-based drugs inside of hydrogel networks.

Acknowledgments

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MASS PRODUCTION OF MULTICELLULAR SPHEROIDS WITH 3D PRINTED LOW-ATTACHMENT POLYURETHANE MICROWELL ARRAYS

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Introduction

3D multicellular structures such as spheroids and organoids better mimic physiologically relevant models by enhancing cell-to-cell interactions compared to 2D cultures. These interactions are crucial for biomedical applications like drug testing and stem cell-derived organoid engineering. Despite their potential, 3D cell culture methods are complex and costly.[1] In this study, we developed a polyurethane microwell array (PMA)-based spheroid generator, utilizing polyurethanes' biocompatibility and tunability properties,[2]. We were able to fabricate precise structures made possible through LCD stereolithography 3D printing.

Methodology

A 3D printed PMA cell culture substrate was developed, offering customizable microcavities and bypassing traditional molding methods. The study focused on the synthesis and optimization of a feedstock resin for LCD printing, assessing PMA substrate properties, and evaluate A549 cell viability and cell-spheroid formation reproducibility. IR and NMR spectroscopy, rheological assessment, tensile properties evaluation, thermal stability testing, water absorption, in vitro degradation, histology examination, and cytocompatibility assessment were used.

Results and conclusions

A 3D printable resin was prepared using a solvent-free, two-step process combining aliphatic isocyanates, polyethylene glycol, and a methacrylate monomer to create a methacrylate-terminated polyurethane oligomer. The resulting 3D printed PMA cell culture platform demonstrated high-throughput spheroid formation capabilities, producing up to 100 spheroids per 45 mm^2 sample. Characterization confirmed the material's stability (less than 4% weight loss per month), non-toxicity (>70% cell viability compared to control), and low-adhesion. Scaffold-free cultivation and cell self-assembly occurred in the PMA device over a week-long culture period, resulting in a fourfold increase in DNA content within one week. Further, spheroid size varied with the initial cell seeding density, and no necrotic core could be observed (see figure). Overall, this approach offers a streamlined process for high-throughput screening of micro- and nanomaterials, potentially advancing drug testing and stem cell-derived organoid engineering.

Acknowledgments

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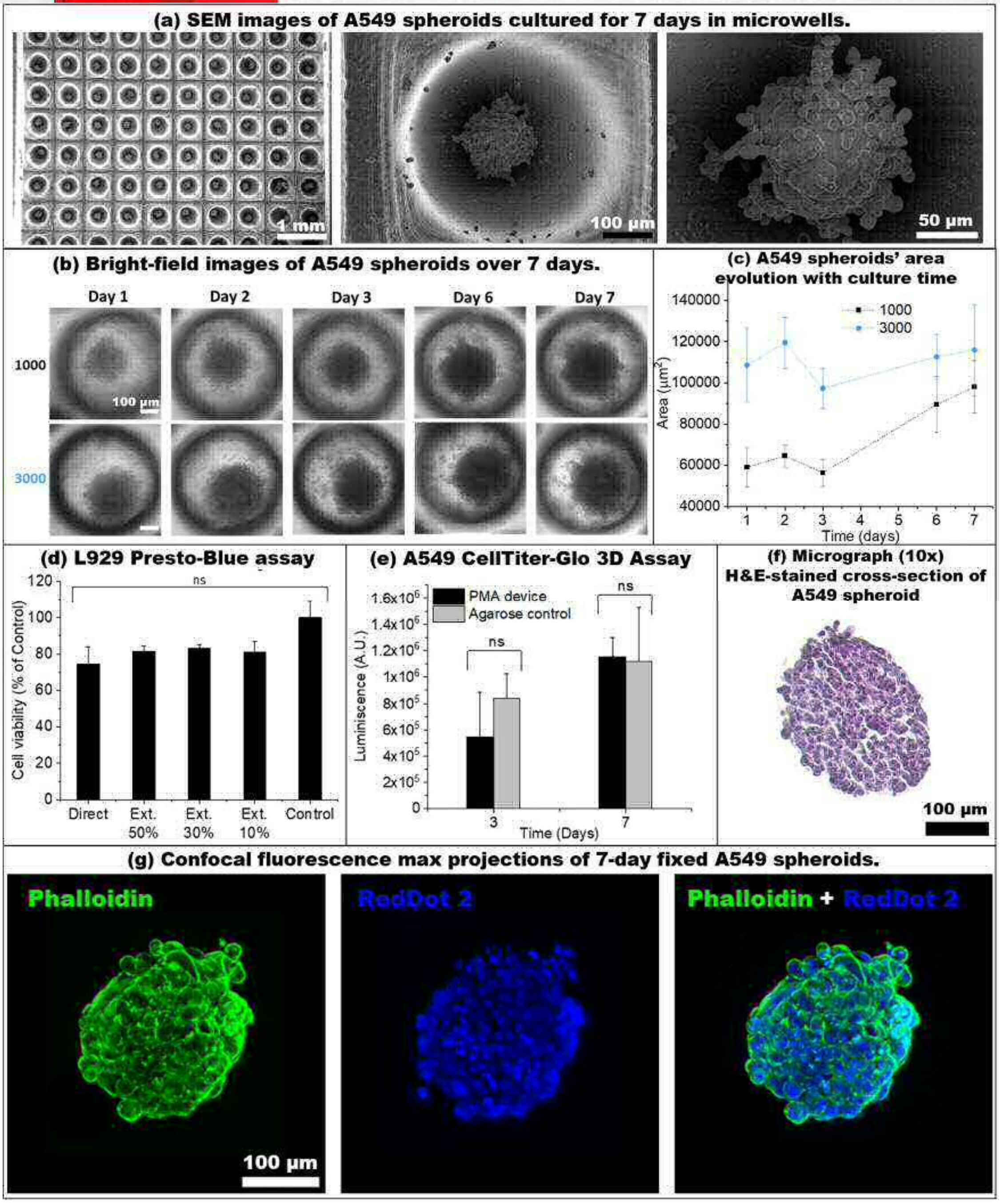

(a) Visualizing A549 spheroids cultured for 7 days in microwells is achieved through SEM images. Spheroids, created with a cell density of 1000 cells per well, exhibit observable morphology, size, and shape. (b) Bright-field microscope images of A549 spheroids on day 1, 2, 3, 6 and 7 at different cell densities (1000/3000 cells/well). (c) The change of spheroids' area with cell culture time. Data represent the mean ± standard deviation (SD) of one experiment ($n = 20$). (d) PrestoBlue assay on L929 cells to determine their tolerance to PMA material and extracts at different concentrations (50%, 30%, and 10%). ns = Statistically not significant difference ($p > 0.05$) from positive controls. (e) Quantification of the metabolic activity of the cells in A549 spheroids after 7 d of culture by using the CellTiter-Glo 3D Cell Viability Assay ($n = 3$). ns = Statistically not significant difference ($p > 0.05$) from positive controls. (f) Microscopic images of 5 um slices of A549 spheroids stained with hematoxylin and eosin showing cell nuclei in dark purple and ECM and cytoplasm in pink. (g) Confocal fluorescence microscopy maximum intensity projections of fixed A549 spheroids cultured for 7 days. Cell density is 1000 cells per well. Utilizing RedDot 2 (blue) and phalloidin (green) staining, cell nuclei and cytoskeletons are distinctly marked. The merged phalloidin/RedDot 2 channels image is presented in the right panel.

CONDUCTIVE TISSUE ENGINEERED SCAFFOLDS FOR SPINAL CORD INJURY REPAIR

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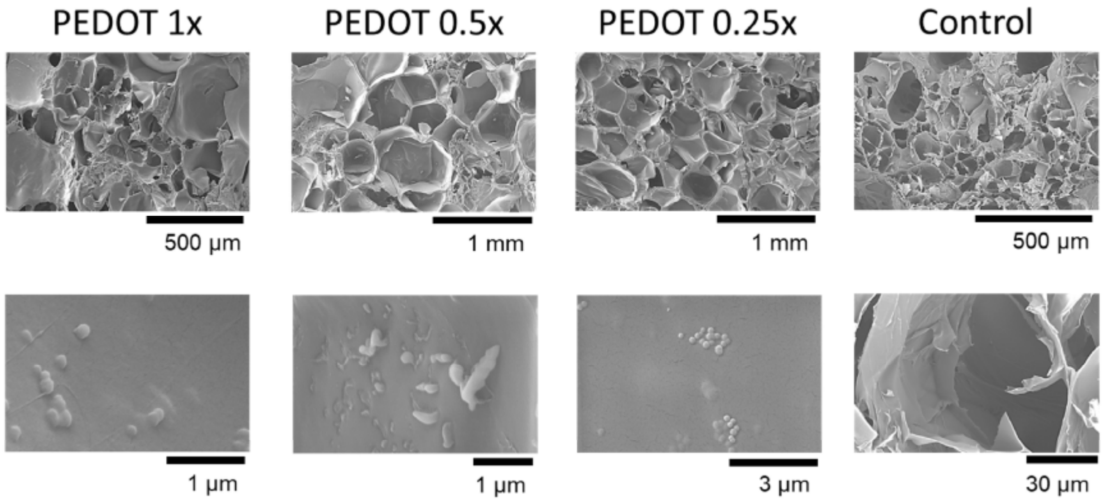
Introduction

Spinal cord injury (SCI) is a debilitating disorder which results in paralysis, with no effective treatment. Tissue engineering (TE) has emerged in the form of conductive biomaterials. It has been known for decades that cells are affected by electrical stimulation, especially cells of a conductive nature such as spinal or nerve cells. The application of conductive TE scaffolds to SCI models aims at repairing and improving the growth and signalling of damaged spinal cells by facilitating electrical stimulation. The major drawbacks of using standard conductive additives arise from low conductivity in neutral pH, insolubility in water and poor biocompatibility. To overcome these limitations, the conductivity of the biomaterials was inferred through the incorporation of novel electroconductive additives such as carbon nanofibers (CNFs), and Poly (3,4-ethylene-dioxythiophene) (PEDOT) and polypyrrole (PPy) nanoparticles synthetised via the mini-emulsion method, as well as naturally present ions to develop ionic based conductivity in completely biodegradable conductive scaffolds. Further incorporation of the CNF/NPs/ions with bioactive components such as gelatin and hyaluronic acid allowed for the development of novel electroconductive biomaterials.

Methodology

Compression, conductivity, FTIR, swelling studies, rheology, 3D printing, in-vitro and in-vivo biocompatibility studies. In-Vitro and In-Vivo Biocompatibility Assessment: Scaffolds were seeded with Mesenchymal Stem Cells. After 96 h, the cells were stained with a LIVE/DEAD assay, as well as fixed in 4% paraformaldehyde, stained with DAPI and DiI and imaged. Implantation of scaffolds into Wistar rats was completed with a complete SCI transection model at T3 level.



SEM images of lyophilised gel:HA:PEDOT-NPs scafolds with diferent PEDOT NPs concentrations (1×, 0.5×, 0.25×and Gel:HA control with no NPs). A-Surface view of gel:HA:PEDOT-NPs scafolds. B-Internal Porosity. C-Magnifcation of PEDOT NPs on the internal surfaces of the gel:HA:PEDOT-NPs scafolds.

Results and conclusions

The CNF biomaterials displayed excellent mechanical results, with the addition of CNFs into the hydrogel increasing the Young's modulus and conductivity to 534.7±2.7 kPa and 4.1x10-4±2x10-5 S/cm respectively for the 5% w/v CNF hydrogel. The morphology of the synthetised PEDOT/PPy NPs was round and stable at 187 nm. The developed PEDOT/PPy NP scaffolds display biomimetic mechanical strength comparable to that of the native spinal cord at 1 MPa, while the conductivity of the scaffolds ranged up to 10-4 S/cm. In-vitro biocompatibility shows that the developed NPs, as well as the electroconductive scaffolds, facilitate MSCs cell proliferation and growth, with 86% viability. In-vivo testing in SCI rat models increased axonal migration towards the lesion, and decreased GFAP positive glial scarring, as well as decreased macrophage and microglia activation, showing great promise for SCI TE strategies.

Acknowledgments and References

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FULLY NATURAL AND FUNCTIONAL POROUS SORBENTS FOR SUSTAINABLE MATERIALS MANUFACTURED VIA POLYMER PROCESSING TECHNIQUES

Antonio José Capezza

KTH Royal Institute of Technology, Stockholm, Suecia

Introduction

Several industries and their respective application areas generate a high environmental impact, using fossil-based resources, generating microplastics, or using high-energy input materials/manufacturing techniques. For example, the sanitary industry market is reaching over 40.000 billion USD, increasing over the years.(1) The primary materials for disposable sanitary items are manufactured from non-biodegradable fossil-based resources, which have been shown that these can release toxic microplastics/PFAS if disposed of in nature. (2)

Methodology

Our approach is to use formulations based solely on proteins, polysaccharides, and lignocellulosic biomass as an alternative to producing fully natural porous functional networks, which can be useful in applications, including disposable sanitary items. The raw materials are obtained from agro-food industry co-streams, contributing to a circular economy and material valorization. Furthermore, the materials are produced as extruded porous filaments and manufactured as sanitary pads using compression molding, opening new avenues into developing porous structures in applications where porosity and encapsulation are required (e.g., GHG remediation materials).

Circular design of new porous sorbent materials in functional applications using biopolymers derived from agro-food waste.

Results and conclusions

All the formulations are plastic and chemical-free, relying on low-energy input manufacturing methods, while the degradation products have been demonstrated as environmentally safe. From the perspective of liquid absorbents, the systems resulted in high and rapid swelling capacity in water, saline solution, and blood, and the swelling uptakes resulted in a ca. 500 % weight increase. The material configurations allowed for blends that resulted in 50 % hydrolytic degradation after 7 days, allowing for the deigning of a future sanitary item that can be flushed. In addition, the material resisted mould growth by adding hydrophobic proteins, providing storage properties to the products. The high-scalable production of bio-based and environmentally friendly materials with potential use as sanitary items and new potential applications to be explored in our recent projects provides an economical and sustainable alternative for producing single-use articles that do not contribute to waste accumulation and do not release harmful leachates to the environment.

Acknowledgments

BioRESorb (FORMAS, Sweden) and PORBioSorb project (M-era.Net 2023 - CSIC, UCLM, Tetis Biotech, IVL, BioExtrax and MedClair) are acknowledged for their contributions to this research and joint projects.

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OXIME METATHESIS: TUNEABLE AND VERSATILE CHEMISTRY FOR DYNAMIC NETWORKS

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Introduction

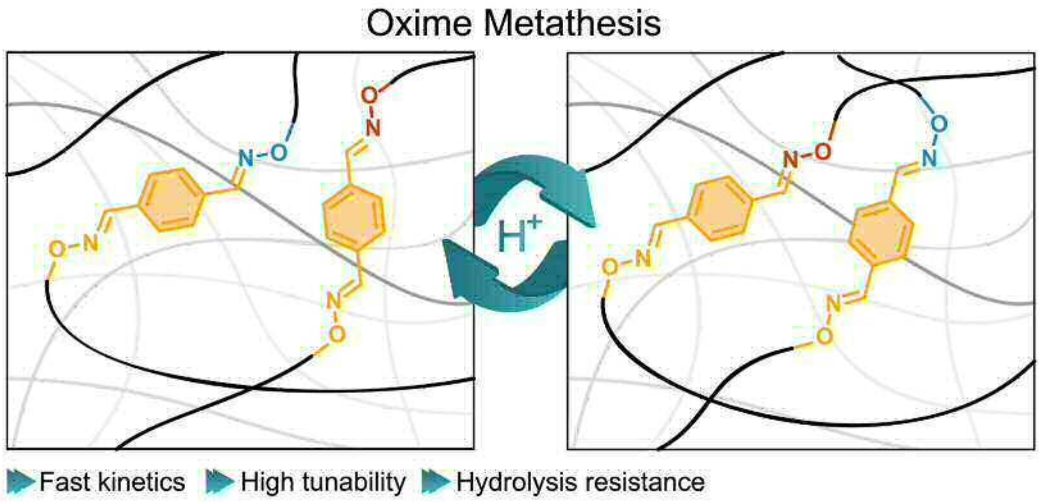
Oxime chemistry has emerged as a versatile tool for use in a wide range of applications. In particular, the combination of oximes with esters and urethanes has enabled the realisation of Covalent Adaptable Networks (CANs) with improved and tunable dynamic properties. [1,2] Nevertheless, an exclusively oxime-based chemistry has not yet been explored in the fabrication of CANs. [3,4]

Methodology

In this work, we investigate the mechanism of the acid-catalysed dynamic exchange of oximes both experimentally and theoretically.

Results and conclusions

We demonstrate an acid-catalyzed metathesis exchange which then we apply in oxime-based vitrimers. The obtained networks are dynamic and can be reprocessed upon heating.



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NANOCELLULOSE-BASED CRYOGELS FOR SUSTAINABLE CULTURAL HERITAGE CONSERVATION

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Introduction

In the last years, the interest in developing effective technologies, tailored materials, and innovative solutions for the conservation of cultural heritage has increased. Currently, developing innovative conservation products that are environmentally friendly and safe for operators remains a serious challenge. Green Chemistry principles that incorporate a life-cycle mindset are becoming key drivers in the development of environmentally sustainable materials for cultural heritage conservation. In particular, bio-based polymers, mostly from lignocellulosic origin, show widespread uses in this field. Our aim is to propose novel sustainable nanocellulose-based materials that show promising properties in the field of art conservation. Besides, the application of these materials has been validated.

Methodology

Nanocellulose-derived cryogels are produced using green cross-linkers and aqueous solutions, instead of conventional methods that involve glutaraldehyde. In particular, dialdehyde cellulose is obtained from cellulose nanocrystals (CNCs), and the effect of modification on the cross-linked materials is evaluated. Additionally, a life-cycle assessment (LCA) is carried out to account for environmental impacts. A cradle-to-gate boundary is established to consider raw material acquisition and cryogel synthesis, and the analysis is performed using OpenLCA software and ecoinvent v3.9 database. The impacts in a wide variety of categories are obtained according to ReCiPe 2016 Midpoint.

Results and conclusions

Our studies suggest that natural diols and triols are effective for the cross-linking of CNC-derived dialdehyde cellulose. Upon freeze-drying, the material can absorb up to 2800% of its mass in water, allowing for salt removal efficiencies of 98.0-99.5% after 3 cycles of only 5 minutes of application onto Roman wall painting mock-ups. Importantly, Energy-Dispersive X-ray Fluorescence mappings confirms that salt removal is uniform throughout the entire thickness of the mock-ups. A CO2 footprint of approximately 50 kg CO2 eq/kg is obtained for cellulosic aerogels, indicating potential for a low-emission material. Overall, the obtained results are encouraging for the removal and cleaning of exogenous materials, such as salts and airborne particulate matter, from wall and canvas paintings.

Acknowledgments

This work has been supported by grant TED2021-129299A-I00, funded by MCIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR. This last grant also funds

RECYCLABLE PHOTORESINS FOR LIGHT-MEDIATED ADDITIVE MANUFACTURING: LOOP 3D PRINTING

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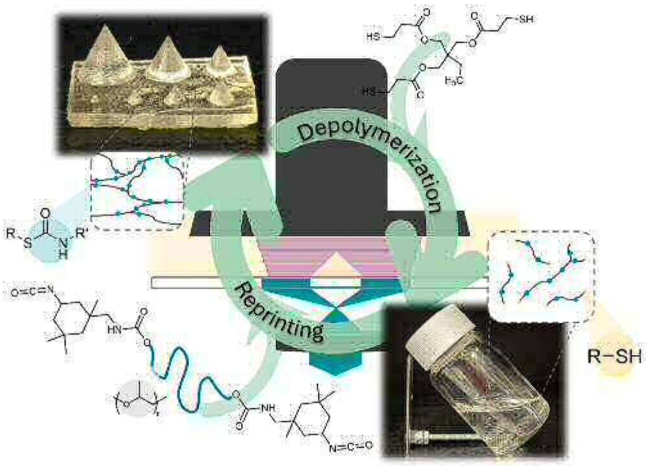
Introduction

Additive manufacturing (AM) of polymeric materials enables the manufacturing of complex structures for a wide range of applications. Among AM methods vat photopolymerization (VP) is desired owing to improved efficiency, excellent surface finish, and printing resolution at the micron-scale. Nevertheless, the major portion of resins available for VP are based on systems with limited or negligible recyclability. Here, we describe an approach that enables the printing of a resin that is amenable to re-printing with retained properties and appearance.

Methodology

For that, we take advantage of the potential of polythiourethane chemistry, which permits the click reaction between polythiols and polyisocyanates in the presence of organic bases, that were liberated on demand by the use of photobase generators.

Results and conclusions



We have investigated the efect of various thiol-isocyanate formulations selecting the most promising ones for their application in vat photopolymerization. By the optimization of printing conditions such as layer exposure time and resin composition fast-printing process was obtained both in the macroscale using digital light processing and in the microscale using direct laser writing. However the resulted prints enabled their chemical recycling, reshaping, and reparation , paving the way toward the development of truly sustainable recyclable photoprintable resins. In summary, we have demonstrated a simple yet versatile platform for recyclable and 3D printable resins based on a thiol-isocyanate polymerization reaction requiring minimal synthetic effort. In particular, the photobase generator activated formulation allowed the fabrication of both macro-featured and micro-featured structures in reasonable time via commercially available DLP or two photon DLW 3D printers, respectively. The stability and photorheological behavior along with the chemical and thermomechanical properties of the prepared materials were studied. Additionally, the dynamic nature of the thiourethane bonds in the network backbone permitted the reparation and chemical recycling of printed structures with identical properties. In particular, the addition of a thiol monomer to printed samples in basic conditions generated thiol terminated oligomers which were utilized to produce reclaimed materials. This process allowed for the unprecedented closed-loop 3D printing of the resin formulations with reduced waste as a circular approach. We therefore believe that this contribution is a significant advancement in the field of sustainable AM.

Acknowledgments and References

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POLIMERIZACIÓN EN SUPERFICIE DE AGRO-RESIDUOS PARA FABRICACIÓN ADITIVA DE MATERIALES COMPUESTOS SOSTENIBLES

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Introducción

El desarrollo de productos más sostenibles es una demanda creciente tanto por parte de la industria como de la sociedad. Un enfoque es reducir el contenido de plásticos derivados del petróleo reemplazándolos con un compuesto bio-basado, de modo que se reduzca su huella de carbono. Otra alternativa es la valorización de agro-residuos integrándolos en nuevos materiales, en un marco de economía circular. La combinación de estas dos estrategias con tecnologías de fabricación aditiva permite generar nuevos materiales y productos sostenibles y atractivos para el consumidor. [1, 2]

Metodología

Se usó polvo de corcho (C) y de hueso de aceituna (HA) como materiales de partida. Estos agro-residuos se hidrofobizaron mediante reacciones de polimerización en superficie, tanto de polimerización radical como policondensación. Después se integraron en varias concentraciones (5 – 15 %p/p) en matrices poliméricas de ASA y PETG mediante extrusión doble husillo y se imprimieron mediante modelado por deposición de fundido empleando tanto filamento (FFF) como granza (FGF). La influencia de la modificación superficial se evaluó mediante ensayos de tracción y microscopía electrónica de barrido (SEM). En el caso del corcho además se estudió su influencia en la conductividad térmica del material.

Resultados y Conclusiones

En este trabajo se demuestra que la modificación superficial, tanto del C como del HA, mediante polimerización en superficie permite compatibilizar estos agro-residuos con la matriz polimérica en la que están embebidos. Esto facilita la impresión 3D de los materiales compuestos, disminuyendo la viscosidad del fundido y mejorando su procesabilidad. Además, también se demuestra que los materiales compuestos con C y HA modificados tienen mejores propiedades mecánicas, dado que estos aditivos se encuentran más dispersos en la matriz polimérica, disminuyendo la aparición de puntos de nucleación de grietas. En conclusión, este trabajo demuestra que la polimerización en superficie de distintos agro-residuos permite conseguir materiales compuestos más sostenibles: Por un lado, se disminuye el contenido de polímero derivado del petróleo y por otro se valoriza un agro-residuo sin que disminuyan significativamente las propiedades mecánicas del polímero matriz. [3]

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INJECTABILITY OF MACRO-HYDROGELS: DEVELOPMENT OF HYALURONIC ACID GRANULAR FORMULATIONS

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Introduction

Hyaluronic acid (HA) is a non-sulphated glycosaminoglycan found naturally in the human body, such as connective tissue, skin, and synovial fluid. This polymer has been extensively studied to produce chemically cross-linked hydrogels, which allow the modulation of mechanical properties, the addition of new functionalities and the prolongation of residence time in the human body. They are promising candidates in various biomedical fields, for example as scaffolds for tissue engineering or carriers for drug or cell deliver [1]. Hyaluronic acid hydrogels has attracted attention in the las decades in the aesthetic field as volume fillers, where stand out as the second non-surgical procedure in the world by plastic surgeons in 2022, with more than 4 million treatments [2][3]. Nowadays, there is a growing demand for injectable hydrogels as they can be administered through needles or small cylinder cannulae, thus avoiding invasive surgery.

Methodology

In this work, we optimized a methodology for the development of injectable granular hydrogels chemically crosslinked by thiol Chemistry [4]. To this end, hyaluronic acid was modified with thiol groups. Subsequently, macro-hydrogels were produced through disulfide bond formation and Michel addition type reactions using PEGs derivatives. Hydrogels were fully characterized as to their viscoelastic properties and hydrolytic stability. Finally, the material was mechanically fragmented and sterilized to produce injectable formulations

Results and conclusions

The resulting formulations exhibited characteristic properties such as shear thinning, recovery after deformation, microporosity and stability. This simple and inexpensive technique multiplies the applications of conventional hydrogels by allowing their injectability

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BIOMIMETIC LINEAR-DENDRITIC HYBRIDS FOR ADHESION: DENDRITIC EFFECT AND SKIN ADHESION

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Introduction

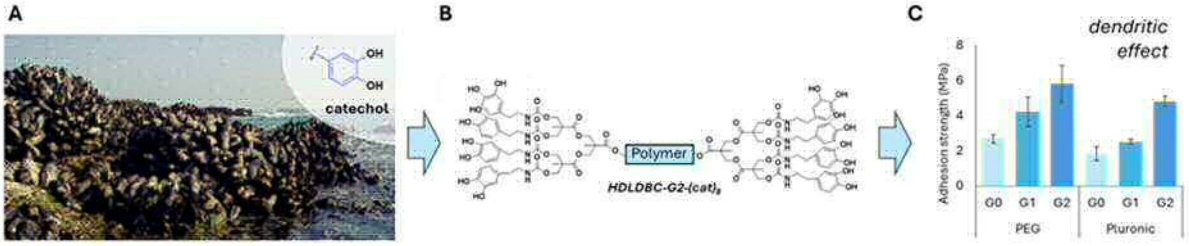
Catechol moieties are found in several proteins secreted by mussels and other bivalves. These proteins, named mussel foot proteins (mfps), allow the mussels to firmly stick on the sea reef in a large variety of conditions and environments (Figure 1A). Indeed, catechols can foster strong adhesive interactions with the reef by means of H-bonding, π-π stacking, metal chelation and covalent bonding. [1] Hence, mimicking the mussels foot proteins, a library of catechol-containing copolymers has been synthesized.[2] These polymers showed good adhesive properties when used in dry conditions and impressive adhesive properties when used underwater. In particular, poly(vinylcatechol-styrene) showed underwater adhesion up to 3 MPa on aluminum substrates, overpassing all the other commercial adhesives tested.[3]

Methodology

In the present work, we designed and synthesized two series of Hybrid Dendritic-Linear-Dendritic Block Copolymers (HDLDBCs) based on: (i) either poly(ethylene glycol) or poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol), aka Pluronic® F-127, (ii) 2,2-bis(hydroxymethyl)propionic acid and (iii) terminal catechols (Figure 1B). Their adhesive forces were tested in dry conditions on aluminum substrates and on porcine skin using a Instron 5544 materials testing system.

Results and conclusions

The hereby presented HDLDBCs showed good adhesive properties on aluminum substrates with values up to 7 MPa. Interestingly, a clear dendritic effect was observed with adhesion strength values increasing with dendron generation for both series (Figure 1C). Additionally, Fe(III) was added to the HDLDBC formulations in order to reinforce adhesion via crosslinking. Also, these HDLDBCs were applied onto porcine skin to study their abilities to be used as biomedical adhesives. Pluronic® derivatives displayed adhesion on skin, with values up to 2 kPa. These values were similar to those of Tisseel, a commercial FDA-approved tissue sealant, paving the way for a possible future application of this HDLDBCs in biomedicine.



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SURFACE-FUNCTIONALIZED THERMOPLASTIC ELASTOMERS AND HUMAN STEM CELLS: A COMBINATORIAL APPROACH FOR NERVE TISSUE ENGINEERING

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Introduction

Thanks to their biodegradability, biocompatibility and tunable mechanical properties, poly(L-lactide-co-ε-caprolactone) copolymers (PLCLs) have attracted enormous interest in the field of tissue regeneration. Their thermoplastic behavior further allows the surface nanopatterning, which can modulate stem cell fate. We have previously demonstrated the capacity of nanostructured PLCL films, functionalized with polydopamine (PDA) and graphene oxide (GO), to support cellular adhesion and differentiation of neural stem cells, as well as a proper biocompatibility with human stem cells.1,2 The main objective of the present work is to study the behavior of human embryonic stem cells (hESCs; ES-2) and induced-pluripotent stem cells (hiPSCs; KiPS-4F-1) on these materials, to evaluate the potential of this combinatorial approach on the field of neural tissue engineering.

Methodology

Nanostructured PLCL films were fabricated and subsequently functionalized with PDA and GO. The obtained material was thoroughly characterized in terms of morphology, physico-chemical and mechanical properties. Cell viability and proliferation assays were utilized to evaluate the biocompatibility of the materials with ES-2 and KiPS-4F-1 cell lines. Immunofluorescence and scanning electron microscopy (SEM) were used to assess cells alignment and migration. RT-qPCR and immunostaining were applied to analyze the pluripotency and differentiation capabilities of the cells.

Results and conclusions

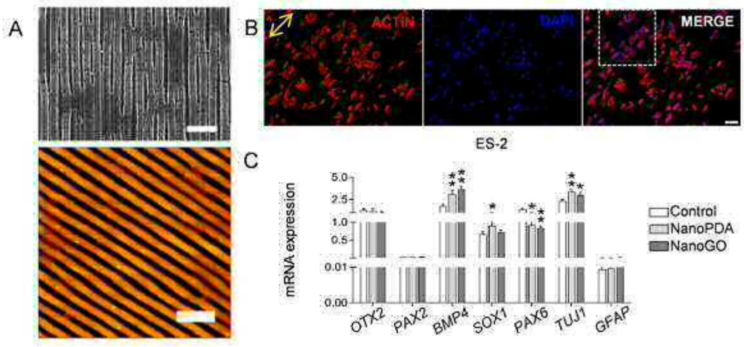

Figure 1: (A) SEM (upper) and AFM (down) micrographs of nanostructured PLCL films functionalized with PDA and GO (NanoGO) . Scale bars, 2 µm. (B) Immunofluorescence micrographs showed hESCs guided alignment in NanoGO structure by the expression of actin protein (red). Scale bar, 100 µm. (C) RT-qPCR results in OTX2, PAX2, BMP4, SOX1, PAX6, TUJ1 and GFAP genes expression that indicate the hESC ectodermal specification. Data are expressed as the means ± SD. (*) Comparison between PDA/GO and control conditions.*p<0.05, **p<0.01, ***p<0.001.

Elastomeric PLCL films functionalized with PDA and GO showing a nanostructured surface were satisfactorily fabricated by thermoplastic techniques (Figure 1A).1 The surface-functionalized nanostructures allowed the proliferation of ES-2 and KiPS-4F-1 cells, even though GO incorporation triggered partial cells apoptosis. The presence of the nanotopography allowed cell attachment, resulting in an ordered cellular distribution along the grooves (Figure 1B). Moreover, the scaffolds maintained and enhanced the pluripotency ability of these stem cells, along with a promotion in their specification towards the neuroectoderm germ layer (Figure 1C). These findings demonstrate the potential of these materials to promote the commitment of hESCs and hiPSCs towards neural lineages, thus supporting the progress in the field of cellular therapy for nerve tissue regeneration.

Acknowledgments

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FIBROUS PLA/FE3O4 NANOCOMPOSITE MATERIALS PREPARED BY SOLUTION BLOW SPINNING AND ELECTROSPINNING: A COMPARATIVE STUDY OF THEIR MECHANICAL BEHAVIOR

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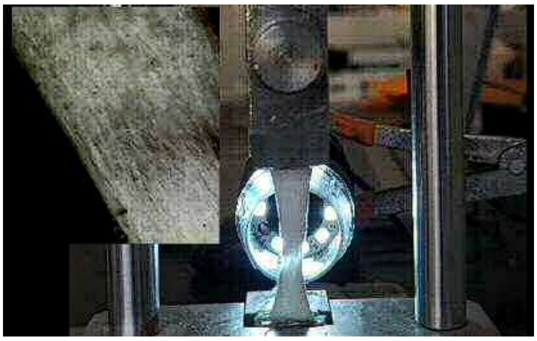
Introduction

Micrometric or even submicrometric polymeric fibrous materials are gaining attention in the fields of wound dressings and scaffolds for tissue engineering [1,2]. They are easy to apply and adaptable to different surfaces, they have a high surface to volume which enhances the interaction material-cells or tissues. Their porosity facilitates nutrients transport and exudate transfer. However, additional properties such as biocompatibility, biodegradability, and mechanical consistency are also crucial. Although for both wound dressings and scaffolds structural integrity is essential, to have other special properties like antibacterial behavior and responsiveness to external stimuli would be also desirable. In this sense, modification of this materials with nanoparticles is a possibility and, among them, magnetic nanoparticles have great potentiality. When subjected to the action of external magnetic fields, they can behave as actuators while, the application of alternating magnetic fields can induce local heating, enabling their use in hyperthermia treatments. Nowadays, although the most commonly used method to prepare nanofibrous materials is electrospinning, solution blow spinning is receiving much attention because of its versatility, low cost and interesting advantages, including high production rates. As far as we know, there is a lack of research focused on understanding the differences between materials prepared by these two different methods. This research aims to address this gap by preparing fibrous materials using both methods. Fibrous materials based on polylacticacid (PLA) modified with Fe_3O_4 nanoparticles have been prepared by ES and SBS, respectively. A morphological and structural analysis was conducted on these two types of materials to understand their mechanical behavior differences.



Methodology

Fibrous PLA filled with Fe_3O_4 magnetic nanoparticles at different concentrations were prepared by ES and SBS. Morphology was studied by field emission scanning electron microscopy. Structure was studied by Fourier transformed infrared spectroscopy and X ray diffraction. Mechanical behavior was studied carrying out tensile tests with a universal testing machine.

Results and conclusions

SBS materials are constituted by thinner fibers than those obtained by ES. In both cases there is a quite uniform dispersion of the nanoparticles within the fibers although certain degree of particle aggregation was not avoided. ES samples showed higher ability for plastic deformation than SBS samples. This behavior can be explained from the differences observed in both, morphology and structure.

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PH-RESPONSIVE AMPHIPHILIC HOMOPOLYACETAL DERIVED FROM GREEN SOLVENT CYRENE

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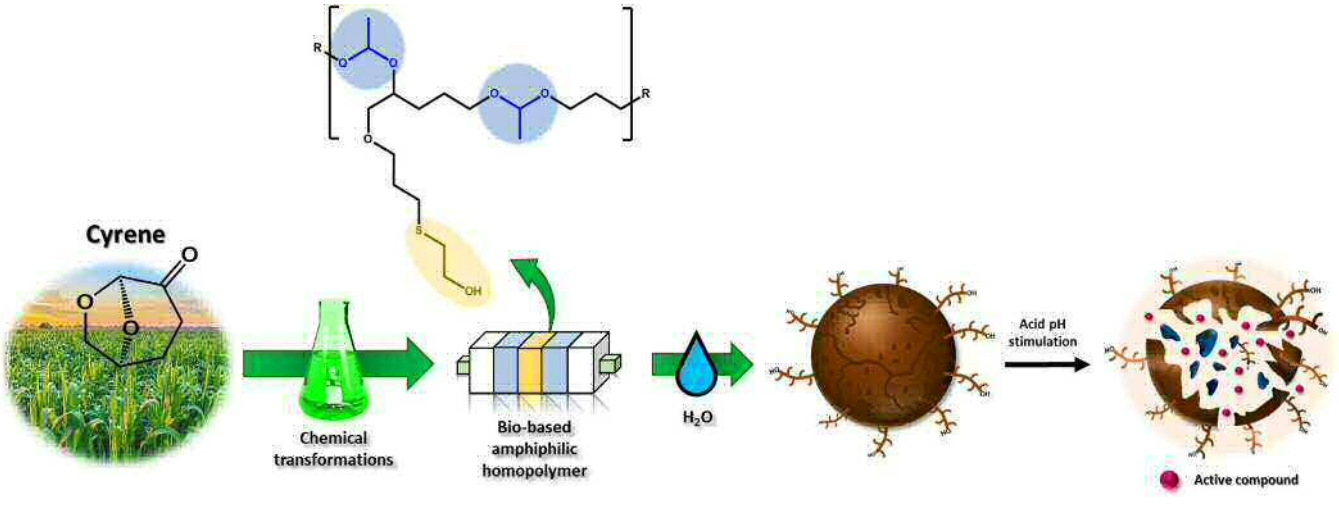
Introduction

To advance the development of hydrolytically degradable functional polymers in a more sustainable manner, we have synthesized and fully characterized a novel amphiphilic homopolyacetal derived from Cyrene, considered a green solvent and eco-friendly alternative to toxic polar aprotic solvents such as DMF. First, a bio-based homopolyacetal was obtained by the polyaddition of an allylic-bearing diol derived from Cyrene with 1,4-butanediol divinyl ether (DVE). Second, bio-based amphiphilic homopolyacetal was created by thiol-ene click reaction with 2-mercaptoethanol. Thereafter, self-assembled in water to afford well-defined nanostructures was performed via solvent-exchange methodology The presence of acetal links in the structure was confirmed to be crucial for the polymer's stimuli-responsive behavior under biologically relevant conditions. More specifically, under acidic pH conditions, the homopolymer underwent site-selective chain cleavage, causing agglomeration and breakdown of the nanoassemblies. Finally, encapsulation and release studies of active molecules confirmed the potential of this Cyrene-derived homopolyacetal for drug delivery applications.

Methodology

Schlenk line techniques applied for synthesis of monomer and polymer. NMR and SEC analysis were used to characterize the amphiphilic homopolymer. DLS and TEM analysis were performed to characterize the nanostructures, and fluorescence experiments were carried out for the study of the potential applications.



Scheme 1. Cyrene used as a precursor to access pH-responsive amphiphilic homopolyacetal for drug delivery applications.

Results and conclusions

The functionalized diol was achieved from Cyrene with 3-step reaction synthesis in high yield. The kinetic studies of the polymerization reaction demonstrate that after 6h an homopolyacetal can be obtained with 97% of conversion and a molecular weight of 16,500 g/mol. Amphiphilic polymer was successfully prepared via thiol-ene click reaction and characterized by NMR and SEC. DLS measurements confirm the formation of stable and monodisperse nanoparticles with a size between 178-180 nm. The analysis of aqueous nanoassemblies dispersion by TEM showed the presence of well-defined spherical shape nanoparticles with different average diameters. DLS measurements confirm the stimuli-response that Cyrene-derived nanoparticles show at acidic pH. A change in the size of the nanoparticles at acidic pH confirms a first swelling of the nanoassemblies, followed by its breakdown after 24h. Encapsulation and release of curcumin as model drug compound was confirmed by fluorescence measurements. After 15h, 90% of the curcumin has been released.

Acknowledgments

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SURFACE MODIFICATION OF PLA-BASED ELECTROSPUN NANOFIBERS MATS WITH HYDROPHILIC POLYMERS.

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Introduction

The electrospinning technique permits the production of fibers from a polymeric solution. Polylactic acid (PLA), a biodegradable and bio-based polymer, is widely used to fabricate electrospun nanofibers mats. However, it is characterized by high hydrophobicity and lack of binding sites. These drawbacks can be improved by depositing a hydrophilic polydopamine (PDA) coating, which presents abundant functional groups that can bind with different substrates [1]. Thus, polyethyleneimine (PEI), which contains primary, secondary and tertiary amines, can react with PDA, improving the antimicrobial properties of the material surface [2]. These materials can find applications such as cleaning surfaces, antibacterial wear and surgical masks.

Methodology

1.5 and 3 wt% of dopamine (DA) relative to PLA were added to PLA solutions (10 wt%) in $CHCl_3$ and stirred at room temperature for 1h. DMF in a $CHCl_3$:DMF ratio of 4:1 was added before electrospinning. Electrospun fiber mats were prepared from solutions by applying a voltage of 20 kV and a flow rate of 1.0 mL h^{-1}. The two mats were cut into 2 cm squares and immersed in a solution of Tris (pH=8.5, 15mM) to obtain PDA-coated nanofibers (PDA1.5, PDA3), and in another similar solution but containing 2 mg mL^{-1} of PEI branched (PEIb), or PEI linear (PEIl), to obtain functionalized PDA-coated nanofibers. After 24 h, the substrates were thoroughly rinsed with deionized water and dried for 72 h in a vacuum chamber at room temperature.

Results and conclusions

The presence of the PDA coating on the substrate surfaces was confirmed by SEM analysis, also revealing the formation of small aggregates. FTIR analysis also showed typical absorption bands of PDA, and additionally, a band related to C=N group formed by Schiff-base reactions in PEIb and PEIl appeared. EDX-SEM analysis corroborated the presence of nitrogen in all of the substrates, which increased by increasing DA content. Furthermore, a significant increase in hydrophilicity of the functionalized PDA-based substrates was observed consistent with a drastic reduction of water contact angle. Antibacterial activity tests are being carried out on all coated and modified materials. Thus, a surface Live/Dead assay has been performed using *staphylococcus aureus* bacteria strain

Acknowledgments

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O-64

COMPREHENSIVE STRUCTURAL CHARACTERIZATION OF DEVULCANIZED RUBBER DERIVED FROM END-OF-LIFE TIRES.

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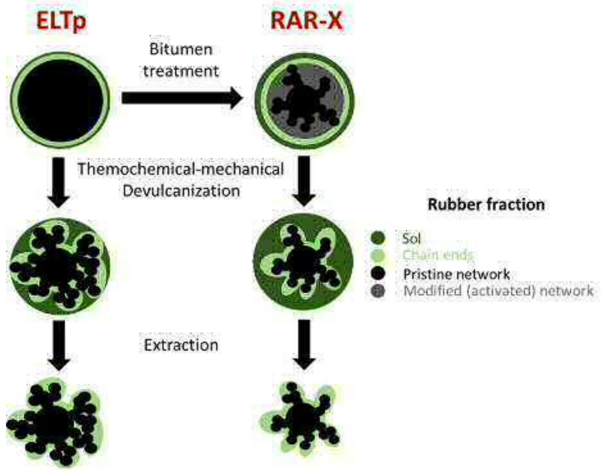
Introduction

Devulcanization processes are some steps forward in terms of sustainability and recycling for end-of-life tires (ELT) rubber. In this field, thermo-mechanical devulcanization methods are the most developed approaches to be exploited on an industrial scale because they allow the continued use of the synergy between thermal energy and high shear forces to break the sulfur bonds while trying to reduce the chain scission and degradation processes [1]. Despite the developments and efforts made in recent years in this field, the rubber devulcanization processes did not achieve the scientific-technical progress needed to reach the degree of devulcanization and selectivity required to be applied in high-content in products with demanding technical requirements [2].

Methodology

Pristine end-of-life tire rubber powder (ELTp) and bitumen-added ELTp (under the trademark RAR-X) were devulcanized via a thermo-mechanical process in an internal mixer. The sample characterization consists of the quantification of oils, additives, and soluble fraction of rubber after the devulcanization by solvent extraction. The structural parameters such as the cross-link degree and the fraction of defects were determined by using 1H DQ-NMR, and the fillers and rubber content were determined by thermogravimetric analysis.



Results and conclusions

The obtained results unveil that the addition of bitumen has a dramatic impact on the reactivity of ELT rubber promoting the devulcanization degree and evidencing that this commercially available product (RAR-X) is a promising alternative feedstock for industrial implementation of a thermo-mechanical process to obtain high quality and added value raw materials from ELT. From the distributions of residual dipolar coupling of RAR-X it can be observed that the devulcanized samples have shifted to the left, which represents a higher devulcanization degree (lower cross-link density), the sample that was thermomechanically devulcanized and extracted by solvents show shifting to the right compared to the pristine one, that behavior is explained by the fact that after the extraction process, the remaining structure is composed by fillers and more crosslinked rubber than the pristine sample.

Acknowledgments

Acknowledgement the financial support from Ministerio de Ciencia, innovación y universidades (RTI2018-096636-J-100, PID2020-119047RB-I00, PLEC2021-007793) and CSIC (EC-22-2021). The authors are members of the SusPlast platform from the Spanish National Research Council (CSIC).

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IMPACT OF ALIPHATIC GLYCOL CHAIN LENGTH IN POLYCAPROLACTONE BASED RANDOM COPOLYESTERS

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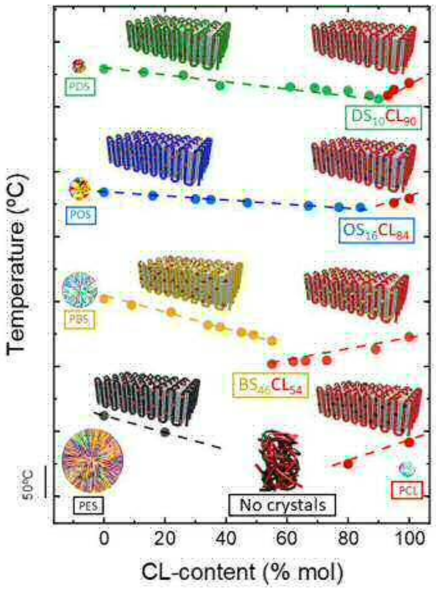
Introduction

Finding new biodegradable materials to avoid plastic pollution is of utmost importance. Aliphatic biodegradable polyesters are very promising in this respect, although in many cases, polymers like polycaprolactone (PCL) may have very slow degradation due to their high crystallinity degree. The properties of these materials can be improved by copolymerizing them with other biodegradable polymers. Recently, PCL-ran-poly (butylene succinate) (PBS) copolymers have shown interesting properties and applications thanks to their isodimorphic crystallization mode. These findings can be the starting point for investigating other PCL-ran-succinic acid-based polyester copolymers (PCL-SAP) [1] We have synthesized and characterized four series of biodegradable copolyesters: poly(ethylene succinate-ran-PLC) (ESxCLy), poly(butylene succinate-ran-PCL) (BSxCLy), poly(octylene succinate-ran-PCL) (OSxCLy) and poly(dodecylene succinate-ran-PCL) (DSxCLy). We have found that the comonomer structure (even succinate part) and composition are essential to determine the random copolyesters' thermal properties, structure, and crystallization modes.

Methodology

The synthesis of the copolyesters was carried out in the whole range of compositions by a first step of transesterification and ring opening polymerization (160ºC,6h,N2) and a second step of polycondensation (220ºC,6h,vacuum). Then, different characterization analyses were performed, such as differential scanning calorimetry, hydrogen and carbon nuclear magnetic resonance, gel permeation chromatography, synchrotron wide and small angle X-ray scattering, Fourier transform infrared spectroscopy, and polarized light optical microscopy.

Results and conclusions



Tailoring isodimorphic PCL-based copolymers properties by varying the chain lenght of the second comonomer

Resultados The isodimorphic behavior of copolyesters with different compositions has been analyzed. Despite not showing crystallization at intermediate compositions, the ESxCLy exhibited changes in its unit cell parameters; thus, it crystallized in a novel mixed isodimorphic/comonomer exclusion mode. The BSxCLy, OSxCLy, and DSxCLy did crystallize in the entire composition range, but with a depression of the melting temperature depending on the composition, leading to a V shape (pseudo-eutectic behavior) trend due to the inclusion/exclusion balance. In addition, as the length of SAP increases, the pseudo-eutectic point shifts to a higher CL content, highlighting the importance of the comonomer nature on the pseudo-eutectic position of the isodimorphic random copolymer. Conclusión The synthesis and characterization of biodegradable PCL-SAP was carried out. The structural properties of the synthesized copolymers showed isodimorphic behavior, depending on the chemical structure of the second copolymer. This chemical structure also influences the pseudo-eutectic point position, crystallinity, structural parameters, and thermal transition. Therefore, this dependence could tailor the PCL biodegradability and thermal and mechanical properties to different applications.

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SÍNTESIS DE BIOPOLIESTERES A PARTIR DE CO_2 Y FURFURAL

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Introducción

El polietilenterfetalato (PET) es uno de los poliésteres derivados del petróleo más utilizados pero tarda en degradarse más de 100 años. Así, encontrar una alternativa sostenible a los poliésteres derivados del petróleo es un objetivo prioritario. A partir de biomasa (azucares) se ha extraído hidroximetilfurfural (HMF, Figura 1a) y se ha sintetizado el diester metílico de furano (FMDE), monómero precursor del polietilenfuroato (PEF), sustituto sostenible del PET, ya que degrada en 1 año y ofrece mejores propiedades [1]. En este trabajo presentamos una estrategia más sostenible para la preparación de FMDE a partir de otra molécula extraída de azucares, el Furfural y CO2 (Figura 1b) que ha sido validado en la síntesis de polipropilenfuroato (CO2-PPF).

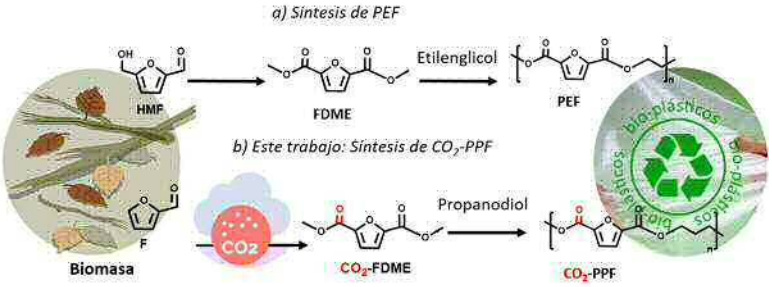

Figura 1. a) Síntesis convencional de PEF b) Contribución de este trabajo. Síntesis de CO2-PPF

Metodología

El CO2-FDME se obtuvo por oxidación (O2) seguida de carboxilación (CO2) catalizada por un polímero poroso hiperreticulado (HCP) de Cu, seguida de esterificación con metanol catalizada por otro HCP sulfonado. Los catalizadores fueron sintetizados por polimerización mecano-química en 1 h seguida de post-funcionalización para incorporar el cobre y los grupos sulfónicos. El biopoliester (CO2-PPF) se sintetizó reaccionando CO2-FDME con propanodiol. Con fines comparativos se sintetizó en mismo poliester (c-PPF) a partir de FDME comercial, derivado de petróleo.

Resultados y Conclusión

Los espectros de 1H-RMN de los dos poliésteres presentaron las mismas señales pero el de CO2-PPF indicó mayor pureza. El CO2-PPF exhibió mayor estabilidad térmica con una descomposición en una sola etapa a 340 ºC mientras que c-PPF mostró dos etapas de degradación, a 185ºC y 350ºC. La Tg de CO2-PPF fue de 40ºC mientras que para c-PPF fue inferior (23ºC). Ambas Tgs son inferiores a los reportadas, 47º [2] y 58ºC [3]. La DSC de CO2-PPF no mostró ninguna otra transición térmica como las reportadas [3] pero la DSC de c-PPF mostró cristalinidad y picos de fusión a 97ºC y 146ºC, respectivamente. En conclusión, se ha desarrollado una nuevo procedimiento termocatalítico para obtener FDME a partir de Furfural y CO2 y con el se ha obtenido el poliester CO2-PPF que mostró una mayor Tg y mayor estabilidad térmica que el PPF sintetizado a partir de FDME comercial. No presentó cristalinidad y se observó mayor pureza por 1H-RMN.

Agradecimientos

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IMPROVING PLA PERFORMANCE WITH BIOBASED PLASTICIZERS: TECHNOLOGICAL ASSESSMENT AND RAMAN SPECTROSCOPY ANALYSIS.

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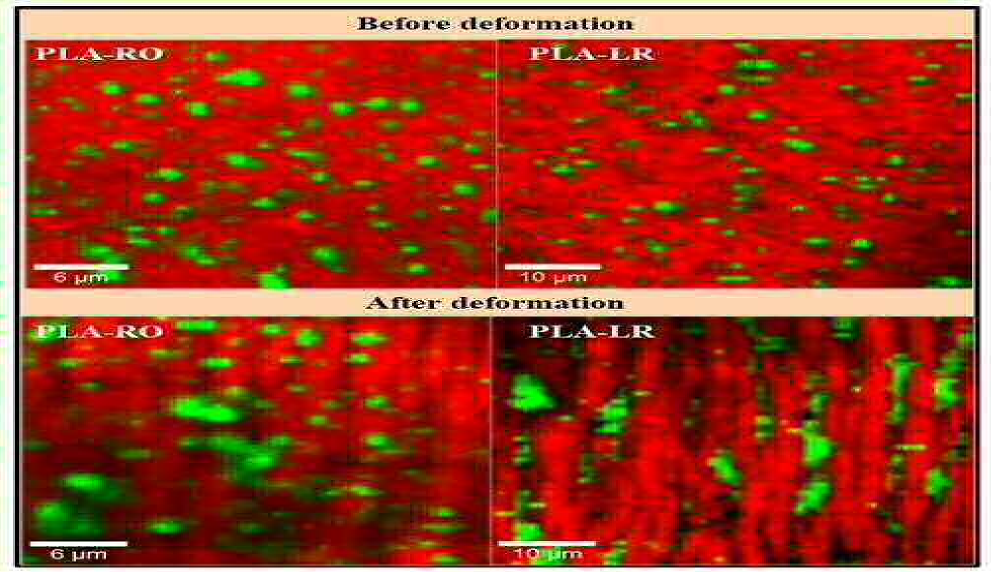
Introduction

Packaging plays a crucial role in protecting, preserving, and containing food throughout the supply chain. However, the migration of unwanted substances from the packaging to the food can negatively affect its safety and quality. Bio-based plasticizers are products that come from biological sources, and their interest comes from their low toxicity and minimal migration. Different derivatives of critic acid bearing free carboxylic acid groups (CITREM-RO, CITREM-VE, CITREM-LR and CITREM-SP), usually used as food additives, were evaluated for the first time as bioplasticizer and compared with another biobased and safe plasticizer, SOFT-NSAFE, which is an acetic acid ester of monoglycerides

Methodology

PLA films containing 10% of biobased plasticizers CITREMs and SOFT-NSAFE were prepared by melt extrusion and compression molding. Thermal properties of plasticized films were evaluated by conventional techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), while the mechanical properties were studied by tensile testing and microhardness; wettability of the samples was also studied by contact angle method. Finally, the antimicrobial properties were evaluated by the standard method E2149-13a against S. aureus and L. innocua and antioxidant properties were analyzed by Bloid's method. To obtain more complementary information about the technological performance of the samples, Raman confocal microscopy was used.

Results and conclusions



Raman microscopy photo of the plasticizer microdomains before and after the tensile test

The results showed that among the CITREMs, the incorporation of CITREM-LR compared to the other plasticizers gives to the films higher antioxidant properties, antimicrobial activity against food-borne bacteria and an enhancement in the mechanical properties, while the thermal properties are almost maintained. The increase in the mechanical properties is attributed to the segregation in microdomains, studied by Raman spectroscopy; segregation that is present in all PLA-CITREM samples. Additionally, CITREM-LR microdomains exhibit higher ductility and can be orientated in the stretching direction. Meanwhile, SOFT-NSAFE compared with CITREM-LR provides lower antioxidant and antimicrobial properties. While the miscibility of this plasticizer is higher and the formation of microdomains is not observed the mechanical properties do not improve significantly with its incorporation. Therefore, the results obtained in this work reveal the potential of these CITREMs as appropriated antioxidant plasticizers for PLA films and then, in its use as food packaging materials.

Acknowledgments and References

This work was supported by the EU H2020 Project, “Characterisation and Harmonisation for Industrial Standardisation of Advanced Materials” (CHARISMA), under Grant Agreement no. 952921.

ANÁLISIS COMPARATIVO ENTRE MOLDEO POR INYECCIÓN Y COMPRESIÓN APLICADO A MATRICES BIOPLÁSTICAS PARA FINES HORTÍCOLAS

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Introducción

El crecimiento de la población mundial requiere un aumento sustancial de la producción agrícola. No obstante, la fertilización, aunque esencial para aumentar el rendimiento de los cultivos, también contribuye a problemas medioambientales como el desequilibrio de nutrientes [1]. Como alternativa, surgen los fertilizantes de liberación controlada para hacer frente a estos problemas [2]. En este sentido, las matrices basadas en proteínas resultan prometedoras por su biodegradabilidad y su capacidad para mejorar la asimilación de nutrientes por las plantas (bioestimulación) [3]. Así, este estudio tuvo como objetivo principal la comparación de dos métodos para la fabricación de dichas matrices: moldeo por inyección y compresión.

Metodología

En este estudio, se empleó un aislado proteico de soja como materia prima y sulfato de hierro heptahidratado como sal portadora del nutriente. El procesado se realizó a diferentes presiones con la finalidad de optimizar el sistema, evaluando sus propiedades mecánicas mediante barridos de deformación y frecuencia en modo de compresión; químicas, mediante FTIR y determinación del grado de entrecruzamiento; morfológicas mediante SEM y, funcionales, determinando la capacidad de absorción de agua y pérdida de material soluble y las velocidades de liberación en agua y suelo

Resultados y Conclusiones

Los resultados mostraron que los sistemas procesados por inyección tienen módulos elásticos inferiores a los sistemas de compresión. No obstante, esta diferencia se contrarresta al aumentar las presiones. En cuanto a la microestructura, las matrices procesadas mediante compresión presentaron una mayor porosidad, siendo coherente con los resultados de las propiedades mecánicas. Las matrices comprimidas presentaron, además, una mayor capacidad de absorción de agua y una liberación del nutriente más controlada. En conclusión, la compresión permite obtener unas matrices más funcionales, en tiempos de procesados más cortos y, por tanto, con mejor perspectiva en el sector hortícola.

Agradecimientos

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EXPLORATION AND SYNTHESIS OF NOVEL POLYOLS OBTAINED FROM BIO-BASED DIOLS

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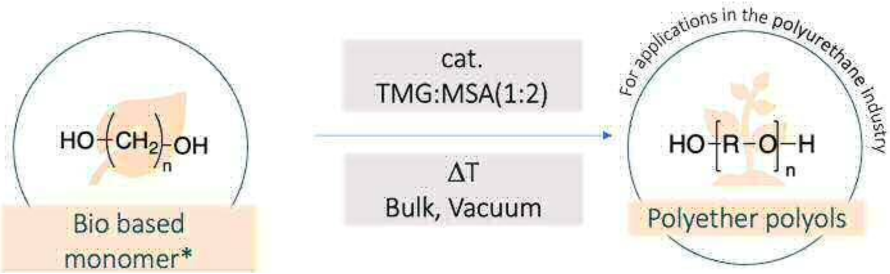
Introduction

Polyurethanes are one of the most important polymers in the world, being the sixth most produced in the world. Polyurethanes are synthesized by reacting polyols and isocyanates, which are typically fuel-based monomers. However, environmental concerns and CO2 releasing related to the extraction of fossil fuels demand a shift toward bio-based sources, such as biomass (1), to obtain new bio-based polyols as a greener alternative (2).

Methodology

Catalyst was prepared by mixing MSA (methansulfonic acid) and TMG (tetramethylguanidine) molar ratio of base to acid of (1:2). 0.025eq. of MSA/TMG (2:1 molar ratio) catalyst were mixed with bio-based diethylene glycol (DEG), 1,3-propanediol (PDO) or 1,6-hexanediol (HDO) in a Schlenk flask under vacuum. The sealed reaction was heated, varying the temperature from 130 to 180 ºC during 96 h. The scale-up of the polycondensation reactions was performed in a pilot reactor of 3 L. 0.025eq. of MSA/TMG organocatalyst were mixed with 1 kg of the bio-based monomer with mechanical stirring under vacuum. The co-polycondensation was carried out by mixing two of the previously mentioned diols in various molar ratios with the organocatalyst under the same conditions as previously reported.



Results and conclusions

PDO, HDO and DEG were synthesized through the model reaction already reported by POLYKEY. The innovative feature of the reaction is the use of an organocatalyst able to resist the high temperature required for the polycondensation of the diols. The organocatalyst was simply prepared by mixing 2eq. of MSA and 1eq. of TMG, resulting in the formation of a stable complex through a proton transfer from the acid to the base, to obtain TMG:MSA (1:2). The monomer conversion as well as the molecular weight were monitored through 1H NMR spectroscopy. The molecular weight was determined by the integration of the signal attributed to the repeating methylene protons of the etheric sequence. Additionally, the molecular weights of the homo- and co-polyethers were determined by SEC (Size Exclusion Chromatography). Conversions between 90-99% were obtained after 96 h of reaction. The homo and co-polymers presented molecular weights of 2 to 3 kDa. The thermal behaviour of all the synthesised polyethers was studied, obtaining a broad range of properties depending on the monomer(s) employed.

Acknowledgments

The authors would like to thank the Spanish government for their financial support through the project DIN2020-011536 of the Ministerio de ciencia e innovacion.

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SILICA BASED PARTICLES AS CARRIERS OF ADDITIVES FOR ENHANCING THE PROTECTION OF RECYCLED MATERIALS

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Introduction

Plastics are highly durable materials and can take hundreds of years to decompose. Without recycling, vast amounts of plastic waste end up in landfills, oceans, and natural environments, causing severe pollution. Recycling is an appropriate alternative, but antioxidants and other additives, as UV stabilizers, are necessary to prevent its degradation [1] during processing and during extension of their shelf life, allowing their use in more recycled cycles, thus contributing to the global sustainability and resources saving. Moreover, avoiding the migration of additives is a challenge [2], which can be solved by incorporation of different inorganic particles [3]. In this study, different amounts of the primary antioxidant Irganox 1076 (A), the UV stabilizer Cyasorb 531 (E), and a combination of them have been incorporated into the polymer matrix through their wet impregnation into two different silica-based particles: mesoporous MCM-41 (M) and nanopowder Aerosil 200 (nS). The prepared films have been exposed to an accelerated degrading test, and then they have been analyzed by means of gas chromatography (GC-MS), oxidation induction time (OIT) and infrared spectroscopy (ATR-FTIR).

Methodology

Recycled polypropylene-based blends and hybrid silica-additive particles (previously prepared by wet impregnation) have been mixed by melt extrusion in a mini-extruder. Then films were made by compression molding and characterized with different techniques. The effectiveness of the additives has been studied by evaluating the effect of an accelerated degrading test performed according to the standard ISO 4892-3.

Results and conclusions

The analysis of the films using GC-MS indicates a correct incorporation of the additives into de polymer matrix, while the OIT tests, carried out to evaluate the thermal stability of the films, show a higher performance of the materials containing Aerosil 200 compared to those with MCM-41. This behavior is observed in both the original materials and in those exposed to accelerated degradation test, as seen in Figure 1. Results also confirm the synergistic action of combined antioxidant and UV protector systems.

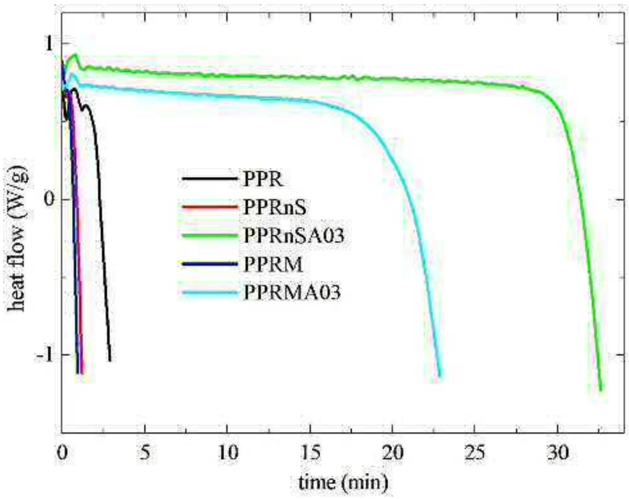

Figure 1. OIT results for PPR (pristine recycled polymer), PPRnS (4 wt.% nS), PPRnSA03 (4% nS and 0.3% of (A), PPRM (4% M), PPRMA03 (4% M and 0.3% of A).

Acknowledgments

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DETECCIÓN DE LA TENSIÓN DE TRACCIÓN EN COMPUESTOS REFORZADOS CON FIBRA DE VIDRIO CON MICROHILOS FERROMAGNÉTICOS INTEGRADOS

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Introducción

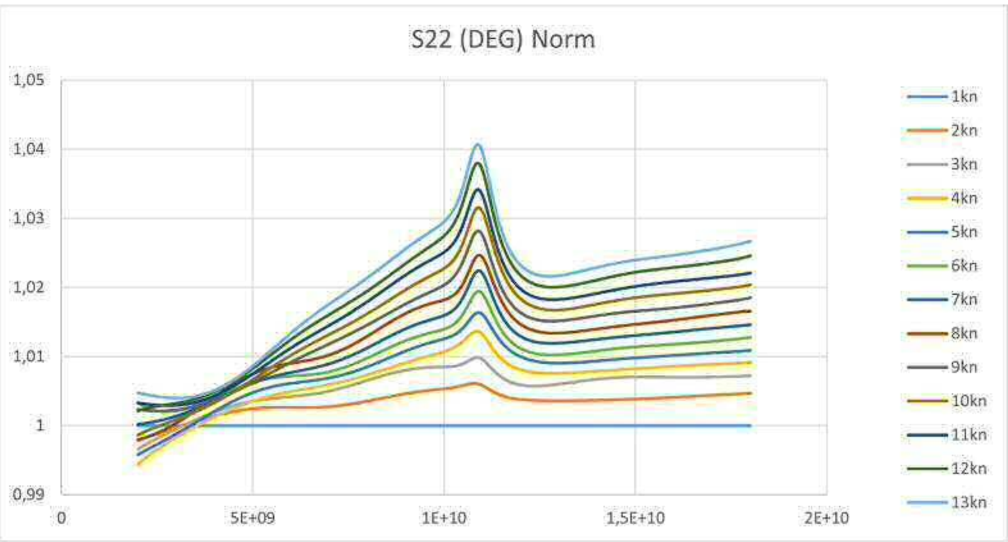
Los materiales magnéticos blandos se usan como sensores en la monitorización de múltiples procesos [1]. Se ha demostrado que los microhilos magnéticos muestran una magnetoimpedancia gigante (GMI) sensible a la tensión aplicada [2,3] y en estudios previos se ha determinado la evolución del ciclo de histéresis y los parámetros S de trasmisión y reflexión en el microondas durante la polimerización de la matriz de un material compuesto [4]. En este trabajo se presentan las variaciones de los parámetros S frente a una carga aplicada en probetas de composites con microhilos ferromagnéticos embebidos.

Metodología

Para la fabricación de las placas de composite con microhilos se ha usado un refuerzo de fibra de vidrio biaxial (NCF), una matriz epoxi y microhilos de CoFeSiB. Para las medidas del parámetro S se ha usado un VNA con las correspondientes antenas montados sobre una máquina de ensayos dinámicos, realizándose las medidas por la técnica del espacio libre. La normalización de los valores obtenidos para la amplitud y la fase de los parámetros de dispersión en reflexión y trasmisión (S11, S12, S21 y S22) permite analizar las diferencias.

Resultados y conclusiones

Tanto en los ensayos a fuerza constante como el aumento paulatino del esfuerzo se observa una clara y fuerte dependencia de los valores del parámetro S con la carga aplicada, planteándose nuevas alternativas que permiten monitorizar los esfuerzos de forma no destructiva y sin contacto.



Variación del parámetro de dispersión en reflexión (S22) normalizado frente a la fuerza aplicada

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PROPIEDADES VISCOELÁSTICAS DE LAS LÁGRIMAS HUMANAS Y ARTIFICIALES: UNA VISIÓN MICRORREOLÓGICA

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Introducción

El estudio de las propiedades viscoelásticas de las lágrimas humanas y los colirios artificiales es fundamental para comprender la fisiología ocular y desarrollar tratamientos efectivos para condiciones como la enfermedad del ojo seco. Hemos explorado estas propiedades utilizando microrreología pasiva basada en dispersión dinámica de luz, ya que son capaces de proporcionar detalles interesantes sobre su comportamiento en condiciones fisiológicas relevantes.

Metodología

Hemos investigado las propiedades reológicas de lágrimas humanas sanas y de colirios artificiales basados en polisacáridos. La técnica, que se basa en el movimiento de nanopartículas trazadoras en el interior de la muestra, proporciona una metodología muy interesante para explorar las características viscoelásticas de fluidos biológicos complejos en pequeños volúmenes. Se ha determinado la respuesta viscoelástica de las muestras en una amplia gama de condiciones, cubriendo, por primera vez, las frecuencias características del proceso de parpadeo. Aplicando la regla de Cox-Merz, hemos calculado la viscosidad newtoniana y el tiempo de relajación para cada muestra utilizando el modelo de Cross. El estudio va más allá, al realizar un análisis exhaustivo de la dependencia de la frecuencia de la viscosidad compleja en un rango de temperatura de 278 K a 313 K. Esta exploración tiene como objetivo descifrar el comportamiento viscoelástico en todo el espectro de aplicabilidad. Discutiremos los resultados obtenidos a la luz de las leyes de escala típicas observadas en las propiedades de disoluciones poliméricas, incluyendo polielectrolitos.

Resultados y Conclusion

Nuestro análisis facilita la comparación entre la huella viscoelástica característica de las lágrimas humanas y la obtenida para un conjunto diverso de lágrimas comerciales. Los hallazgos revelan un comportamiento no newtoniano en ambos casos, aunque con distinciones notables entre los diferentes sistemas. Los resultados obtenidos sirven como una puerta de entrada para obtener los parámetros reológicos básicos de las lágrimas humanas contribuyendo a la comprensión de sus propiedades viscoelásticas, y ofreciendo implicaciones para la salud ocular y posibles avances en la formulación de lágrimas artificiales.

Agradecimientos

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IMPROVED POLYURETHANE BASED ADHESIVES FOR SATIN XPS-SANDSTONE INSULATION PANELS.

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Introduction

Well isolated facades [1] are a key point to harness energy and to reduce the environmental impact of our societies. Extruded polystyrene panels (XPS) are excellent insulators [2], which can be combined with sandstone, a natural material that protects the XPS from atmospheric deterioration and improves aesthetical appearance with minimal environmental footprint. Polyurethane (PU) adhesives are suitable to fix XPS and sandstone together due to their excellent endurance [3], generally when using surface sanded XPS. In terms of cost saving and material waste reducing, 6 different PU-based adhesives have been developed to produce XPS-sandstone isolating panels from extruded "satin skin" XPS.

Methodology

Six PU-based catalyst-free adhesives were synthesized with different polyols. In a jacketed glass flask, 86 g of polymeric MDI were added with variable quantities of polyols of different molecular weights (~400, 1000 and 2000 g/mol) and 2 chemical structures (PEG and PPG), to maintain a 25% NCO index in every adhesive, i.e., the ratio between isocyanates and hydroxyl groups. After the mixture, it is magnetically stirred for 3 hours at 60 °C under a nitrogen atmosphere. The adhesive is applied with a roller and then the catalyzing solution, containing 0.330 mL of triethylamine in 5mL of water, is sprayed over before bonding XPS and sandstone.

Results and conclusions

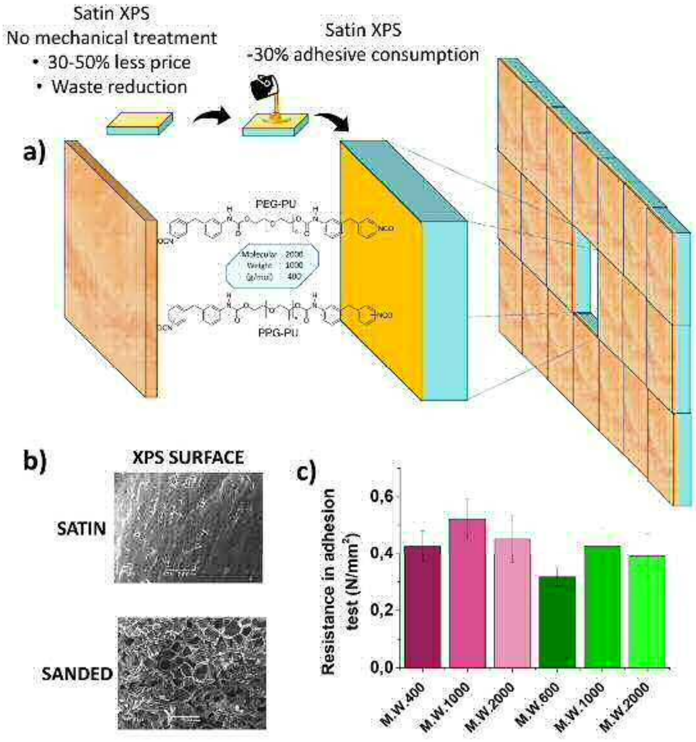

FIGURE 1. a) Insulating XPS panels concept, b) SEM image of XPS panels surface, and c) adhesion resistance results

There is a tendency that around 1000 g/mol the equilibrium between flexible and hard moieties in the PU structure provides a maximum in adhesion resistance. Moreover, PPG-based adhesives present better performance when compared with PEG-based ones, being 0.52±0.08 N/mm2 the highest resistance to adhesion for PPG 1000 g/mol PU adhesive. Satin finished XPS has lower adhesive consumption. Regarding thermal conductivity, the insulating capacity of the panels falls on the foam (sandstone presents a value of 1.43 W/mK, while satin XPS foam is 0.05 W/mK), however, both values are within the standard limits. These results pave the way to utilize satin-finished XPS foams, offering a 30-50% cost savings over current sanded foams.

Acknowledgments and References

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SYNTHETIZING SUSTAINABLE THERMOSETTING POLYMERS: THE ROLE OF DIFFERENT VEGETABLE OILS

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Introduction

In the modern age, there is a growing trend in the synthesis of polymers from renewable resources to mitigate the environmental concerns of petroleum-based products. In the field of thermoset polymeric materials field, which are used for multiple purposes like coatings, furniture, electronics, etc., the sustainability is still an objective [1]. In this sense, the use of vegetable oils as raw materials to synthetize biopolymers for thermosetting applications is a very interesting option to promote the sustainability. Their outstanding properties, like functionality or biodegradability, make them suitable for chemical modifications, thus extending their range of the use in multiple applications via chemical crosslinking to cover from lubricant formulations with liquid-like properties to coating with solid-like characteristics [3]. In this work, polyester-polyether materials with sustainable characteristics were synthetized in order to study the influence of their composition, i.e. the nature of vegetable oil chemical structure varying the number of functional sites susceptible to chemical modifications, on the rheological properties, which defines their field of application.

Methodology

Vegetable oils with different unsaturation points were selected to synthetize the biopolymers via chemical crosslinking with two crosslinking agents (named compounds A and B). The reaction was performed in an open vessel by mixing all the reagents at 100 ºC for 20 min. When a viscous solution was obtained, sample was poured into silicon moulds and cured in an oven for 20 hours. Characterization techniques. Differential scanning calorimetry and rheological tests were used to fully characterize the new synthetized bio-based polymers.

Results and conclusions

Upon the synthesis process, fully cured polymers materials were obtained, regardless the number of unsaturation the vegetable oil used as raw material has. A well-structured three-dimensional network was verified by the evolution of glass transition temperature analyzed by means of differential scanning calorimetry tests. However, the viscoelastic properties of the formulations varied depending on the type of oil employed to synthetize the polymers. Both viscoelastic parameters increased as the number of functional sites in the oil fraction rose. For example, when using oils comprising 9 reactive moieties, the highest values of both rheological moduli were obtained. Glass transition and the rheological characteristics also verified the completion of the curing process and the formation of a well-crosslinked microstructural network with gel-like characteristics after 6 hours of curing.

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TOWARD SELF-DRIVING LABORATORY FOR THE DESIGN OF MULTIFUNCTIONAL NANOCOMPOSITES

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Introduction

Advanced polymer nanocomposites are relevant to a broad spectrum of applications, from clean and efficient industrial separations through innovative medicine to safe commodity products with low-impact life-cycles. We specifically focus on sustainable and multifunctional nanocomposites incorporating bio-based polymer matrixes and multiple advanced functional components such as 2D materials and/or metal-organic frameworks. Formulating the composition of such nanocomposites tuned to a specific application poses a significant challenge as they need to include the appropriate components to ensure desired performance while simultaneously addressing constraints regarding the physicochemical compatibility between them and the overall dependence on the processing involved. We are streamlining this process by developing a dedicated material acceleration platform (MAP). The MAP is a closed-loop experimental setup where laboratory work related to the preparation and characterization of samples is performed by a robot. At the same time, machine learning algorithms dictate what experiments to perform to achieve desired results with a minimal number of experiments. Unlike other emerging MAPs that work with solution or thin-film chemistries, our MAP focuses on thermoplastic materials, which are processed in a pelletized form and require solid specimens for property testing.

Methodology

Our presentation will introduce the concepts behind our nanocomposite MAP and summarize the recent progress in its development, which so far has included (i) an automated twin-screw extrusion process for nanocomposite preparation, (ii) a nested Bayesian optimization loop for 3D printing of testing specimen executed on a pellet 3D printer farm, (iii) a collaborative robot-operated analog Charpy impact test instrument and (iv) an outer Bayesian optimization loop for navigating the nanocomposite formulation space.

Results and conclusions

Our presentation will demonstrate the initial results obtained by our MAP, such as the autonomous optimization of 3D printing parameters used to produce material test specimens and highlight other ongoing efforts in optimizing nanocomposite composition to achieve desired mechanical and thermal properties.

Acknowledgments

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HIGH RESOLUTION MOLDS, SACRIFICIAL IN AQUEOUS MEDIA, OBTAINED BY VAT PHOTOPOLYMERIZATION 3D PRINTING

Pedro Liz Basteiro, Raúl Sanz Horta, Felipe Reviriego , Enrique Martínez Campos, Helmut Reinecke , Carlos Elvira , Juan Rodríguez Hernández, Alberto Gallardo

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Introduction

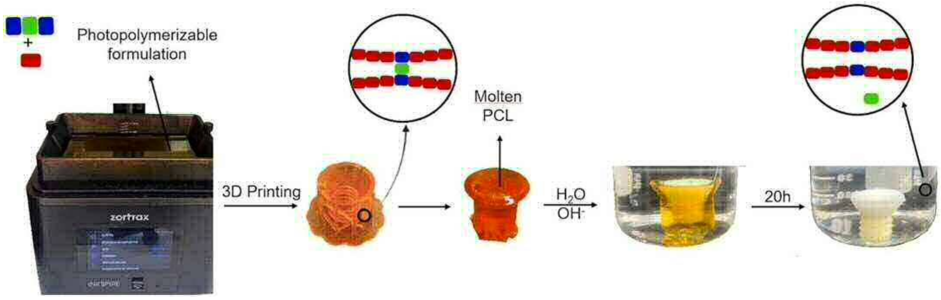
Vat photopolymerization 3D printing (VPP) techniques based on the use of UV-light to solidify a liquid resin layer-by-layer. A minimum amount of crosslinkers is required to obtain pieces with a suitable resolution and desirable mechanical properties. Indeed, VPP resins are usually formulated with a high content of multifunctional crosslinkers to form stable non-swellable structures, that is, covalently linked polymer networks that remain unaltered during the lifetime of the 3D printed object. Therefore. it is explored here the design of sacrificial printed parts in VPP, as the design and fabrication of 3D parts based on the use of labile crosslinkers. In this manner, the resin would comprise enough crosslinker for printing, but the printed part could be sacrificed by breaking the labile crosslinker's bridges and converting the polymer network into soluble chains. If the crosslinker is hydrolysable, like those used in this work, the printed part will be dissolved in water. In this work methacrylic crosslinkers containing hydrolysable β-amino esters were employed[1].

Methodology

The 3D printing parameters selected were: layer height 100 µm, layer exposure time 20 s, exposure off time 5 s, bottom layer exposure time 60 s, bottom layers 5 pcs, platform lower speed 100 mm/min and 5 platform lift speed 100 mm/min. The printer used was the Zortrax Inkspire. After printing, a washing step in 2-propanol was carried out for 5 min and a post-curing process for 30 min at room temperature in a UV-curing chamber.

Results and conclusions

The 3D printing of these resins, through VPP, has given rise in all cases to sacrificial pieces in basic water, that is, soluble, fulfilling the starting hypothesis that sacrificial networks could be obtained using hydrolysable crosslinkers. The versatility of the approach was shown when it comes to intervening in the components of the formulations, which has allowed the properties of the printed parts to be tuned in terms of mechanical performance. In addition, the molds has been proven successful for different uses such as theirfilling with a molten thermoplastic, followed by cooling and solubilization, as shown in Figure 1.



Strategy to prepare sacrificial (in water) 3D printable polymeric materials from resins containing an hydrolysable crosslinker.

Acknowledgments

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OPTIMIZING THE PROCESSING PARAMETERS OF PEEK ADDITIVE MANUFACTURING THROUGH DESIGN OF EXPERIMENTS

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Introduction

PEEK is a high-performance engineering thermoplastic with high strength to weight ratio, reported as an excellent candidate for metal replacement in a variety of applications, including space, aerospace, automotive, medical and dental.

AM of PEEK for high performance parts is promising, yet challenging, stemming from the semi crystallinity and high melting temperature of PEEK and the strong temperature gradient arising in FFF [1]. Reported knowledge gaps and research needs include optimising the temperature difference between nozzle and bed/chamber, more research on the microstructure, fracture phenomenon, rheological behaviour, and crystallisation of PEEK, and the interactive effects of the printing parameters [1].

In this work we explore the contribution of different processing parameters (nozzle temperature, bed temperature, chamber temperature, during-print annealing and print speed) to the mechanical properties of printed parts through design of experiments (DoE) as to allow their optimization. In-depth analysis of the microstructure allows to correctly interpretate the role of each process parameter on the resulting mechanical properties. This work provides new insights in order additive manufacture PEEK parts with equivalent properties to bulk PEEK.

Methodology

A 2^{5-1} fractional factorial design was undertaken. Five dog-bone samples and 1 cantilever DMA sample was printed for each set of parameters (16 sets) in a Creatbot PEEK-300 printer, with Evonik INFINAM PEEK 9359 F. WAXS, SAXS and X-ray tomography was undertaken in dog-bone samples prior mechanical testing. Tensile test of all dog-bone samples was undertaken in an Instron universal testing machine with a displacement rate of 1 mm/min. DMA Q800 from TA Instruments was used, with a 3ºC /min ramp up to 220ºC.

Results and conclusions

The porosity of the parts plays a mayor role in the resulting mechanical properties, together with the level of crystallinity. Crystallinity can improve the mechanical properties as long as the porosity remains low. The during-print annealing used in our work is compared with traditional post-print annealing. A model for the optimization of print parameters will be presented and discussed.

Acknowledgments

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3D BIOPRINTED SCAFFOLDS USING FIBRILLAR COLLAGEN BIOINKS FOR TISSUE ENGINEERING: NEW APPROACHES IN CARDIAC AND CARTILAGE TISSUE REGENERATION.

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Introduction

The importance of 3D models for regenerative medicine therapies is increasingly recognized. Within these models, one crucial aspect is the adequate recapitulation of a native-like ECM, important for cell-cell and cell-ECM interactions, and overall 3D tissue performance. Amongst the available ECM-mimics, collagen is one of the most used, but it is usually available in the market in a soluble state. However, native, fibrillar collagen has a much more complex structure than the soluble form, potentially allowing an improvement in the rheological properties andgeneral biomimicry of the scaffolds.

Methodology

Here, we present the use of a native and fibrillar collagen bioink in cardiac and cartilage 3D tissue engineering applications, 2 tissues where collagen is of paramount importance. Fibercoll-Flex-N®, a commercially available 3D collagen bioink, was used to encapsulate human induced pluripotent stem cell-derived cardiac fibroblasts and cardiomyocytes (5M/ml and 25M/ml respectively) and human nasal septum chondrocytes (0,5M/80µl) to establish the most appropriate in vitro model for each tissue.

Results and conclusions

To characterize the mechanical properties of the collagen bioinks, rheological properties such as Young's modulus and viscosity, as well as Fiber length were determined. Printing speed, pressure and shape were also controlled during 3D scaffold fabrication process to ensure shape fidelity and absence of batch-to-batch variability. Cellular viability and material biocompatibility were confirmed by alamarBlueTM and Live-DeadTM assays, DNA quantification (PicoGreenTM) and immunofluorescence, together with gene expression studies (qPCR). Bioink characterization showed 1124 Pa G' and 186 Pa G'' in terms of rheology, 1,5 McP in viscosity and a mean value of the median value of 200 µm. Viability, DNA content and biocompatibility assays showed high levels of cell viability, harvested DNA and an increase of cell metabolism when compared to the control. Moreover, the gene expression studies also showed an increase of expression in genes of interest.

These results confirm the suitability of Fibercoll-Flex-N® for both in vitro models, with high levels of cell survival and metabolism, as well as an adequate gene-expression profile and cellular architecture. In conclusion, this bioink permits the generation of functional cardiac tissue by supporting the two main cardiac cell types. It also supports the expression of type II collagen by human nasal septum chondrocytes corroborating the great potential of this bioink for cartilage regeneration.

HYDROGEL-BASED 3D PRINTED CANCER MODELS FOR SERS SENSING AND IMAGING

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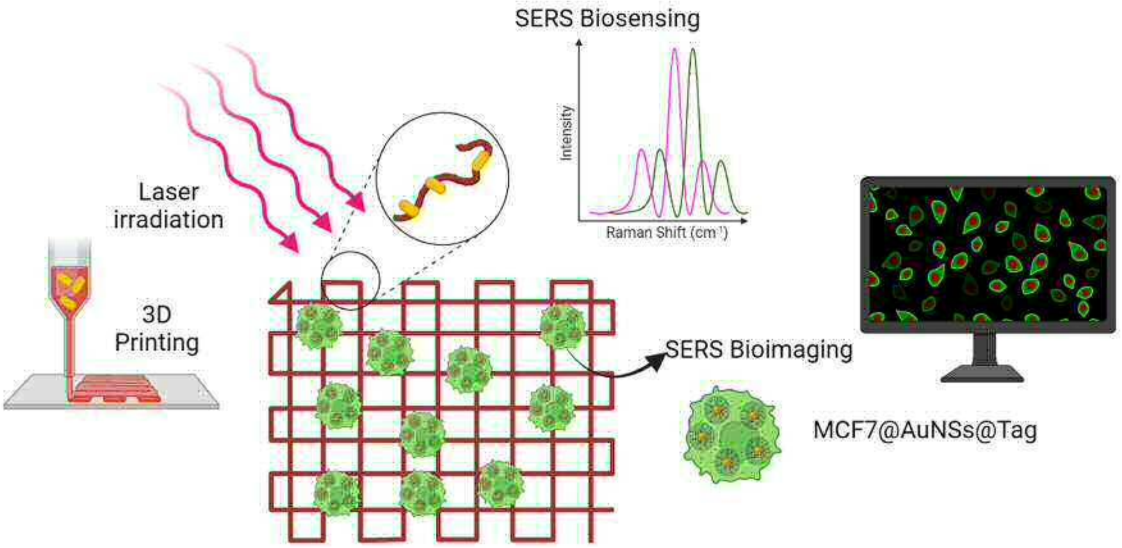
Introduction

Bioprinting shows great promise for fabricating supportive scaffolds for tissue or tumor growth. While number of biopolymer and hydrogel-based inks are available to create complex 3D cell models, there is a pressing need for non-invasive tools to monitor cell behavior in 3D environments over extended periods. To tackle this, sensors can be incorporated into the printable ink formulations to create scaffolds able to monitor tissue growth or disease evolution. In this work, we explore the potential of incorporating plasmonic nanoparticles to different ink formulations to perform sensing and imaging within 3D printed tumor models by means of Surface-Enhanced Raman Scattering (SERS). Noble metal nanoparticles with localized surface plasmon resonances (LSPR) absorb and scatter light, boosting Raman scattering of molecules near the metal surface for sensitive detection and multiplex imaging. Different material compositions, printing setups and nanoparticle combinations were explored in order to perform sensing as well as multiplex imaging of different cell populations in a 3D fashion.

Methodology

Various 3D models were developed using biopolymers (methacrylated hyaluronic acid, methacrylated gelatin), synthetic polymers (polyethylene glycol diacrylate) or decellularized extracellular matrix (dECM)-based inks containing gold nanostars or nanorods for in vitro sensing and imaging. For cell-secreted metabolite detection, bare gold nanoparticles were employed whereas SERS imaging was performed using gold nanoparticles decorated with SERS tags that can be also internalized by cells. Printing of the different models was achieved using a RegenHU 3D Discovery bioprinter.



Results and conclusions

Scaffold-assisted cell growth was achieved using MCF7 cancer cells and fibroblasts as single cells or as preformed spheroids. SERS was used to monitor the scaffold for up to 21 days . dECM was employed for the creation of core-shell tumor models mimicking a cancer core and a healthy stroma to study cell migration by SERS imaging. Sensing platforms can also be printed in this core-shell models to monitor changes between the different tumor regions. In this work, the potential and versatility of SERS as a sensing and imaging tool in 3D complex cell models is demonstrated.

Acknowledgments

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IMPRESIÓN 3D DE FILAMENTO FUNDIDO DE POLICAPROLACTONA CARGADA CON RESINA EPOXI RECICLADA

Iker Razquin [1], Leire Mediavilla [1], Mónica Cobos [1], Itziar Insua [1], Itxaso Calafel [1], Nora Aramburu [1], Izaskun Larraza [2], Loli Martin [3], Alba Gonzalez [1], Lourdes Irusta [1]

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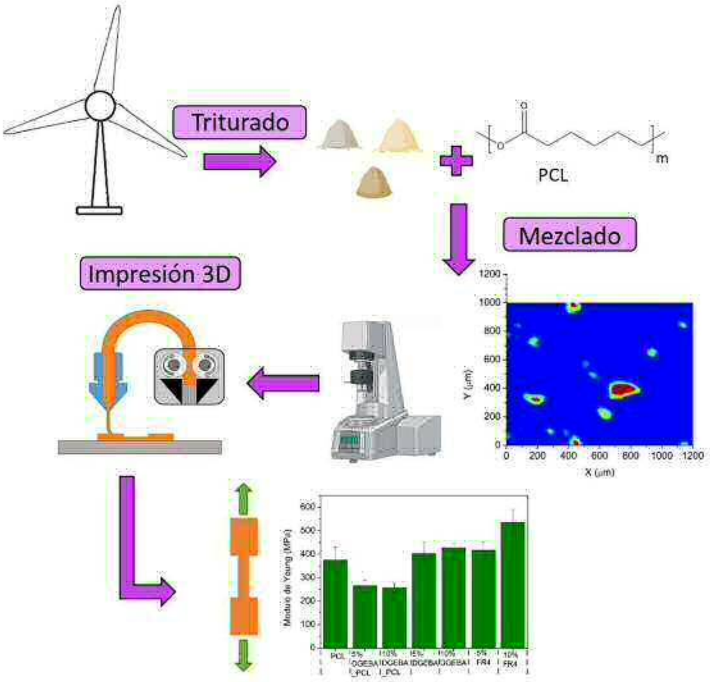
Introducción

Los materiales termoestables están limitados en términos de reciclado porque no pueden fundir ni ser reprocesados. Uno de los materiales termoestables mas utilizados es la resina epoxi que frecuentemente se encuentra reforzada con fibra de vidrio, formando un composite. Este composite es muy utilizado en las palas de los aerogeneradores, las cuales, al finalizar su vida útil, se acumulan en vertederos con el consiguiente impacto medioambiental negativo [1]. Por lo tanto, existe una creciente necesidad de recuperar y reciclar estos materiales e incorporarlos en nuevos productos útiles.

Metodología

Con el objetivo de reciclar las resinas epoxi mediante reciclado mecánico, se mezclaron diferentes tipos de resinas epoxi reticuladas a modo de refuerzo como carga con PCL de alto peso molecular (Mn=50.000 g/mol). Se utilizaron tres materiales epoxídicos diferentes como carga. Los dos primeros fueron DGEBA y mezclas de DGEBA_PCL curadas en el laboratorio [2]. El tercero un compuesto epoxidico comercial que contenía fibra de vidrio (FR4). Estos tres termoestables se molieron y se mezclaron con PCL en fundido para fabricar piezas mediante impresión 3D por deposición de filamento en fundido. El análisis de imprimabilidad predijo la obtención de una buena adherencia entre capas y la no obstrucción de la boquilla por presencia de carga.



Resultados y Conclusiones

Una vez se imprimieron en 3D las probetas, se analizó la distribución de la carga en la matriz de PCL mediante FTIR acoplado a un microscopio. La distribución de la carga en la matriz depende de la rigidez de la carga empleada. Así, cuando se usó DGEBA y FR4 se obtuvo una buena distribución. Sin embargo, la carga mixta DGEBA_PCL resultó difícil de dispersar. Las muestras cargadas obtenidas mediante impresión 3D mostraron un aumento en el módulo de Young y una disminución de la elongación a rotura con respecto a la PCL pura. La muestra cargada con FR4 resultó especialmente interesante mostrando propiedades similares a las de la misma formulación inyectada. Como conclusión general se puede decir que, el uso de resina epoxi como refuerzo de piezas para impresión 3D es una alternativa sostenible que permite dar un segundo uso a los cada vez más abundantes residuos de resina epoxi. Por lo tanto, el método desarrollado ofrece una solución al problema medioambiental asociado a la acumulación de ese residuo.

Agradecimientos

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PHBV FILMS LOADED WITH PHA MICROPARTICLES FOR PACKAGING APPLICATIONS

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Introduction

Due to the environmental concerns and the shortages of fossil resources, the interest is growing in developing materials from biopolymers such as poly-(3-hydroxyalkanoates) (PHAs) to replace synthetic non-degradable materials (1). In this work, biocomposites made from PHBV modified with PHA Microparticles were produced and tested towards their suitability as a substitute for commercial plastics in packaging applications.

Methodology

The biocomposites were produced with Poly-(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (88/12 HV, Goodfellow), Polyhydroxy-butyrate (PHB) (Biomer), Polyhydroxy-butyrate-hexanoate PHBH (Maip) were used. The PHB and PHBH microparticles were produced by miniemulsion-evaporation-technique. The biocomposites were produced by pre industrial melt processing via extrusion (Haake Lab and injection (Minijet) .The prepared particles were characterized respecting their morphology and their thermal properties using SEM and DSC. Their effects on the thermal properties on the biocomposites were investigated by using DMA and TGA.

Results and conclusions

PHB and PHBH particles were spherical shaped with different diameters in a micrometric range. The PHBH particles showed a lower crystallinity resulting in a lower melting temperatures compared to PHB particles due to their higher complexity of the molecular structure. The incorporation of particles in the PHBV matrix showed no effects on their thermal stability but reduced their glass transition temperatures and their phase shift due to hindering of the molecular chain movement. Furthermore, higher storage moduli for all biocomposites were observed demonstrating the reinforcing effect of the particles in the composite. It can be concluded that the PHA particles can be successfully included in the PHBV matrix by preindustrial melt processing techniques.

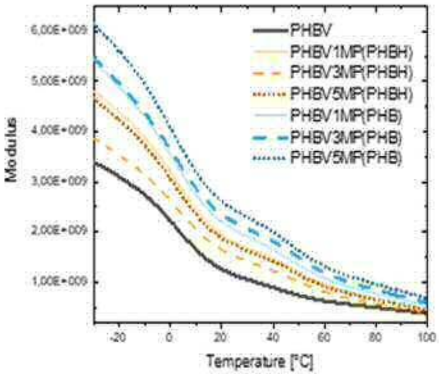

Figure 1: DMA curve of storage modulus

Acknowledgments

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APLICACIÓN DE LOS PHA AL SECTOR DEL ENVASADO: MEJORAS EN LA USABILIDAD Y CONTROL DE LA BIODEGRADACIÓN

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Introducción

Los polihidroxialcanoatos (PHA) son una familia de polímeros biobasados y biodegradables que, debido a su carácter termoplástico, combinación de propiedades y capacidad natural para biodegradarse ubicuamente, se están posicionando como la opción más prometedora para aplicaciones plásticas de corta vida útil, como el envasado alimentario. Sin embargo, existen problemas técnicos que limitan su aplicabilidad y dificultan su implantación. Estas limitaciones pueden abordarse desarrollando formulaciones que mantengan los beneficios medioambientales del PHA mientras mejoran su comportamiento y procesabilidad. Además, aunque el PHA puede biodegradarse, esto no garantiza que los residuos de productos fabricados con PHA no presenten desafíos en cuanto a su gestión, la estimación del tiempo de biodegradación y la seguridad ambiental. Por ello, es necesario estudiar el proceso de biodegradación y su aplicación tecnológica.

Metodología

La fragilidad intrínseca del PHA, su estrecha ventana de procesado y baja estabilidad térmica son limitaciones técnicas significativas para el envasado alimentario. Presentaremos el desarrollo de mezclas con otros materiales y aditivos funcionales como una herramienta eficaz para mejorar el comportamiento del PHA. Se mostrarán resultados de mezclas con varios tipos de polímeros, destacando la importancia de una correcta compatibilización y las limitaciones de esta estrategia. Además, se presentará cómo el uso de aditivos puede mejorar el comportamiento de estas mezclas.

Resultados y Conclusiones

Los polímeros biodegradables, como los PHA, ofrecen ventajas medioambientales significativas en dos aspectos: la gestión de residuos mediante reciclaje orgánico y la capacidad de biodegradarse en entornos naturales, lo que puede reducir la acumulación de plásticos. Sin embargo, ser biodegradable no garantiza por sí solo una ventaja medioambiental; se requiere un mayor conocimiento y evaluación de la biodegradación para asegurar que un producto hecho a partir de estos materiales es mejor para el medio ambiente. En esta comunicación se presentarán los resultados de estudios de compostabilidad, biodegradación en el medio ambiente y análisis de ecotoxicidad de materiales desarrollados y formulaciones basadas en PHA que muestran mejores propiedades y usabilidad.

Agradecimientos

El trabajo presentado se ha realizado en el marco de la Unidad Asociada de Investigación UJI IATA-CSIC en Tecnología de polímeros. Los resultados que se presentan son parte de distintos proyectos: proyecto de I+D PID2021-128749OB-C32, financiado por MICIU/AEI /10.13039/501100011033 y por FEDER, UE, proyecto INNEST/2023/69 AVI-COMBOOST financiado por la Agencia Valenciana de Innovación (AVI) y fondos FEDER de la Unión Europea, y proyecto PDC2022-134006-C22 financiado por MCIN/AEI /10.13039/501100011033 y por la Unión Europea Next GenerationEU/PRTR.

RECYCLING GROUND TYRE RUBBER VIA THEIR BLENDING WITH NATURAL RUBBER MATRIX FOR ELASTOCALORIC APPLICATIONS

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Introduction

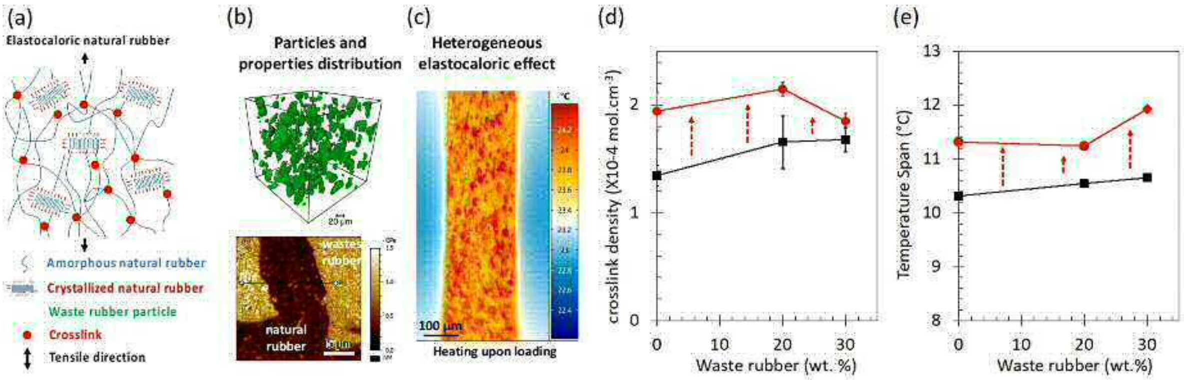
The efforts of the scientific community toward a responsible waste management in the rubber are encouraged by a shift toward Circular Economy as demanded by the 2030 UN Sustainable Development Goals (SGD) and the 2050 European Green Deal. One employed strategy is to devulcanize these GTR particles, i.e., to break the chemical crosslinks between the rubber chains, then to blend them into a fresh polymeric matrix and finally to (statically or dynamically) revulcanize them, with the final ambition to get novel materials with high mechanical performance.

Methodology

In line with this strategy, in this work, we prepared rubber blend containing rubber waste from tires (GRT) for high mechanical performance. To do so, GTR particles had been first devulcanized (by mechanical or physical treatment), then blended with a fresh natural rubber (NR) matrix in an internal mixer and the obtained blend had been vulcanized (by dicumyl peroxide) to obtain a mechanically resistant rubber blend with a high deformability.

Results and conclusions

The natural rubber had been chosen as a matrix as it shown strain induced crystallization (SIC) and elastocaloric effect (eC), that we aim to tune via the incorporation of the GTR particles. These two properties are crucial as their attest for a high fatigue performance of the material. The obtained blends incorporating a maximum of 30 wt.% of GTR were found to "accelerate" the SIC, i.e., that SIC appears at lower deformation as compared to the pristine NR (250% against 300% respectively). They were found to also improve the eC behaviour, via the generation of a heating of 8 °C of the blend during its tensile loading and a cooling of – 8°C during its unloading (against +6°C/-6°C for the pristine NR). The preparation of rubber blends incorporating devulcanized GTR particles from wastes is hence a strategy of interest to provide them a high added value, especially for materials with high fatigue performance. In a future investigation, we aim to explore the possible improvement of both SIC and eC effect in NR/GTR blends during multiple cyclic loading, to clearly demonstrate their effect on the fatigue life of the NR.



Acknowledgments and References

We acknowledge the Spanish Ministry of Science and Innovation (Project TED2021-129952A-C33, and the group eb-POLICOM / Polímers i Compòsits Ecològics i Biodegradables, a research group of the Generalitat de Catalunya (Grant 2021 SGR 01042).

RECYCLED POLYOLEFIN BLENDS AND GROUND TIRE RUBBER (GTR): FROM POST-CONSUMER WASTE TO 2ND GENERATION FUNCTIONAL MATERIALS

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Introduction

Discarded tires are one of the biggest groups of polymer waste, and wide research is performed to find alternatives to their incineration. One alternative is mechanical recycling, i.e., shredding those tires to fine particles that can be then used, for example, in the manufacture of asphalt, but many other applications are also being studied, including their blending with different polymers [1]. Plastics coming from municipal waste streams are also a challenging group of wastes, given that their sorting in separate homopolymers is not always simple. In fact, commercial grades of blends based on recycled polyolefins are available in the market and find application in several sectors. This work aims to explore the blends resulting from the combination of these two families of materials. The materials used were 100% recovered from post-consumer waste streams and processed using the most usual techniques in plastic industry. The ultimate goal is to develop new materials with competitive mechanical properties for their use in several applications, for example, as potential thermoplastic elastomers.

Methodology

Three commercial polyolefin blends (named rPO hereafter) kindly supplied by Borealis (Austria) and based on recycled polyethylene (rPE) and recycled polypropylene (rPP) coming from municipal waste streams were selected: Purpolen PP-70 (rich in rPP), Dipolen S-70 (roughly 50:50 rPP:rPE), and Purpolen PE (rich in rPE). Shredded ground tire rubber (GTR) coming from discarded tires and kindly supplied by GMN (Spain) was added to the blends at a 30 wt% content. Additionally, an EVA copolymer was added as a potential compatibilizer at 7.5 and 15 wt% contents. All the materials were prepared using melt mixing and the required specimens were injection molded.

Results and conclusions

The stiffness of the materials decreased after GTR addition (Figure 1a). Ductility also decreased significantly in the case of rPO/GTR blends based on Dipolen S-70 and Purpolen PE. However, the formers remained quite ductile, showing strain at break values around 50% (without EVA) and 90% (with EVA). Interestingly, in all cases the impact strength increased after GTR addition (Figure 1c), even more in the presence of EVA. All compositions - except Purpolen PP-70 - showed partial break after impact. In conclusion, blending rPO with GTR seems an approach worth exploring deeper to develop 2nd generation functional materials. Particularly, Dipolen S-70 blends show promising mechanical performance to be used as a thermoplastic elastomer.

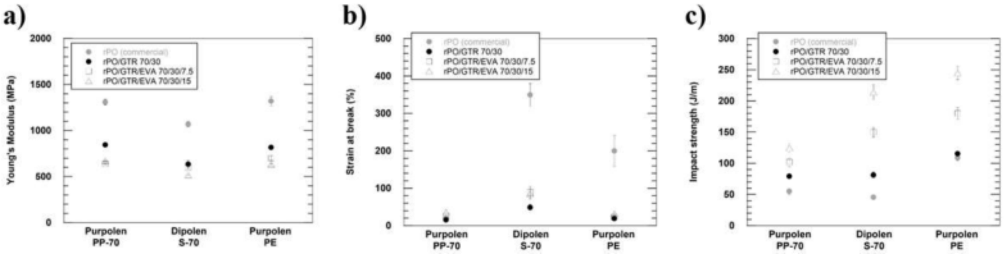

Figure 1. a) Young's modulus, b) strain at break and c) impact strength of the rPO/GTR blends as a function of the rPO matrix type.

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FUNCTIONALIZATION OF POLYMER NANOPARTICLES WITH CATALYTICALLY ACTIVE ORGANIC AND METALLORGANIC MOIETIES

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Introduction

The functionalization of polymer nanoparticles with catalytically active organic and metallorganic moieties represents a promising approach to developing highly efficient and sustainable heterogeneous catalysts. Utilizing polymeric supports functionalized with organic ligands offers enhanced catalytic performance due to increased accessibility to active sites and improved structural stability. Miniemulsion polymerization, noted for its versatility and efficiency, enables the production of polymer particles with defined size, morphology, and large surface areas, which are crucial for maximizing catalytic efficiency. This work focuses on synthesizing polymer nanoparticles by miniemulsion polymerization and functionalizing their surfaces with two types of catalytic ligands: Schiff-base-type metal complexes and xanthene derivative fluorophores.

Methodology

The general strategy was copolymerizing the supporting monomer (typically styrene) with a catalytically active functional comonomer. For the Schiff-base-type systems, styrene was copolymerized with polymerizable Schiff bases, specifically synthesized in our laboratory. Subsequently, the surface ligands were complexed with Mn(III). For the xanthene-systems, rhodamine B was reacted with 2-hydroxyethyl methacrylate (HEMA) by a Steglich esterification reaction to form an ester and obtain a comonomer suitable for subsequent radical polymerization. In this case, nanoparticles were prepared by miniemulsion polymerization of styrene, divinylbenzene, and the synthesized rhodamine B-containing comonomer. The catalytic performance was monitored either by high performance liquid chromatography (HPLC) or by NMR spectroscopy.

Results and conclusions

After successful synthesis of the functional comonomers and the resulting catalytic nanoparticles, the prepared systems were assessed for suitable organic reactions. On the one hand, the Schiff-base systems were shown to be effective catalysts for the asymmetric epoxidation reaction of styrene and indene. The kinetics of the reactions was followed by chiral column chromatography to analyze the enantioselectivity of the prepared catalysts. According to the findings, all catalytic systems achieved substrate consumption yields of at least 90%. Additionally, it was found that the catalysts with the greatest steric hindrance were the most selective, showing the highest conversion rate and reaction yields of at least 99% for all systems after 24 hours. On the other hand, the xanthene systems were proven as very effective photocatalysts for the dehalogenation reaction of meso-1,2-dibromo-1,2-diphenylene. Overall, a very important advantage of the prepared catalysts is the easy separation and recyclability.

Acknowledgments and References

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DOUBLE-SHELLED HOLLOW PARTICLES BASED ON POLYESTER GRAFTED BACTERIAL CELLULOSE FOR TRAPPING BIOACTIVE CARGOES

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Introduction

Biocarrier design is a highly effective method for preserving bioactive elements under adverse conditions and achieving controlled release in specific environments, thereby increasing efficacy. Bacterial polymers, known for their advantageous properties, give rise to strong and stable structures and are among the most widely used sources for developing new materials [1]. This study describes the development of particles based on bacterial cellulose (BC) and bio-based polyhydroxybutyrate (PHB) as bionanocarriers. BC, a hydrophilic porous biopolymer, exhibits high water holding capacity and tensile strength, while PHB, a hydrophobic polymer, offers excellent barrier properties and UV stability. In this work, we aim to develop a protective coating on BC microparticles with a biodegradable PHB coating to control bacterial release.

Methodology

One of the main challenges is the compatibility of both polymers in a stable device [2]. To solve this, the two polymers were covalently bonded to form the core particle (BC-PHB). Subsequently, we applied a one-step coaxial electrospray-based strategy for the preparation of original spherical-shaped double-shell hollow particles (DSHP), consisting of a PHB outer surface shell and a BC-PHB inner shell with a hollow core capable of entrapping live bacterial cells.

Results and conclusions

These DSHP are stable microparticles and spherical in shape, with an outer PHB surface coating and an inner BC-PHB layer capable of housing living cells. The inner cavity can accommodate bacteria up to 1.4 ×108 CFU/mL, while the thin outer PHB layer acts as a barrier, contributing to the protection, stability and controlled sustained release of the enclosed live cargo. Given the biodegradability and low toxicity of the components, BC-PHB DSHP have potential applications in the biomedical or environmental fields.

Acknowledgments and References

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USING NANOPARTICLES OF SEPIOLITE FOR DESIGNING ADVANCED POLYSTYRENE CELLULAR MATERIALS

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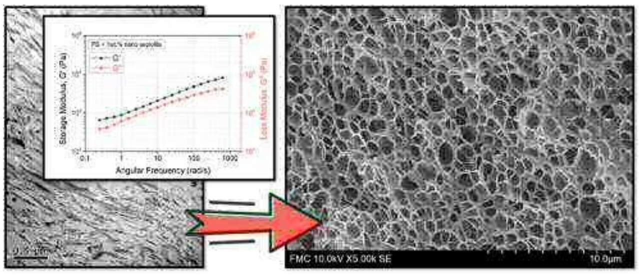
Introduction

Polymer characteristics can be modified by the inclusion of nanoparticles. Even small amounts can enhance or impart new properties compared to neat polymers and conventional composites. However, nanocomposites are strongly affected by nanoparticle dispersion and adhesion within polymer matrix. When these parameters are carefully controlled, nanoparticles can form a percolation network -an interconnected structure where nanoparticles contact throughout matrix- significantly enhancing material properties. Within this framework, our research focuses on designing PS/nano-sepiolite composites using in-situ polymerization. Inclusion of well-dispersed and well-adhered nano-sepiolite enhances polymer properties, which can be exploited in the preparation of advanced cellular materials. Cellular nanocomposites are foams produced from polymer nanocomposites. Beyond enhancing the morphology and properties of the polymer, nanoparticles act as nucleation sites, modifying the cellular structure and resulting in smaller cell sizes and higher cell nucleation densities. Nanoparticles also influence polymer rheological properties, crucial in foaming mechanisms, affecting cell size, structure homogeneity, and foam density. In this study, the inclusion of nano-sepiolite by in-situ polymerization was enhanced through silanisation to improve the properties of PS for the preparation of advanced polymeric cellular materials.



Methodology

Nano-sepiolite was modified with vinyl silanes. Silanisation was studied using Design of Experiments (DoE). Styrene underwent polymerization via suspension technique and was expanded through gas dissolution in an autoclave employing scCO2. Characterization techniques included TGA, DSC, FTIR, GPC, rheological tests, X-ray radiography, TEM, density measurements, and SEM analysis.

Results and conclusions

Nanoparticles of sepiolite were grafted with vinyl silane groups. Grafting was controlled using DoE. A grafting degree of up to 3.5wt.% was confirmed by TGA. PS/nano-sepiolite composites were successfully obtained by in-situ polymerization with 1, 3, and 6wt.%. GPC measurements showed a bimodal Mw distribution for neat PS and unmodified nanocomposites, which shifted to a single peak with grafted nano-sepiolite. Shear dynamic rheology indicated a percolation network at 1wt.% nano-sepiolite. TGA results demonstrated higher thermal stability for the nanocomposites compared to neat PS. Nanocomposites with unmodified sepiolite did not foam, whereas the foam containing 6wt.% of grafted nano-sepiolite showed the highest expansion ratio and cell nucleation density. It had an expansion ratio 3.5 times higher and a cell nucleation density 2 times higher than foam produced with neat PS. This improvement is attributed to the chemical bonds formed between grafted nano-sepiolite and the PS matrix, made possible by silanization and in-situ polymerization.

Acknowledgments and References

The authors are grateful to the Complementary plans of research and development with the autonomous regions in actions of R&D, C17,I1, for financial support.

OPTIMIZATION OF PROCESSING CONDITIONS AND THEMAL/MECHANICAL PROPERTIES FOR PEEK/PEI MULTILAYERED BLENDS AND THEIR CF COMPOSITES.

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Introduction

Developing advanced polymer blends and composites relies on combining multiple polymers to enhance final properties. The properties of these materials depend on morphology, processing history, formulation, and interactions between components. Creating layered structures can significantly improve various properties. For over six decades, multilayer films have been essential in the market due to their excellent optical, gas barrier, mechanical, and dielectric properties, finding applications in light reflectors, toughness-enhancing films, selective radiation filters for windows, flexible food packaging barriers, and medical uses.

Polyetheretherketone (PEEK) is a high-performance, semi-crystalline thermoplastic with excellent mechanical, chemical, and temperature resistance. Polyetherimide (PEI), an amorphous thermoplastic, has high strength and rigidity at high temperatures but limited solvent resistance. PEEK/PEI blends have been studied for their high miscibility, balance properties, and minimize drawbacks. Studies show that high miscibility affects PEEK crystallization, decreasing its rate and crystallinity, especially at high PEI content. Maintaining some crystallinity is crucial for mechanical, thermal, and solvent resistance, making multilayer stacking a promising processing method. This strategy to preserve high crystallinity in PEEK/PEI blends using multilayer films is the aim of this work and the first result of this method in carbon fibre (CF) composites.

Methodology

The PEEK/PEI multilayer and their CF composites were prepared by hot press and studied by a combination of mechanical properties, DMA, DSC, and X-ray diffraction, among others.

Results and conclusions

The adhesion and PEEK crystallinity depended on temperature processing and time. At a temperature higher than the PEEK's Tm, longer processing times reduced PEEK crystallinity and crystallization temperature, affecting the mechanical properties. WAXS and SAXS studies confirmed that unaltered PEEK regions exist in the multilayers, despite global crystallinity reduction. PEEK/PEI multilayers processed for 10 minutes at 380°C retained excellent mechanical properties, close to pure PEEK; however, for the CF composite production, a lower temperature was necessary due to the fluidity of PEI. (1,2)

A good selection of temperature and time for the processing, may produce excellent multilayer PEEK/PEI and CF/PEEK/PEI composites, retaining a high PEEK crystallinity and superior mechanical properties.

Acknowledgments and References

SAXS/WAXS experiments were funded by the Diamond Light Source Synchrotron (grant number SM20494). S.A. Toro is grateful for the support of the ANID-BECAS CHILE/2018-72190509 from the Government of Chile.

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IMPROVING NA-O2/AIR BATTERIES: OVERCOMING OXYGEN CROSSOVER AND FUTURE CHALLENGES WITH SOLID-STATE POLYMER ELECTROLYTES (SSPE).

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CIC-EnergiGUNE, Vitoria-Gasteiz, España

Introduction

Energy storage is crucial for achieving climate neutrality, particularly by integrating more renewables and greening the industry and transport sectors. While lithium-ion (Li-ion) batteries have been the standard, they face limitations such as limited lithium supply, cobalt scarcity, and restricted energy storage capacity. Sodium-air/O2 Batteries (NaBs) offer a solution with abundant, low-cost sodium, no need for cobalt, and high theoretical energy density due to a lightweight air cathode. NaBs provide 5-10 times higher theoretical capacities than Li-ion and Na-ion batteries. However, research has predominantly focused on improving electrodes rather than electrolytes, leading to challenges such as oxygen crossover causing anode passivation and the instability of liquid electrolytes with sodium and reactive species, resulting in battery failure.

Methodology

To address these challenges, the oral presentation will give an overview on how to overcome the O2 crossover and mitigate side reactions by designing and developing more stable solid-state electrolytes based on a highly porous conducting membrane separator. Furthermore, special focus will be given on the chemistry of discharge products and O2 crossover, exploring the relationship between electrolyte properties, the stabilization of NaB chemistry and Na+ transport.

Results and conclusions

The main goal is to enable the development of high-energy-density batteries and deepen the understanding of fundamental mechanisms in NaBs using this kind of membranes, an area that remains largely unexplored as a solid-state electrolyte for NaBs. Overall, this talk aims to identify and demonstrate solid state polymer electrolytes to achieve stable and high-performing solid-state NaBs to advance the commercialization of emerging NaB technologies and strengthen the impact of research and innovation.

Acknowledgments

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DETERMINATION OF BETALAIN CONTENT IN COOKED BEETROOTS USING SMART POLYMERS

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Introduction

Betalains are pigments derived from the amino acid tyrosine, found in plants of the order Caryophyllales, such as beets and some fruits [1]. They are commonly classified into two groups: betaxanthins, (yellow-orange), and betacyanins, (red-purple). The stability of these compounds can be affected by pH, oxygen, light, and temperature [2]. Temperature changes can lead to color alterations, impacting consumer preferences. Therefore, there is an industrial need to predict when these changes will occur. In this way, color can be used as a quality indicator in the beet processing industry [3]. We propose a novel methodology using a sensory polymer in film form to rapidly quantify betalains in processed beets.

Methodology

The film-like smart polymer was prepared by bulk radical polymerization. As monomers, NNDA, 2-HEA, and MMA were employed in a molar ratio of 45/45/10. NNDA generates, after protonation, the positive charges, necessary for the electrostatic interactions with betalains.2-HEA and MMA have structural functions. Additionally, a 15% of crosslinker and a 1% w/w of AIBN were added. The oxygen-free polymerization was carried out in a 100 µm thick mould. The solid film was washed, protonated, and cut into 8 mm diameter discs, which were then introduced into beetroots' purees, acquiring the corresponding color, which was analyzed with the "Colorimetric Titration" app [4], for extracting the color parameters.

Results and conclusions

The results showed that only one specific color parameter exhibited correlation with the calibration betalain content calculated using the traditional method. Subsequently, the rest beetroot puree samples were analyzed. No statistically significant differences were observed when evaluating the correlation between total betalains derived from the reference method and the different color parameters determined with our material. In conclusion, this study presents a new material for the quantification of betalains in processed beetroot in combination with a smartphone application.

Figure 1: Comparison between the proposed methodology with the traditional method for betalain quantification.

Acknowledgments and References

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POLY (METHYL METHACRYLATE) FOAMING BY ONE STEP PROCESS WITH SCCO2 AND WATER

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Introduction

Poly(methyl methacrylate) (PMMA) is a synthetic and amorphous polymer that belongs to the acrylate family. Very promising application have been developed in recent years through the polymer foaming [1, 2]. This work studies the foaming of PMMA with supercritical CO2 in different conditions to obtain microcellular polymers in short times. Also, recent research showed no PMMA modification under hydrothermal conditions [3], so the use of subcritical water has been included, as a novelty, in this process to improve the pressure drop rates and cell parameters.

Methodology

Foaming was carried out in autoclave vessel. PMMA and water in different ratios were placed in the autoclave and CO2 pumped to pressurized the system. After desired saturation time, pressure was suddenly released. Different experimental conditions were analyzed such a pressure, particle size and time. Temperature was set above effective glass transition temperature of the polymer.

Results and conclusions

Multilayered structures were observed after the PMMA's foams analysis. Homogeneity of the foams changed as a function of saturation pressure. The cell size of the cellular materials decreased, and the cell nucleation density increased, as the pressure increased. The experiments in aqueous medium presented higher pressure drop rates and quicker decrease of cell size at the lowest pressures (Fig. 1). Moreover, plasticizing effect of water was able to reduce the structural defects in samples. Further experiments will be conducted to reach the best foaming conditions. To conclude, the novel one step process proposed in this work provides satisfactory results for PMMA foaming. Reduction of saturation time to 60 minutes was achieved without loosing foaming effectivity.

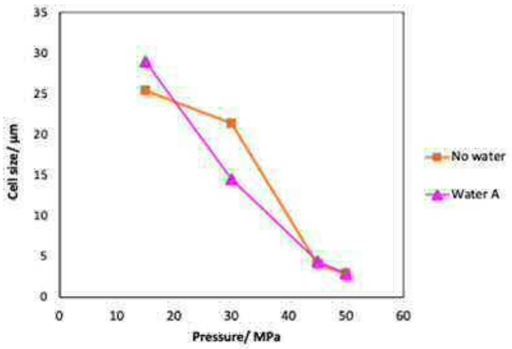

Fig.1. Cell size as a function of pressure for each condition.

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ADVANCEMENTS AND CHARACTERIZATION OF POLYMER GEL ELECTROLYTES FOR SODIUM BATTERIES

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Introduction

Sodium may be considered as excellent alternative to lithium batteries because of its natural abundance, non-toxicity, low cost, light weight and high electrochemical potential. In the SuSaNa project, we work to develop polymer-containing electrolytes for safer sodium batteries. Gel polymer electrolytes based on polymers and liquid electrolytes can make these batteries safer, by avoiding liquid leaks, and mitigating dendrite growth[1] and subsequent short-circuits. At the same time, they can reach conductivities close to those of a liquid and show excellent electrode wettability.

Methodology

The gels have been prepared by mixing UHMW PEO in the liquid electrolyte $NaPF_6$ in diethylene glycol dimethyl ether. The method is fast, simple and sustainable (does not require auxiliary solvents). First, they are mixed at RT until a good powder dispersion is obtained, followed by heating them up to 65°C while continuously stirring to melt and dissolve the polymer. The stirring continued for another 10 min at 65°C.[2]

Results and conclusions

Different polymer concentrations have been studied, up to 5 wt%. It has been observed that after standing overnight the gels with concentration below 5 wt% exhibit a white precipitate that will be characterized. The gels prepared by mixing PEO with 10 wt% of PVC, didn´t show this white precipitate.

To qualitatively assess the rheological properties of gel electrolytes, the inverted cup test is employed. For a better understanding of ion mobility in these gels, the ionic conductivity and the diffusion coefficients, DH^+ and DF^-, have been measured. Both ionic conductivity and diffusivity decrease with the viscosity of the gel, but still remain quite close to those of the liquid electrolyte, making them valid as gel electrolytes for sodium batteries.

In conclusion, gel polymers with UHMW PEO up to 5 wt% have been prepared and demonstrate promising rheological properties and ionic mobility, making them strong candidates for use in sodium batteries.

Acknowledgments

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FLASH PRESENTATIONS

LONG TERM-DISPERSIBLE AND METAL-FREE-SINGLE-CHAIN NANOPARTICLES (SCNPS)

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Introduction

Single chain nanoparticles (SCNPs) are soft nano-objects formed by folding individual polymeric chains via intra-chain interactions, exhibiting promising properties for potential applications in catalysis and biomedicine [1]. One of the most used synthetic pathways for SCNPs is Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) using polymers as precursors [2]. However, this method can cause metal-induced aggregation in SCNPs limiting their use in some applications due to metal traces. To overcome these limitations, we synthesized metal-free SCNPs via strain-promoted azide-alkyne cycloaddition (SPAAC) using sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DIBOD) as a bifunctional cross-linker.

Methodology

A random copolymer of styrene (S) and chloromethyl styrene (CMS), P(S-co-CMS), was prepared via reversible addition-fragmentation chain-transfer polymerization (RAFT) in bulk. Subsequently, it was azidated to obtain a PS-based precursor, P(S-co-AMS). Finally, metal-free SCNPs were synthesized through SPAAC using DIBOD as an external cross-linker and characterized by different techniques.

Results and conclusions

The synthesized P(S-co-CMS) contained 27 mol% CMS (1H NMR). It showed a weight-average molecular weight (Mw) of 100.5 kDa and a hydrodynamic radius (Rh) of 8.2 nm (SEC in THF). After azidation, the resulting P(S-co-AMS) maintained a similar Mw and Rh to the original copolymer. The complete replacement of -Cl units with -N3 was confirmed by NMR. Metal-free SCNPs were synthesized using P(S-co-AMS) as precursor, via SPAAC employing DIBOD as a bifunctional cross-linker, preventing effectively any aggregation phenomena. The successful formation of SCNPs was confirmed by SEC through a decrease in Rh (6.9 nm) and an increase of molecular weight was observed due to the intrachain cross-linker. The resulting SCNPs exhibited excellent long-term stability against aggregation phenomena as studied by small angle X-ray scattering (SAXS) measurements. This study presents an innovative approach for the synthesis of stable, dispersible and metal-free SCNPs using intramolecular metal-traceless azide-alkyne click chemistry. By employing DIBOD as external bifunctional cross-linker in combination with azide-containing polymers, a new pathway is created to metal-free SCNP via intramolecular folding/collapse. Besides their suitability for applications in which total absence of metal traces is essential, these SCNPs exhibit long-term stability against aggregation phenomena.

Acknowledgments and References

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KINETIC STUDY OF THE BULK THERMAL POLYMERISATION OF MALONONITRILE DIMER BY DIFFERENTIAL SCANNING CALORIMETRY

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Introduction

Cyano chemistry is an important mean for the construction of aromatic heterocyclic structures. On the one hand, this chemistry is widely used in the field of drug design; and on the other hand, it is also play a relevant role in the field of materials science. In this context, malononitrile dimer, also known as 2-amino-1,1,3-tricyanopropene (ATCP), is a white to yellow powder with a melting point about 170–173 °C, which can be easily prepared by dimerization of malononitrile in the presence of bases [1,2]. In this communication, the study of the bulk thermal polymerization of ATCP basically by DSC is presented

Methodology

DSC measurements of ATCP were carried out at different heating rates (2.5-25 °C/min) from room temperature to 350 °C, under nitrogen atmosphere. Complementary, TG and DTA studies were performed, and a coupled TG-MS system was employed to analyse the main volatiles evolved during the heating of the ATCP samples. A structural and morphological characterization by FTIR and SEM was also conducted.

Results and conclusions

The results indicated that this thermally stimulated polymerization is initiated at relatively low temperature after its melting point, and a kinetic model can be used to appropriately describe, determining the kinetic triplet, including the activation energy, the pre-exponential factor and the mechanism function ($E\alpha$, A and $f(\alpha)$) at different heating rates. The apparent $E\alpha$ was calculated by differential and integral iso-conversional methods for the effective generation of nitrile-based polymers prepared from ATCP, with spectral characteristics very similar to those exhibited by other cyano polymers, such as diaminomaleonitrile-derived polymers. This study demonstrated the, highly efficient and straightforward character of ATCP melt polymerization, and to the best of our knowledge, describes for the first time a systematic and extended kinetic analysis to gain mechanistic insights into this process. The latter was done through the help of simultaneous TG situ MS technique to investigate the gas products generated during these polymerizations. These results prove the successful ATCP melt polymerization, increasing our knowledge about the complex and rich cyano chemistry in polymerization.

Acknowledgments

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PLASMA-DERIVED FIBRIN HYDROGELS WITH PERFUSABLE MICROCHANNELS FOR VASCULARIZED SKIN TISSUE ENGINEERING APPLICATIONS

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Introduction

Skin disorders have a significant impact on patient well-being, with limited drugs available on the market to combat them. Over the last few years, several advances have been made toward the development and production of in vitro human skin models for the analysis and testing of cosmetic and pharmaceutical products. However, these skin models are cultured under static conditions that make them unable to accurately represent normal human physiology. Recent interest has focused on the development of different platforms integrating skin equivalents with a perfusable vasculature allowing dynamic and more sophisticated systems. Including vascularization which plays a key role in skin homeostasis and disease progression is a crucial issue [1].

Methodology

Human plasma-derived bilayered skin substitutes were successfully used by our group to produce human-based in vitro skin models for toxicity, cosmetic, pharmaceutical testing and for clinical use [2]. The lower layer comprises a human plasma-derived fibrin hydrogel populated with fibroblasts, while the upper layer houses keratinocytes. Our goal is to improve this model by recapitulating skin vasculature using different bioprinting approaches based on 3D gel extrusion [3].

Results and conclusions

In this work, we present several approaches to obtain plasma-derived fibrin hydrogels with bioengineered channels mimicking vasculature including the employment of hydrogel lithography on 3D printing molds and approaches based on the so-called FRESH methodology. Channel characterization of the final gel architecture and the potential applications of this work will be demonstrated.

Acknowledgments

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MATERIALS BASED ON MODIFIED PLA WITH BIOCIDE PROPERTIES FOR THE PRODUCTION OF CERTIFIED FILTERS FOR PPES AND AIR-CONDITIONING SYSTEMS

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Introduction

The search for new environmentally friendly biocidal activity materials, which prevent the bacterial adhesion and can be used as certified filters, has gained importance in recent years, especially since the SARS-CoV-2 pandemic for applications such as surgical mask, personal protective equipment (PPE), and air-conditioning systems. Polylactic acid (PLA) is a soluble and biodegradable polymeric material, which can be processed as fiber mats by electrospinning technique.(1) The surface modification of PLA by a polydopamine (PDA) coating layer makes it possible to change its hydrophobic character and, even, functionalize it with polyethyleneimine (PEI), an amino-rich polymer that enhances the antibacterial properties of the coated surface.(2)

Methodology

In this work, in order to optimize the conditions of the PDA coverings on the surface of mats, dense films of PLA have been prepared by casting as they facilitate the characterization of the coatings. A PLA solution in chloroform, with a 50 mg/mL concentration, was poured onto a leveled glass. The most of solvent was evaporated at 30C, then the transparent colorless membrane was dried at 37C under vacuum for 72 h to eliminate any trace of solvent. The film was cut into rectangular strips of 1 x 7 cm and they were immersed in PDA solutions varying parameters such as concentration, immersion time and pH. The best coatings were obtained when the samples were immersed in a solution of PDA (2mg/mL) in a Tris buffer solution (pH=8.5, 15mM) at room temperature for 24 h. Afterwards, some of the coated films were immersed in a solution of lineal PEI or branched PEI in distilled water (2mg/mL) at room temperature for 6 h to obtain functionalized PDA-coated films. Finally, all of the samples were washed with distilled water using ultrasonic stirring, and they were dried at 30 C under vacuum for 72 h.

Results and conclusions

The films were characterized by FTIR and SEM-EDAX to confirm the modification of their surface with PDA and PDA/PEI. Contact angle measurements revealed the more hydrophilic character of the coated surfaces. Biocide activity of these materials is being studied by LIVE/DEAD assay using staphylococcus aureus bacteria strain as probe.

Acknowledgments

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BIOCOMPATIBILITY, ANTIBACTERIAL AND ANTIOXIDANT POTENTIALS OF MICROFLUIDIC-ASSISTED CANNABIDIOL-LOADED PLGA NANOPARTICLES

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Introduction

Cannabidiol (CBD) presents diverse therapeutic effects, including anti-inflammatory and antioxidative properties[1]. However, its clinical application is hindered by low solubility and bioavailability[2], driving the quest for innovative delivery methods. Poly(lactic-co-glycolic acid) (PLGA)-based nanoparticles (NPs) are esteemed for their biomedical and pharmaceutical roles. CBD-loaded PLGA NPs synthesized via emulsion solvent evaporation have shown sustained antibacterial effects[3] and intraperitoneal CBD delivery in ovarian cancer treatment[4]. This study investigates the biocompatibility, antibacterial, and antioxidant properties of novel microfluidic-assisted CBD-loaded PLGA NPs (CBD-NPs).

Methodology

CBD underwent purification using flash chromatography, and its structure and purity were analyzed via various techniques. CBD-NPs were synthesized using a microfluidic mixer from Elveflow (France), with PLGA504 and different CBD proportions relative to total polymer as the polymeric phase. Physical characteristics of CBD-NPs were evaluated post-synthesis, including size distribution, zeta potential, and morphology using dynamic light scattering, laser Doppler electrophoresis, and scanning electron microscopy. Encapsulation efficiency and radical scavenging activity were assessed. Antibacterial properties against Staphylococcus aureus were determined by minimum inhibitory concentration evaluation and agar diffusion method, along with cytotoxicity against various eukaryotic cell types using the Alamar blue assay.

Results and conclusions

CBD purification achieved a purity exceeding 99%. CBD-NPs exhibited stable physical parameters for at least 56 days post-synthesis, with encapsulation efficiency exceeding 90% in certain formulations. Antioxidant activity depended on CBD percentage, with higher activity in CBD-NPs containing 5% CBD. Antibacterial activity was evident immediately after synthesis, with ongoing studies to assess long-term effectiveness. Formulations demonstrated no cytotoxicity against fibroblasts. These findings underscore the potential of CBD-NPs for effective CBD drug delivery.

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TRHCROSS® SYNTHESIZED USING SARE® TECHNOLOGY: THE BEST COMMERCIAL VISCOSUPPLEMENT FOR KNEE OSTEOARTHRITIS SUPPORTED BY IN-VITRO EVIDENCE

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Introduction

Osteoarthritis (OA) affects millions globally, disabling 25% of the population over 18 since 2017, with prevalence expected to double by 2030.[1] OA, particularly common in the knee, occurs when joint cartilage deteriorates. Intra-articular hyaluronic acid (HA) injections are a common treatment, aiming to restore HA concentration in synovial fluid. HA provides viscoprotection[2] by enhancing functionality, lubrication, impact absorption, nutrient regulation, proteoglycan synthesis, pain desensitization, and inflammation reduction. The effectiveness of viscosupplementation is linked to the longer residence time of HA in the knee joint,[3] but the most effective commercial HA viscosupplement for knee osteoarthritis (KOA) remains unclear.

Methodology

Four different chemically crosslinked HA commercial KOA viscosupplements were compared: TrHCROSS® (SARE® technology), Regenflex®Bio-Plus (BIORIVOLUMETRIA® technology), Durolane® (NASHA® technology) and Monovisc® (unknown), through enzymatic degradation test, in depth physicochemical characterization, rheological studies and biocompatibility (ISO10993).

Results and conclusions

TrHCROSS® and Monovisc® had the highest HA quantity per treatment (88 mg). TrHCROSS® showed significantly higher enzymatic stability (remaining hydrogel mass after 7 days: 82 ± 2.20%) compared to Regenflex® Bio-plus (77.81 ± 0.76%), Monovisc® (72.77 ± 1.65%), and Durolane® (69.09 ± 2.49%). These results correlate with the degree of modification (MoD), with Durolane® having the lowest MoD (6.8 ± 0.7%) and Regenflex® Bio-plus the highest (20.7 ± 2.8%). All tested HA viscosupplements demonstrated non-Newtonian shear thinning behavior, confirming injectability. TrHCROSS® had the highest viscosity at shear rates 1 (walk) and 1000 s – 1 (sports) (154.81 Pa·s and 1.22 Pa·s), followed by Regenflex® Bio-plus (60.17 Pa·s and 0.52 Pa·s), Durolane® (44.53 Pa·s and 0.44 Pa·s), and Monovisc® (3.80 Pa·s and 0.15 Pa·s). Viscoelastic properties indicated effective chemical crosslinking and gel-like elastic behavior in TrHCROSS®, Regenflex® Bio-plus, and Durolane®, whereas Monovisc® exhibited characteristics of a non-chemically crosslinked viscous hydrogel. The biological safety of TrHCROSS® is reinforced compared to other commercial viscosupplements, as it complies with the more stringent endotoxin regulatory requirements for ophthalmic devices (0.2 EU/mL).

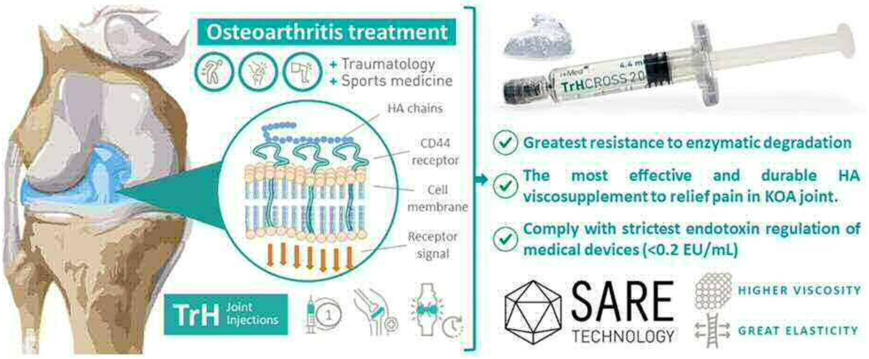

Fig 1.- General scheme and best findings of TrHCROSS injectable hydrogel synthesized with SARE® technology.

TrHCROSS® can be concluded as the most remarkable commercial HA viscosupplement to combat more effectively and durably KOA. This success is attributed to SARE® technology that enhances TrHCROSS® rheological properties and resistance to enzymatic degradation, increasing the implant's lifespan and the duration of pain relief and shock absorption.

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LONG-TERM OXYGEN REDUCTION REACTION ELECTROCATALYSIS USING ROBUST AMIDE-LINKED FLUORINATED COVALENT ORGANIC FRAMEWORKS

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Introduction

The energy demand of the evolving world opens the door to develop more sustainable and environmentally friendly energy sources [1]. Oxygen reduction reaction (ORR) is a promising candidate, being the 2e− pathway of great interest for the green production of hydrogen peroxide [2]. Metal-free covalent organic frameworks (COFs) electrocatalysts present a alternative to noble-metals more commonly employed [3]. However, the lability of the linkages building up the framework raises an issue for their long-term use and application [4]. Herein, a stable amide-linked COF is reported through post-synthetic modification of a previously reported imine-linked COF proven to be effective as an electrocatalyst, enhancing its chemical stability and electrochemical response. The new electrocatalyst displays a higher selectivity toward H2O2 production (98.5%) and an enhanced TOF of 0.155 s−1, among the bests reported to date for metal-free COF based electrocatalysts.

Methodology

This project is based on obtaining an imine-linked fluorinated COF (imine-F-COF) and post-synthetically oxidize the imine bonds to amide-bonds (amide-F-COF). The imine-F-COF was obtained by the Schiff's base condensation reaction between a trigonal-amine and a linear-dialdehyde and characterized by solid-state techniques. The post-synthetic modification was carried out by solid-state transformation of the imine-F-COF to an Amide-F-COF using NaClO2, studying this reaction by the aforementioned techniques. The polymers were exfoliated, obtaining nanomaterials which and drop-casted onto glassy carbon electrodes. Finally, the electrocatalytic properties were analyzed corroborating that the linkage transformation enhances the performances in terms of activity and stability.

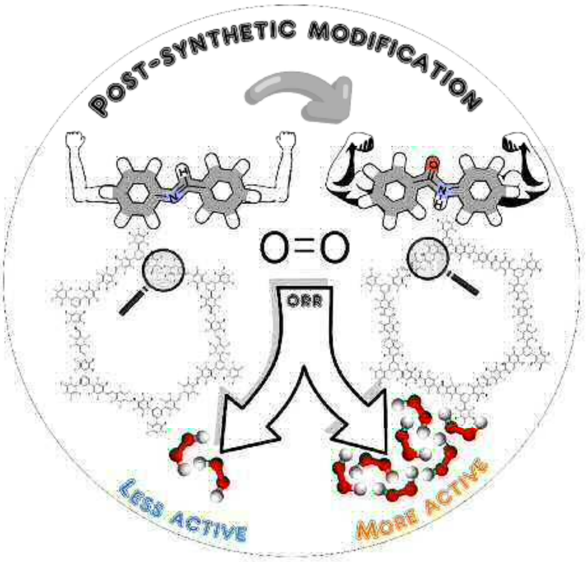

Figure 1. Schematic representation of the postsynthetic linkage modification and its effect enhancing the ORR electrocatalytic performance.

Results and conclusions

We have investigated the post-synthetic modification of linkages in a fluorinated COF, transforming it into its amide derivative, which serves as a good ORR electrocatalyst. Our study reveals that the linkage modification, while preserving most of its original properties and improving its chemical stability, also induces a change in carbon-site adsorption within the framework, enhancing the selectivity, activity, and stability of the new catalyst. These findings underscore the suitability of the COF platform for developing new catalysts with high activity and long-term operability.

Acknowledgments and References

This work was financially supported by Research Project TED2021-129886B-C43 granted by MCIN/AEI/10.13039/501100011033 and the European Union NextGeneration EU/ PRTR; and Research Project PID2022-138908NB-C33 granted by MCIN/AEI/10.13039/ 501100011033/ and FEDER A way to make Europe, by the Spanish Ministry of Economy and Competitiveness (PID2020-116728RB-I00, TED2021-129738B-I00, PID2022-142262OA-I00, RED2022-134120-T, PID2020-113142RB-C21, PLEC2021-007906 and TED2021-129416A-I00)), Community of Madrid (REACT-UE NANOCOV-CM, TRANSNANOAVANSENS, S2018/NMT-4349; 2021–5A/BIO-20943 and SI3/PJI/2021-00341).

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SUSTAINABLE CORE-SHELL STRUCTURES DERIVED FROM LIGNIN FOR SODIUM-ION BATTERIES

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Introduction

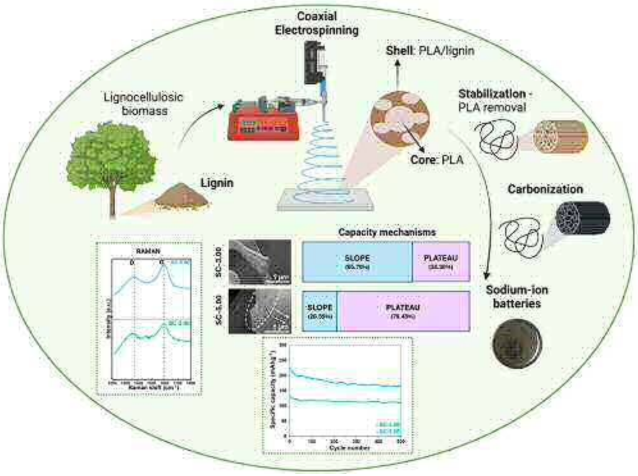
Due to the current high demand for battery energy storage systems and lithium-ion scarcity, there is a transition from the use of lithium towards other, abundant elements such as sodium. However, sodium ions are relatively large (1.02 Å for Na+ versus 0.76 Å for Li+) and have more complex storage mechanisms [1]. The aromatic nature of its structure enables lignin to be used as a natural and sustainable hard carbon precursor after a carbonization process. Lignin-derived hard carbon has shown potential as a sodium-ion battery anode [2].

Methodology

In this work, coaxial electrospinning is used to create hollow carbon structures with different morphologies to improve sodium-ion storage and diffusion. Employing Organosolv lignin as a carbon precursor and PLA as a sacrificial blend, coaxial electrospinning was performed followed by stabilization and carbonization at 900 °C. Using different flow rates for the core and the shell solution, novel nanostructures are obtained. Post-mortem studies confirm that the different nanostructures are maintained after electrode assembly and testing.

Results and conclusions

The Raman presented characteristic bands at 1350 and 1580 cm-1, corresponding to the D and G bands in hard carbon. The XRD peaks were present at 22° and 43°, corresponding to the (002) and (100) crystal planes of graphitelike carbon and cubic amorphous carbon, respectively [3]. SEM pictures confirm the existence of two morphologies, nanochannels within the fibers (SC-5.00) and hollow structures with partial melting (SC-3.00). Long-term cycling was performed at 100 mA g−1 as shown in Figure 10A. SC-5.00 electrode exhibits a stable capacity of 184.7 mAh g-1 with 99.90% Coulombic efficiency (C.E.) during charge between cycles 100 and 500. SC-3.00 electrode exhibits a stable capacity of 115.6 mAh g−1 with 99.98% Coulombic efficiency (C.E.) during charge between cycles 100 and 500. In addition, SC-5.00 is characterized by a 79.45% plateau capacity and 20.55% slope capacity. This innovative and green approach enables new strategies to obtain sustainable materials for sodium ion energy storage applications.



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This research was conducted thanks to the support of the School of Engineering, University of Limerick.

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COVALENT ORGANIC FRAMEWORKS BASED ON MULTI-COMPONENT SYNTHESIS FOR PHOTOCONDUCTIVITY

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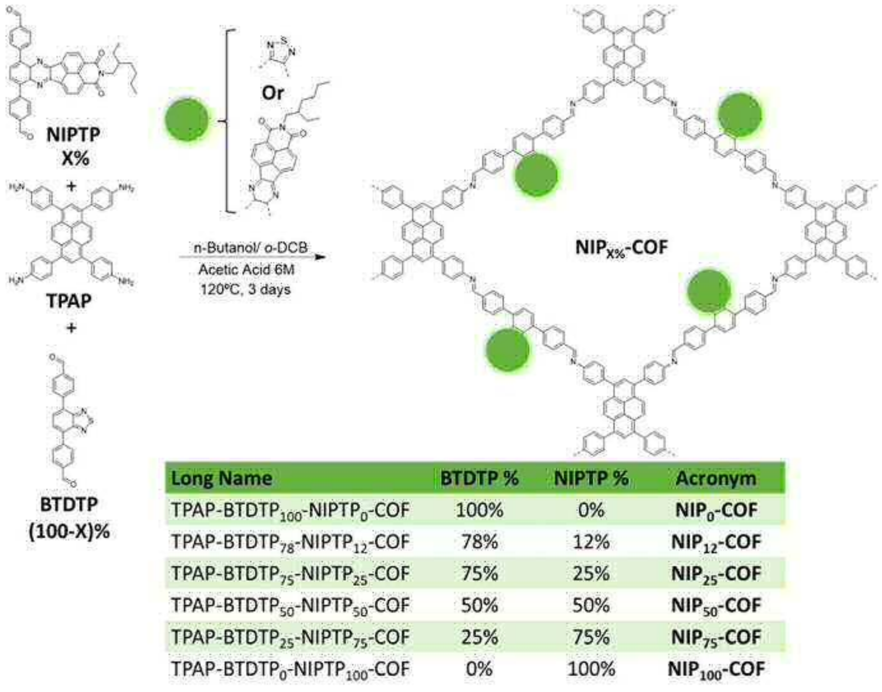
Introduction

Covalent Organic Frameworks (COFs) are a series of porous and crystalline polymers which present properties like pre-designability and the ability to fine-tune the pore wall interface.1 This allows for the synthesis of bespoke materials with tunable properties. Furthermore, multi-component reactions are gaining popularity as a new approach to obtain modified compositions of the aromatic skeleton without the loss of porosity or long-range order associated with post-synthetic modifications.2,3 Additionally, integration of chromophores into the framework has been shown to affect optical properties of the material,4 which is why, for the first time, NIPTP, an electron deficient chromophore, has been synthesized to be introduced into a framework in varying proportions.

Methodology

In this project, first, necessary monomers were synthesized by use of the Suzuki cross-coupling reaction. COFs have been synthesized de novo by using multi-component condensation reactions, under solvothermal conditions, between one tetratopic tetraamine (TPAP) and two different linear aldehydes (BTDTP and NIPTP). Both aldehydes have been introduced in the framework with varying ratios, giving way to six different NIPX%-COFs. The obtained materials were characterized by Fourier Transform Infrared (FTIR), Powder X-Ray Diffraction (PXRD), solid state 13C nuclear magnetic resonance, N2 sorption isotherms at 77 K and Electron Microscopies (SEM and TEM). Furthermore, the photoconductivity of these polymers is currently being studied in Rajendra Prasad's research group in Kyoto University.



Long Name	BTDTP %	NIPTP %	Acronym
TPAP-BTDTP$_{100}$-NIPTP$_0$-COF	100%	0%	NIP$_0$-COF
TPAP-BTDTP$_{78}$-NIPTP$_{12}$-COF	78%	12%	NIP$_{12}$-COF
TPAP-BTDTP$_{75}$-NIPTP$_{25}$-COF	75%	25%	NIP$_{25}$-COF
TPAP-BTDTP$_{50}$-NIPTP$_{50}$-COF	50%	50%	NIP$_{50}$-COF
TPAP-BTDTP$_{25}$-NIPTP$_{75}$-COF	25%	75%	NIP$_{75}$-COF
TPAP-BTDTP$_0$-NIPTP$_{100}$-COF	0%	100%	NIP$_{100}$-COF

Scheme 1. General synthesis procedure of the different NIPX%-COFs.

Results and conclusions

In a nutshell, the work done in this project has allowed for the synthesis of six COFs with varying composition by using a multi-component synthesis approach. The obtained materials were characterized and their photoconducting behavior has been analyzed. Preliminary results show COFs to be hole-carrier materials, showing the NIP25-COF as the most promising one out of the series.

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ENCAPSULATION OF ORGANIC PHASE CHANGE MATERIALS IN POLY(3,4-ETHYLENEDIOXYTHIOPHENE) NANOPARTICLES FOR ENHANCED THERMAL ENERGY STORAGE COATINGS

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Introduction

The rising energy demands and environmental concerns have driven research into innovative energy storage solutions, with phase change materials (PCMs) being highly promising for their ability to store and release thermal energy [1]. PCMs, particularly those with phase change temperatures close to ambient, such as hexadecane and octadecane, offer a great potential due to their ability to store and release thermal energy efficiently. A promising strategy involves encapsulating these PCMs within conductive polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT). This encapsulation enhances their processability, stability, and heat transfer capabilities, addressing key challenges and optimizing the interaction between the energy storage system and its environment [2].

Methodology

This work focuses on the encapsulation of two organic phase change materials (PCM), hexadecane and octadecane, through the formation of nanocapsules of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT), obtained by oxidative miniemulsion polymerization, using iron(III) p-toluenesulfonate hexahydrate as an oxidant and poly(diallyldimethylammonium chloride) (PDADMAC) as a stabilizer. The obtained materials were morphologically characterized by scanning and transmission electron microscopy (SEM and TEM, respectively). The encapsulation efficiency of in the context of latent heat storage was determined by differential scanning calorimetry (DSC). Finally, the energy storage capacity of the nanocapsules was evaluated by preparing polymeric films on copper substrates.

Results and conclusions

The results obtained indicate the effective encapsulation of the two PCMs, revealing that the conductive nanoparticles formed possess a spherical and homogeneous morphology without the presence of aggregates. The applicability of the prepared PEDOT/PCM nanoparticles in coatings was demonstrated by preparing polymer layers on substrates. The thermal studies conducted exhibit not only satisfactory but also reproducible outcomes over time, providing evidence of the robustness and reliability of the developed systems in storing thermal energy through latent heat. In conclusion, this study provides insights into the encapsulation of phase change materials within conductive nanoparticles, offering opportunities for improve the energy storage efficiency and thermal management of this type of systems.

Acknowledgments

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FORMULATION OF ANTIBACTERIAL CREAM CONTAINING IMIDAZOLIUM-TERMINATED CARBOSILANE DENDRIMERS FOR WOUND TREATMENT

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Introduction

Skin and soft tissue infections (SSTIs) are one of the most typical microbicides infections that require medical treatment and affects patients of all ages causing significant morbidity and, in severe cases, mortality of these. [1,2] This is due to the ability of pathogenic microbes present in wounds to form biofilms, which offer resistance mechanisms against most microbicidal agents, thus hindering wound healing. [3] In this way, the development of topical antiseptic formulations with new active ingredients is advocated as a promising alternative to prevent infections on the outermost surface of the skin or to eliminate bacteria present in wounds, thus minimizing the increase in bacterial skin diseases and reducing the unnecessary use of antibiotics. [4] One attractive option is the application of multivalent dendrimers functionalized with imidazolium groups as antibacterials and active molecules. [5]

Methodology

Herein, we have evaluated the antimicrobial activity against Gram- negative and Gram- positive bacteria and the toxicity in red blood cells of imidazolium carbosilane dendrimers with different branch lengths. This modification of the branches lengths of dendrimers induces the modification of their hydrophobic-hydrophilic balance.

Results and conclusions

After these experiments, we have selected the best dendrimer as active ingredient to formulate topical biocide cream. In the end, the in vitro antibacterial activity of this cream was evaluated against S.aureus bacteria, since this bacterium is widely involved in wound infections. [6]

Acknowledgments and References

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AQUEOUS SEEDED RAFT POLYMERIZATION FOR THE PREPARATION OF SELF-ASSEMBLIES BASED ON 2,6-DIACYLAMINOPYRIDINE FOR BIOMEDICAL APPLICATIONS

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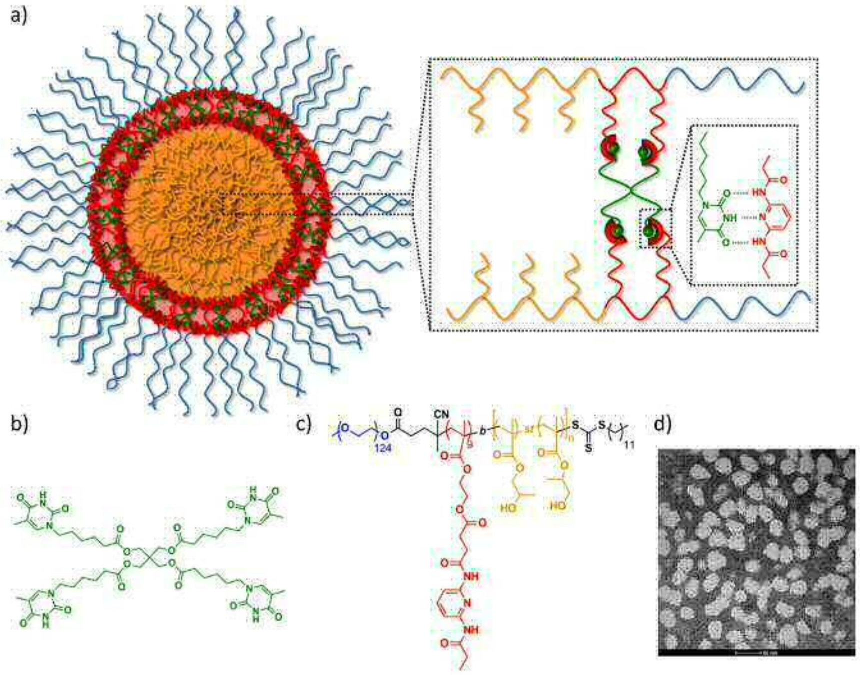
Introduction

Amphiphilic block copolymers (BCs) are able to self-assemble in aqueous solutions giving raise to different nanostructures, whose morphology and size depend on the length of the blocks, their chemical structure, the hydrophobic/hydrophilic ratio and the preparation methodology. These nanostructures can be employed for biomedical applications since they are able to encapsulate drugs, bioactive molecules or other compounds of interest in therapy, as we recently demonstrated with Pd nanomaterials for photothermal therapy. [1] The 2,6-diacylaminopyridine (DAP) unit is an adenine analogue able to interact with metal ions or molecular recognition by hydrogen bonding. These properties can be employed to introduce functionality into BCs or cross-linking, which constitutes a more versatile approach than covalent chemistry.

Methodology

This work explores the preparation of highly concentrated aqueous self-assemblies dispersions containing DAP moieties, using the PISA methodology, and their supramolecular H-bonding functionalization with thymine based cross-linkers, in order to be employed for biomedical applications. [2]



a) Supramolecular recognition through a triple H-bond between DAP units (red) from PEG-b-PDAP-b-PHPMA and thymine moieties (green) of the cross-linker (T4). Chemical structure of b) the thymine based cross-linker (T4) and c) the BC (PEG-b-PDAP-b-PHPMA). d) TEM image from PEG-b-PDAP-b-PHPMA micelles cross-linked with T4 and loaded with Nile Red.

Results and conclusions

Due to the poor water solubility of DAP based methacrylic monomer, a synthetic strategy for preparing nanoparticles was devised. First, the chain extension of a PEG chain by conventional RAFT polymerization was undertaken to obtain an amphiphilic BC containing DAP units. This amphiphilic BC was then employed as a macro-CTA for the aqueous seeded RAFT polymerization of 2-hydroxypropyl methacrylate (HPMA). In this manner, different morphologies were observed (spherical micelles, worms and vesicles) from the resulting BCs (PEG-b-PDAP-b-PHPMA) by modifying the length of PHPMA block and solids concentration. H-bonding supramolecular functionalization of the DAP repeating units during aqueous seeded RAFT polymerization has been studied. For that purpose, the supramolecular cross-linking of the resulting self-assemblies dispersions with a cross-linker with terminal thymine groups (T4) has been carried out and optimized. In addition, their ability to encapsulate molecular cargoes, including fluorescent probes, drugs or Pd nanosheets has been examined. Besides the loading, the subsequent release of these molecular cargoes has been proven in both supramolecular cross-linked and non-cross-linked self-assemblies. It can be concluded that aqueous RAFT-PISA is a suitable methodology for obtaining highly concentrated polymeric self-assemblies dispersions that can be loaded with molecular cargoes or cross-linked in one-step.

Acknowledgments

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LIGNIN-BASED MAGNETICALLY SEPARABLE CATALYSTS FOR THE DEGRADATION OF NITROAROMATIC POLLUTANTS

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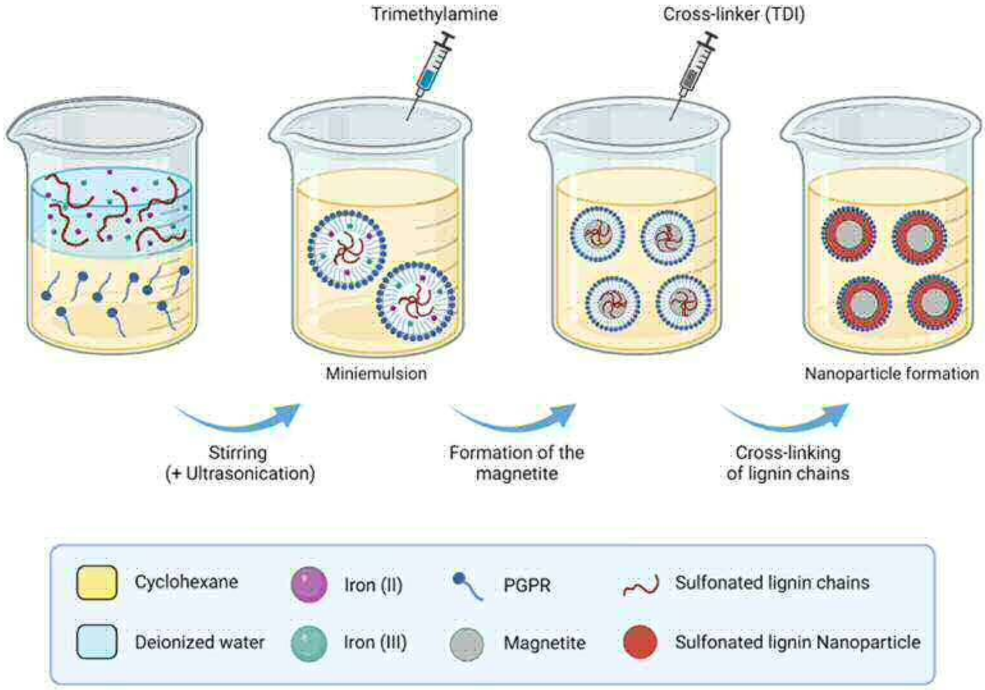
Introduction

The degradation of nitroaromatic pollutants is crucial from both an environmental and an industrial perspective. In particular, 4-aminophenol, formed as the reduction product of 4-nitrophenol, acts as an important industrial precursor in the synthesis of analgesic and antipyretic medications, anticorrosive lubricants, and hair dyeing agents. The catalytic reduction stands as one of the most effective methods to carry out the removal of such nitro pollutants [1].

Methodology

An inverse miniemulsion strategy was used to prepare biopolymeric nanoparticles while synthesizing magnetite in situ. The experimental procedure, partially based on a strategy previously reported by our group [2], consisted of mixing an aqueous phase, containing iron(II) chloride tetrahydrate and iron(III) chloride hexahydrate as precursors of magnetite, and the sulfonated lignin dissolved in water, with an organic phase, containing polyglycerol polyricinoleate (PGPR) dissolved in an appropriate organic solvent. After applying ultrasonic high-shear forces to the mixture, miniemulsions containging the magnetite precursors and sulfonated lignin in the dispersed phase were obtained. Subsequently, trimethylamine and a diisocyanate were added under an inert atmosphere, the former to promote a basic medium and initiate the formation of magnetite, and the latter to cross-link the lignin chains (see figure). Interfacial reactions at the droplet interface take place. As a result, hybrid nanoparticles comprised of magnetite and cross-linked lignin are formed.



Preparation of lignin/magnetite hybrid nanoparticles by inverse miniemulsion

Results and conclusions

The morphology and composition of the materials have been characterized by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) and inductively coupled plasma-mass spectrometry (ICP-MS). Copper was successfully incorporated on surface of the prepared lignin/magnetite hybrid nanoparticles and the catalytic activity was evaluated for the reduction of 4-nitrophenol by sodium borohydride. Our results indicate a promising catalytic potential of the prepared systems in the degradation of environmentally relevant pollutants. Therefore, we provide a new valorization route for lignin, contributing to the circular use of resources and decreasing the environmental impact of material production.

Acknowledgments and References

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).

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EFFECT OF BIO-BASED SIZING ON THE INTERFACE OF CARBON FIBRE-REINFORCED COMPOSITES

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Introduction

Carbon fibre is a well-known reinforcement material for composites, known for its excellent mechanical properties and strength-to-weight ratio. Its extensive use in aeronautics, automobiles, and wind turbines has significantly impacted daily life. The high mechanical strength of carbon fibre-reinforced polymer (CFRP) is attributed to a sizing coating (Montes-Morán et al. 2002) on the carbon fibres (CF), which enhances adhesion between fibre and matrix and allows for avoidance of delamination. Currently, the fossil-based sizing agents used on CF are environmentally harmful but essential for maintaining mechanical performance. Despite their reinforcement properties, CFRP exhibits poor ductility, leading to unpredictable failure. Embedded damage detection membranes could improve safety and reliability. Piezoelectric materials, which generate electric voltage under mechanical stress, can detect failure in CF structures.

Methodology

The study focuses on developing bio-based sizing and producing a nanoscale fibre membrane for CF coating, which can be embedded into a bio-sourced matrix for mechanical sensing. Polyvinylidene Fluoride (PVDF) offers advantages such as mechanical flexibility, low cost and sustainability, making it suitable for creating nanofiber membranes via electrospinning (Kalimuldina et al. 2020).

Results and conclusions

The first step involves synthesising a PVDF solution for coating via electrospinning. Figure 2 presents characteristic peaks commonly associated of PVDF: unspun PVDF exhibits α-phase peaks, while electrospun PVDF shows β-phase peaks, indicating piezoelectric properties. This confirms that electrospinning produces PVDF with optimal piezoelectric properties. Once the PVDF nanofiber coating is applied to the CF, it is embedded in a bio-sourced epoxy for piezoelectric testing. Given the increasing use of CF in daily life, developing an environmentally friendly, non-fossil-based sizing is crucial. The next phase involves applying these biobased sizing to lignin-derived CF, creating fully biobased, reversible composites. These composites will replace non-recyclable, fossil-based materials, supporting a circular economy. Integrated PVDF sensors into these materials will monitor structural damage, enabling parts replacement before failure.

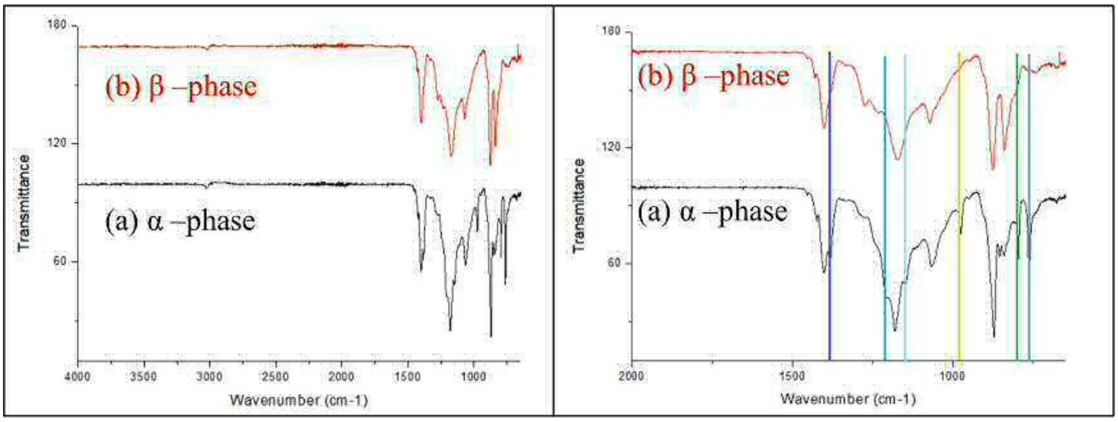

Figure 1: FTIR spectra of (a)a-phase: unspun PVDF and (b)ß-phase: electrospun PVDF

Acknowledgments

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WET SPINNING OF LIGNIN BASED PRECURSORS FIBRES FOR CARBON FIBRE PRODUCTION

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Introduction

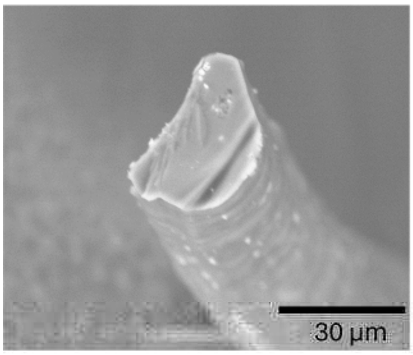
Carbon fibre reinforced polymers (CFRP) find widespread applications in aerospace, automotive and high-quality sports gear. Nowadays, over 95% of commercial carbon fibres (CF) for CFRP are made from polyacrylonitrile (PAN) (Beaucamp et al. 2024). However, the use of PAN is associated with various disadvantages such as high cost indexed on petrol and environmental impact. Given the rapid market expansion of CFRP, forecasting 285 000 tons for 2025 (Zhang et al. 2023), CF production conflicts with initiatives aimed at mitigating global warming. Lignin as a biopolymer and by-product from wood pulping process, can be considered as a “green” and cost-effective alternative for CF production.

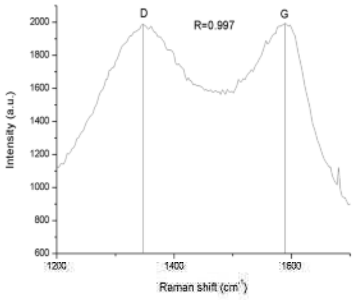
Methodology

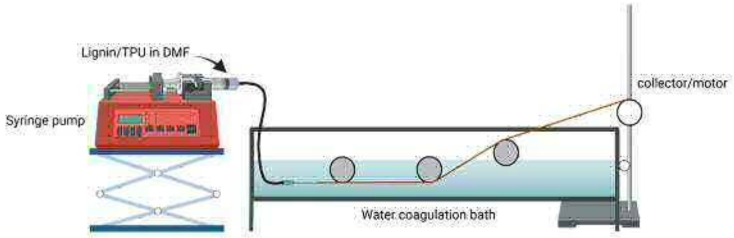
A spinning solution using a blend of kraft lignin and Biobased TPU solution is created by dissolving TPU in DMF under stirring and adding lignin afterwards. A lignin/TPU solution using 50:50 ratio and 16% solid content is extruded through a 25 Gauge tip in a water coagulation bath.

Results and conclusions

Due to high viscosity, solution exhibits unstable behaviour during the extrusion with tip diameters larger than 27 Gauge. Raman presented characteristic bands at 1350 and 1590 cm-1, corresponding to the D and G bands with a ratio of 0,997. A potential carbon yield of 28% was determined using TGA where the sample was heated under nitrogen to 950 oC at a heating rate of 10 oC/min. Tensile strength of 1,01 Gpa and Young modulus of 28,7 Gpa have been measured using single fibre tensile strength machine with a fibre diameter of 30 µm measured using SEM (Figure 1). As wet spinning is currently industrially used for PAN precursor fibre production, lignin/TPU solution could potentially be directly integrated into existing production lines, offering a lower risk and cost for companies. The next phase involves upscaling on a lab-scale production line, optimising both solid, lignin content and viscosity for a multifilament extrusion aiming to decrease the fibre diameter under 10 µm.







Acknowledgments

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LIGNIN-BASED ENCAPSULATION OF AGROCHEMICAL COMPOUNDS BY SPRAY DRYING

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Introduction

The increasing population and, consequently, the demand for food and agricultural production have intensified the environmental impact due to the overuse of plant protection products (PPPs). Therefore, there is a pressing need to develop innovative strategies that minimize agrochemical usage while providing effective, durable, and controlled delivery to plants. One promising solution is the encapsulation of agrochemicals using biomass-based materials, such as lignocellulosic polymers, which can improve the PPPs delivery and prevent their degradation form the environmental conductions.

Methodology

This study focuses on the encapsulation of difenoconazole, a plant protection product with biocide properties, within micro- and submicrometric capsules of kraft-type lignin by spray drying. The particle morphology was analyzed using scanning electron microscopy (SEM), revealing the structural characteristics of the encapsulated product. Thermogravimetric analysis (TGA) was used to estimate the encapsulation efficiency, while liquid chromatography coupled with mass spectrometry provided a detailed assessment of the encapsulation efficiency. Furthermore, the release profiles of the encapsulated difenoconazole were analyzed by ultraviolet-visible spectroscopy.

Results and conclusions

The results showed that difenoconazole was nearly quantitatively encapsulated within the lignin capsules. SEM images confirmed the formation of well-defined micro- and submicrometer particles. Moreover, TGA measurements and liquid chromatography coupled to mass spectrometry confirmed the successful encapsulation. The PPP release in aqueous media was shown to be retarded and more prolonged, as compared to the rapid release in ethanol. In summary, the proposed method is promising for the effective encapsulation of PPPs, underlining the capability of lignin as a suitable material for agrochemical applications. This approach has significant potential to reduce the environmental impact of agricultural practices by improving the efficiency and durability of agrochemical applications.

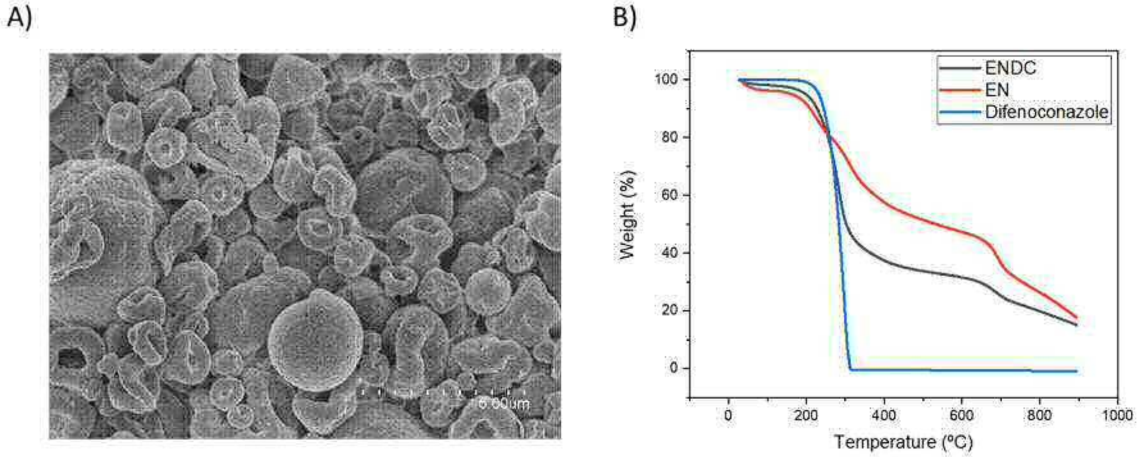

Figure 1. Characterization of the prepared lignin/difenoconazole capsules by SEM (A) and TGA (B).

Acknowledgments and References

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.

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DLP 3D PRINTING OF REPROCESSABLE SEMI-INTERPENETRATING NETWORKS BASED ON HIGH MOLECULAR WEIGHT LATEXES

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Introduction

Vat photopolymerization (VP) is a high-resolution additive manufacturing technique that faces two major limitations: the need for low-viscosity materials, which excludes high molecular weight substances, and the production of non-reprocessable thermosets, which conflicts with circular economy goals. This study addresses these issues by using a latex printing strategy to print high molecular weight methacrylic latexes with varied glass transition temperatures (Tg). For the first time, high Tg and high molecular weight materials like Poly Methyl Methacrylate (PMMA) were printed with high resolution using Digital Light Processing (DLP) and Direct Laser Writing (DLW). A drying process post-printing led to the formation of a Semi Interpenetrating Polymer Network (SIPN), maintaining the 3D structure's integrity. Furthermore, using low scaffold content (5 wt.%) enabled the creation of "thermoplastic rich" SIPNs, which can be reprocessed through classical processing methods, thus supporting circular economy initiatives.

Methodology

In this work three methacrylic latexes with varying Tg's (from 0 to 120 degree celsius) were prepared by seeded emulsion polymerization. Subsequently, light-curable resins were prepared with each of these three latexes by dissolving a crosslinker and a photoinitiator in the aqueous phase of the latex. Finally the photocurable resins were priinted in a Digital Light Processing (DLP) printer.

Results and conclusions

After synthetising the latexes, preparing the photocurable resins and optimizing the printing process, the three synthesized latexes were successfully printed, achieving micrometer-scale resolution. Post-printing, the printed pieces were thermomechanically characterized for each of the three latexes, revealing a wide range of both mechanical and thermal properties. The printed materials exhibited varying glass transition temperatures (Tg) as expected. Mechanically, the properties ranged from elastomeric behavior in the low Tg latex-printed material to very rigid behavior in the high Tg latex-printed material. Finally, the printed materials were reprocessed using various traditional techniques such as extrusion and hot pressing, resulting in materials with properties similar to the original pure materials. This work successfully achieved the first-time vat printing of a high Tg latex, such as PMMA, and additionally developed a strategy for reprocessing the printed pieces.

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NUEVO ACCESORIO DE LIMPIEZA Y PREPARACIÓN DE MUESTRA EN ENSAYOS DE REOLÓGICA DE CIZALLA

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TA INSTRUMENTS, Cerdanyola Del Valles, España

Introducción

Uno de los problemas experimentales más importantes a la hora de la falta de reproducibilidad en las medidas reológicas es la carga de la muestra.

Sobre todo, cuando se produce en caliente. El retirado del sobrante o Trimming puede afectar de manera crucial a la precisión y reproducibilidad de la medida. Es por esto por lo que en el presente trabajo presentamos un nuevo accesorio que automatiza este proceso.

Metodología

Se han realizado multitud de ensayos con diferentes tipos de polímeros tanto amorfos como semicristalinos, utilizando el método convencional de carga de muestra (ya bien sea carga de pellets o fabricación de disco) asimismo como el accesorio propuesto.

El accesorio puede trabajar en caliente directamente cuando la muestra está posicionada entre los dos platos y no es necesario abrir el horno para realizar el trimming.

Resultados y Conclusiones

Los resultados muestran que la reproducibilidad de la medida tanto en viscosidad como en módulos viscoelásticos aumentan enormemente cuando se utiliza el accesorio.

DESARROLLO DE POLÍMEROS DE FUENTES RENOVABLES CON PROPIEDADES MEJORADAS PARA SU APLICACIÓN EN SECTORES INDUSTRIALES DE ALTO CONSUMO Y VALOR AÑADIDO

RED MARFIL

Instituto Tecnológico del Plastico (AIMPLAS), Paterna (Valencia), España
Fundación AITIIP, Zaragoza, España
Fundación para la Investigación y Desarrollo en Transporte y la Energía (CIDAUT), Boecillo (Valladolid), España
Fundación GAIKER, Zamudio (Bilbao), España

El Instituto Tecnológico del Plástico (AIMPLAS), la Fundación AITIIP, la Fundación para la Investigación y Desarrollo en Transporte y la Energía (CIDAUT) y la Fundación GAIKER constituyen la RED MARFIL centrada en intensificar el uso de bioplásticos, aditivos y refuerzos procedentes de fuentes renovables como materiales innovadores en sectores clave, como es el caso del sector del envasado de alimentos, y en sectores industriales de alto valor añadido, como el transporte o la agricultura. El objetivo es incrementar significativamente su uso en aplicaciones donde sean la mejor opción desde el punto de vista medioambiental, técnico y económico.

Para ello, la Red MARFIL está llevando a cabo un programa estratégico de investigación, desarrollo, innovación y formación centrado en fortalecer las capacidades de estos centros para el desarrollo de plásticos biobasados, principalmente a partir de residuos, subproductos agroindustriales o biomasas alternativas. Las capacidades adquiridas se difundirán a diferentes niveles para promover la colaboración con grupos de investigación punteros, incrementar el interés de la industria en el desarrollo de materias primas y productos sostenibles, atraer talento y concienciar a la sociedad sobre las ventajas medioambientales de los bioplásticos para su uso en aplicaciones como la seguridad alimentaria en envases, el aligeramiento en componentes para el sector del transporte y la mejora de las prácticas agrícolas, asegurando la resiliencia de la cadena de suministros.

El objetivo es que el uso de polímeros procedentes de fuentes renovables suponga más del 5% (unas 200.000 toneladas) del total en España en 2030. El éxito de la Red MARFIL contribuirá en gran medida a reducir la dependencia del petróleo, a valorizar los subproductos agrícolas (contribuyendo así a reducir la despoblación en las zonas rurales) y a limitar la cantidad de residuos que van a parar a los vertederos sin ningún tipo de valorización.

El proyecto Red MARFIL forma parte de la convocatoria Cervera Centros Tecnológicos de Excelencia 2023 publicada por el Ministerio de Ciencia, Innovación y Universidades, y financiada con fondos europeos del Plan de Recuperación, Transformación y Resiliencia. El programa está gestionado por el Centro para el Desarrollo Tecnológico y la Innovación (CDTI).

POSTER PRESENTATIONS SESSION 1

(September 16th)

DEVELOPMENT OF LOW-DENSITY FOAMS FROM LIQUID BIOPOLYMERS AND BIO ADDITIVES TO STABILIZE THE CELLULAR STRUCTURE

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Introduction

Today, the extensive use of conventional plastics poses a significant threat to our environment, ecosystems, and human health. These concerns have sparked renewed academic and industrial interest in biobased and biodegradable polymers, offering an eco-friendly alternative to traditional fossil fuel-derived synthetic polymers. One application of these materials is in the production of plastic foams. Given the aforementioned concerns, low densities are highly desirable as they result in lightweight products, reduce plastic consumption, and lower costs.

Methodology

This research focuses on developing biofoams from liquid-based biopolymers using a two-step process: firstly, aeration to produce a liquid foam, secondly microwave heating for drying and sample stabilization. The use of this method not only enables biofoam creation but also provides a more energy-efficient approach [1].

Results and conclusions

This research examines various liquid-based biopolymers, including natural rubber latex with different water contents and polyvinyl alcohol (PVA) with different molecular weights [2]. In both cases the aim is to analyse the effect of initial liquid viscosity on final foamability during aeration and microwave steps. Moreover, stabilizing bioadditives such as egg white powder are introduced into the formulations to improve the stability of the foam and the final cellular structure [3]. In this case, egg white protein, which is normally used in edible foamed products, will improve the aeration because of its surfactant effect and will promote stability in the microwave heating step due to protein denaturalization and viscosity increment of the liquid medium. As a result, stable foams with densities as low as 50 kg/m3 are obtained. Starch is also used as vegetable-based stabilizing additive to enhance the stability of the liquid foam in the microwave step due to gelatinization process it undergoes on heating within a liquid medium. The density and the main structural parameters of both liquid and solid foams are studied to understand the effect of protein and polymer molecular weight/viscosity in the stabilization mechanisms involved in their production. The biofoams obtained could be promising for various applications, such as replacing conventional flexible PU foams in the automotive and comfort sectors, and typical polystyrene and polyolefin foams in the packaging sector.

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THE USE OF BIODEGRADABLE POLYESTER MATRICES FOR MAGNETIC NANOCOMPOSITES

Eider Matxinandiarena [1], Agurtzane Múgica [1], Manuela Zubitur [2], Alejandro Jesús Müller [1,3]

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Introduction

Three types of magnetic nanoparticles (NdFeB, $SrFe_{12}O_{19}$ (SFO) and $SrFe_{12}O_{19}/CoFe_2O_4$ (SFO/CFO)) are employed to prepare nanocomposites based on two biodegradable polymers (Polycaprolactone (PCL) and Poly(butylene succinate-ran-butylene adipate) (PBSA). By DSC experiments all thermal properties were studied. A morphological study was performed by PCLM.

Methodology

PCL and PBSA were employed to prepare nanocomposites with 1%, 5%, 10%-90% of three types of nanoparticles: recycled NdFeB, $SrFe_{12}O_{19}$ (SFO) and $SrFe_{12}O_{19}/CoFe_2O_4$ (SFO-CFO 50/50 wt%). Homopolymers are weighted in aluminum pans and melted in a hot stage. Then, nanoparticles are added and mixed mechanically in the melt, and samples are cooled to room temperature. Six sets of samples are obtained: PCL or PBSA with NdFeB, SFO, or SFO-CFO nanoparticles. The non-isothermal crystallization behavior was determined by DSC using a temperature range between -20 ºC and 80 °C (PCL) or 120 ºC (PBSA) and a rate of 20 °C/min. Morphology at room temperature was analyzed by phase-contrast microscopy (PCM).

Results and conclusions

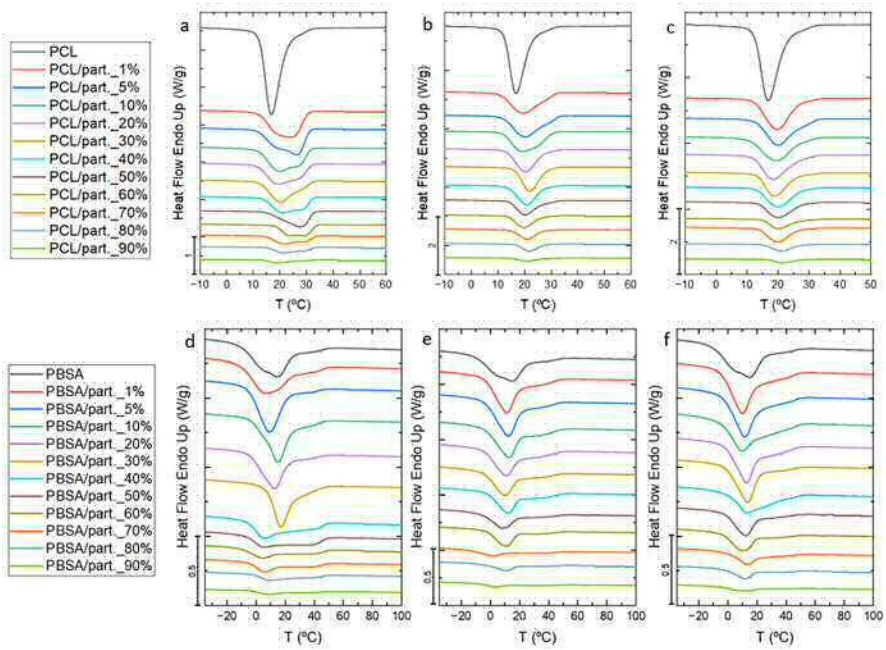

Figure 1. DSC cooling curves at 20 ºC/min of PCL nanocomposites with 1a) NdFeB, 1b) SFO, 1c) SFO/CFO nanoparticles; and PBSA with 1d) NdFeB, 1e) SFO, 1f) SFO/CFO nanoparticles.

Figure 1a, 1b and 1c show DSC cooling scans of PCL nanocomposites with NdFeB, SFO, and SFO/CFO nanoparticles. In Figure 1a, the crystallization exotherms show a bimodal distribution; this may be related to the dispersion of the nanoparticles. There is a fraction of well-dispersed particles that can nucleate a fraction of the material (as the crystallization temperature increases significantly), while sections with particle agglomeration do not significantly nucleate the remaining fraction1. The same behavior is observed in Figure 1b as well as in Figure 1c. Figure 1d, 1e and 1f show the cooling scans for PBSA nanocomposites with the same three nanoparticles. The nucleating effect of nanoparticles is less significant in comparison with PCL nanocomposites. The morphology was analyzed by Phase-Contrast Light Microscopy (PCLM). Although differences are subtle in PCL or PBSA nanocomposites with 1% of different nanoparticles, dispersion seems better when employing NdFeB nanoparticles, thus improving the nucleating effect of such nanocomposites.

Acknowledgments

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DEVELOPMENT AND CHARACTERIZATION OF ELECTROSPUN FILMS OF BIOPOLYESTERS BLENDS OF APPLICATION INTEREST IN FOOD PACKAGING

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2. *Universitat Jaume I (UJI), Castellón, España*

Introduction

Polyhydroxyalkanoates (PHA) are promising candidates to replace petroleum-derived plastics in packaging applications due to their bio-based, biodegradable, hydrophobic, thermoplastic, non-toxic properties and good optical and barrier properties. However, the often inadequate mechanical properties of these polymers limit their applications. Polybutylene succinate (PBS) and poly(butylene-co-butylene succinate adipate) (PBSA) are partially or fully biobased biopolymers, which have been receiving significant attention in the packaging industry for their compostability and balanced mechanical properties. The aim of this work is the development of electrospun PHAs blends with PBS and PBSA and the characterization of their physical properties.

Methodology

Polymeric solutions were prepared for the pure polymers as well as for the blends with different PHAs (PHBV with 2 mol% of 3HV and two grades of PHBH), which were processed by electrospinning in a Fluidnatek LE-500 (Bioinicia S.L.) with control of temperature (27ºC) and relative humidity (30%). The fiber mats were subjected to a mild post-thermal treatment process below the melting point of the polymers in order to obtain continuous films and the obtained materials were characterized in terms of morphology, thermal, WAXS, optical, mechanical and barrier properties.

Results and conclusions

Electrospun fibers of the pure biopolymers as well as their blends with PHAs across the whole composition range were obtained by selecting appropriate solvents and processing conditions, and yielded mats with an average fiber diameter of around 1 µm. The obtained fiber mats were successfully transformed into continuous films. The study of the films by SEM, WAXS, DMTA and DSC allowed us to assess the phase morphology and compatibility between the components in the different blends and as well as to elaborate the discussion about the unique structure-properties relationship found for some of the materials. The produced films for the optimal compositions showed good optical properties and enhanced mechanical properties while retaining to a large extent the good barrier properties of the pure PHAs. As the main result of the study, it was found that the blends with 30% of PBS and PBSA generated the optimal material compositions for the application.

Acknowledgments and References

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PRODUCCIÓN ACUOSA DE HILOS PARA TEXTIL A PARTIR DE NANO/MICROCELULOSA Y BIOPOLÍMEROS

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Introducción

La celulosa es el biopolímero más abundante de la Tierra. Además, su generación captura CO2 atmosférico y es un material sostenible. Sin embargo, su procesado tradicional en forma de fibras textiles supone un gran consumo de recursos y contaminación. Aquí estudiamos un proceso sencillo de hilado a partir del procesado de nanocelulosas/microcelulosa.

Metodología

Con el fin de obtener nanocelulosa, se han estudiado dos vías hidrolíticas: (1) enzimática, empleando una Endoglucanasa, obtenida a través de su reconstrucción ancestral1,2, y (2) únicamente mediante tratamiento mecánico (Fig. 1a). Se ha cuantificado el rendimiento de las reacciones con y sin enzima, y las nano/microcelulosas obtenidas se han caracterizado mediante metodologías como FTIR, XRD, TGA y análisis morfológico. A partir de ellas, se han preparado una serie de dispersiones compuestas de distintas proporciones de nanocelulosa y alginato. Finalmente, mediante un sistema de hilado por coagulación3 en CaCl2, se ha conseguido fabricar monofilamentos de 50-100 micras de diámetro (Fig. 1b). Dichas fibras se han caracterizado mediante ensayos mecánicos de tracción y FTIR.

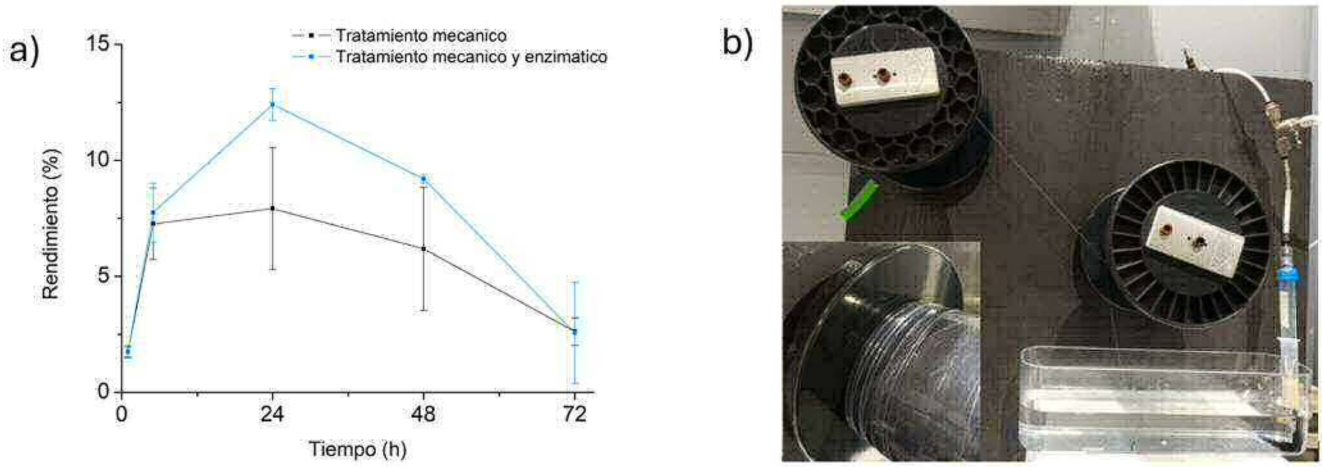

Figura 1. a) Rendimiento de la reacción de hidrólisis en presencia y ausencia enzimática; b) Imagen del montaje empleado en el hilado por coagulación.

Resultados y Conclusión

Los resultados apuntan a que la enzima mejora ligeramente el rendimiento de obtención de nanocelulosa. En lo referente a la fabricación de hilos, los resultados indican que los hilos más ricos en nano/microcelulosa exhiben mayor módulo elástico, resiliencia y tensión de rotura respecto a las fibras de alginato puro. Sin embargo, la deformabilidad disminuye respecto a éstas. Las propiedades mecánicas son comparables a otras fibras empleadas en el sector textil y los resultados son muy prometedores a la hora de diseñar procesos limpios para la producción de biofibras sostenibles.

Agradecimientos

Quiero agradecer al CIC nanoGUNE y a la Universidad del País Vasco por darme la oportunidad de desarrollar mi proyecto, al Gobierno Vasco por otorgarme la beca del programa BIKAINTEK 2021 para financiar mi investigación. Agradecemos al Sincrotrón ALBA y el Programa Tama TA-INOV-20230724-0932-24CB por la financiación del Tiempo de Luz en la línea BL13 (SAXS y WAXS). También a mis tutores, Borja Fernández d'Arlas Bidegain y Arantxa Eceiza Mendiguren por dirigir mi Tesis.

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NOVEL ROOFING BINDERS AND THEIR APPLICATION IN ECO-FRIENDLY CONSTRUCTION

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Introduction

Green construction is dedicated to the implementation of eco-friendly practices, including the minimisation of pollutants, the reduction of materials usage, and the promotion of the reuse and recycling of materials [1]. It emphasises energy savings, environmental preservation, and overall sustainability. In this work, the researchers aim to develop bituminous and non-bituminous binders with recycled or bio-based feedstocks. This will not only improve binder performance but also contribute to the transition to a circular economy, fostering energy savings, and environmental preservation.

Methodology

To assess the viability of the binders, a series of comprehensive tests were conducted. These binders underwent rigorous evaluations of their rheological behavior, thermal conductivity, and response to solar irradiation. The results from these tests were then meticulously compared with those of a reference polymer-modified bitumen to establish a baseline for performance. The primary objective of these tests was to analyze the temperature performance of the binders and determine their suitability for roofing applications, ensuring they can withstand varying climatic conditions. In addition to the experimental tests, Computational Fluid Dynamics (CFD) simulations were employed. These simulations served a dual purpose: first, to validate the experimental setup for solar radiation, ensuring that the tests accurately reflect real-world conditions; and second, to model the ongoing heat transmission mechanism within the binders. By integrating CFD, the study provided a comprehensive understanding of the thermal behavior and overall performance of the binders under actual environmental conditions, thereby enhancing the reliability and applicability of the findings.

Results and conclusions

In line with these principles, those novel binders sourced from bio-based and waste materials emerge as an alternative to petroleum-based bitumen, offering the potential for environmentally friendly roofing materials. They have demonstrated improved energy efficiency, attributed to their colour. This characteristic has led to a notable 14% reduction in heat conduction through the material compared to a traditional bitumen membrane of the same thickness under fixed experimental radiant flux conditions. In summary, these findings suggest that the developed materials could present a more sustainable and eco-friendlier alternative to traditional construction materials.

Acknowledgments

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THE MESOPHASE OF PLA IN MATERIALS WITH ATBC AND MCM-41

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Introduction

The great concerns about environmental pollution and sustainable development is one of the reasons for the success of poly(L-lactic acid) (PLA), a biodegradable polymer produced from renewable resources. PLA can crystallize in different polymorphs, being the α form and the disordered α’ the most important ones. Moreover, a strain-induced mesophase has been also reported [1], which is a kind of solid mesophase [2,3]. This research aims to study the mesophase of PLA, spontaneously developed in materials with acetyl tri-n-butyl citrate (ATBC) and MCM-41 mesoporous silica just by standing at room temperature. Real-time X-ray scattering at both small (SAXS) and wide angles (WAXS), and Infrared spectroscopy with Fourier Transform (FTIR) are employed for that study.

Methodology

Several materials of PLA with ATBC and/or MCM-41 were prepared by melt extrusion and subsequent compression molding. The samples were named as PLAMxAy, being x and y the values, in wt.%, of MCM-41 and ATBC, respectively, in the material. Real-time SAXS/WAXS experiments were carried out with synchrotron radiation in beamline BL11-NCD-SWEET at ALBA.

Results and conclusions

Figure 1 shows the WAXS profiles for the binary materials PLAM0A10, PLAM0A20 and the composites PLAM5A10 and PLAM5A20 during first melting. Specimens PLAM0A10 and PLAM5A10 are initially amorphous, while PLAM0A20 and PLAM5A20 display the mesophase at room temperature. The four samples exhibit a clear cold crystallization on heating, these crystalline phases melting totally at around 162 °C. Relevant information [4] about the degree of order in PLA has been also provided by FTIR measurements. The characteristic band at 916 cm-1 was found for the mesophase [5], and peaks at 923 and 921 cm-1 for the α' and α modifications.

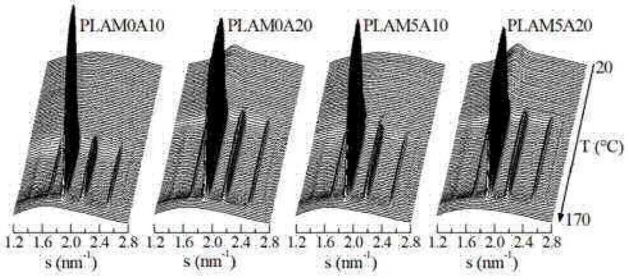

Figure 1. Synchrotron WAXS profiles for the indicated materials.

Acknowledgments

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CELLULOSE NANOCRYSTAL ENABLED SHEAR-THINNING INKS WITH EMBEDDED AU NANOPARTICLES FOR 2D PRINTED PHOTOTHERMIA APPLICATIONS

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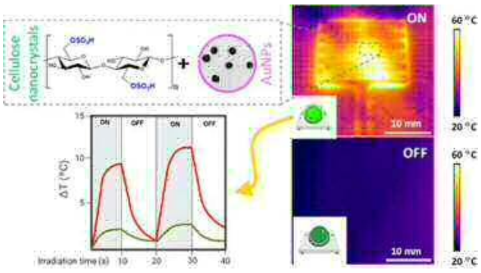
Introduction

Conventional methods of producing photothermally active materials are expensive, time-consuming, and environmentally harmful. Transitioning to a circular biobased economy using renewable materials including cellulose nanocrystals (CNCs) offer potentially sustainable solutions with versatile functional properties. Shear-thinning inks composed of CNCs with embedded active nanoparticles can provide an eco-friendly and efficient approach for printing technologies, with potential applications in biomedicine and flexible electronics. Our aim is to emphasize the intersection of sustainable materials and photothermal microdevices to create innovative and environmentally friendly solutions.

Methodology

Inks are prepared by combining CNC dispersions with gold nanoparticles. The process includes dispersing CNCs in water, followed by the incorporation of spherical gold nanoparticles, coated with PVP for stability, to form stable colloidal inks. The inks are screen-printed onto cellulose acetate substrates and characterised by TEM, FE-SEM, TGA, tensile test, and rheological analysis. Additionally, the photothermal properties are assessed through UV-Vis spectroscopy and thermal imaging, to evaluate their efficiency and potential applications. The study emphasizes eco-friendly practices throughout the synthesis and application processes.



Results and conclusions

Our studies demonstrate that the inks composed of CNCs and gold nanoparticles exhibit excellent photothermal properties and shear-thinning behaviour, making them suitable for screen printing. In fact, after printing and irradiating them with visible light, significant temperature increases of 12 ºC could be achieved. The printed materials were transparent, mechanically robust, and stable in water, suggesting potential applications in sustainable agricultural sensing, smart packaging, and biomedical actuators, emphasizing their biodegradability and non-toxicity.

Acknowledgments and References

The authors acknowledge the funds from the University of the Basque Country (Convocatoria de Ayudas a Grupos de Investigación GIU21/010), the Basque Government under the PIBA (PIBA_2022_1_0047) program, and the Spanish State Research Agency (AEI) through the projects PID2019-106099RB-C43/AEI/10.13039/501100011033, PID2022-139467OB-I00/AEI/10.13039/501100011033, and CNS2023-144447/MICIU/AEI/10.13039/501100011033 /NextGenerationEU/PRTR. Technical and human support provided by SGIker (UPV/EHU, MICINN, GV/EJ, EGEF, and ESF) is gratefully acknowledged.

EXPLORING BORON-BASED MATERIALS AS A PROMISING PLATFORM FOR THE DEVELOPMENT OF DYNAMIC MATERIALS

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Introduction

Vitrimer materials emerged as a potential remedy for the recyclability issues associated with thermosets.1,2 Despite their early potential, creating vitrimers that are genuinely practical has proven to be a difficult task. A common challenge lies in the observation that the dynamic chemical bonds employed either exchange too slowly, necessitating elevated catalyst levels and temperatures for flow induction, or too rapidly, resulting in creep at operational temperatures.3

Methodology

In this project, boron will be introduced to exploit its Lewis acidity, enabling its use as a crosslinking moiety in a polymer network. Utilizing a combination of DFT (Density Functional Theory) calculations allows for the screening of numerous possibilities, enabling the identification of the most promising candidates for further experimental investigation.

Results and conclusions

Leveraging the Lewis acidity of boron, we introduce it as a crosslinking moiety within the polymer matrix. The incorporation of boron enables dynamic covalent bonding, allowing for self-healing properties, reprocessability, and adaptability in response to external stimuli. Through a series of synthesis and characterization techniques, we demonstrate the successful interaction between Lewis Bases and polymer chains doped with boron-containing molecules. The versatility of boron chemistry in these polymers paves the way for innovative applications in sustainable materials, flexible electronics, and advanced coatings. Our findings suggest that boron-containing polymers hold significant potential as a foundational material for future dynamic network applications, offering a promising avenue for advancing the field of smart and sustainable materials.

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CHEMICAL RECYCLING TO MONOMER OF POLYAMIDE 6 WITH SULFONIC ACIDS

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Introduction

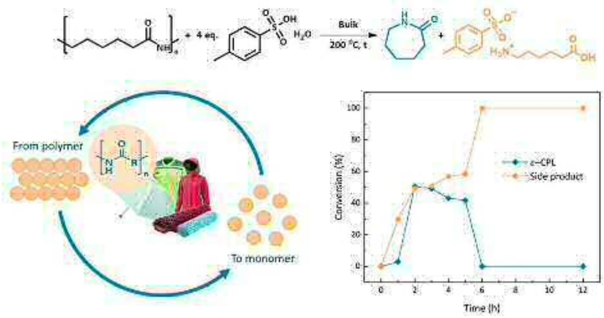
Polyamides (PA) are an important family of polymers used in a wide range of everyday applications due to their excellent properties.1 However, while this high durability makes them suitable for many applications it is also related to its resistance to degradation and depolymerization, so typically, harsh conditions are required to cleave the strong amide groups. For environmental and economic reasons, it is essential to find alternative technologies to recycle PAs efficiently, as recycling rates are critical. 2 Here, we investigate the depolymerization of polyamide 6 (PA6) under simple and easy conditions. We explore different organic acids and reaction conditions to understand the reaction mechanism and optimize it to recover molecules that can be employed in PA6 repolymerization.

Methodology

The depolymerization reactions were carried out employing commercial PA6 and different organoacids. Model reactions were performed using ε-caprolactam (ε-CPL), the direct precursor of PA6, and monohydrated para-toluene sulfonic acid (pTSA·H2O). The nature of the recovered products and the reaction rate (kinetics) were followed by means of 1H-NMR.

Results and conclusions

Different organic acids were tested to assist the hydrolysis of PA6. Among all of them, pTSA·H2O was selected as the best-performing acid as it led to 40 % of ε-CPL conversion and its low cost of production makes it suitable at an industrial scale. Results from the kinetics of the hydrolysis of PA6 with pTSA·H2O showed that the maximum yield of ε-CPL was achieved after 3 hours. At the same time that the monomer was formed, it reacted with the pTSA·H2O resulting in the formation of the salt of aminocaproic acid and PTSA, which was the only product recovered from the depolymerization after 6 hours at 200 °C. In this project, it was proved the potential use of sulfonic acid to assist the hydrolysis of PAs. We reported the depolymerization to the monomer of PA6 at the lowest temperature to date. Additionally, studies of the mechanism of reaction revealed the formation of an ionic compound between the acid and linear version of the PA6 monomer. The recovered compound is likely to be cyclized back to ε-CPL, completing a close loop for the recycling of PAs.



Schematic representation and kinetic analysis of the chemical recycling back to monomer of polyamides

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HIGH-PERFORMANCE ELASTOMERIC COMPOUNDS MADE FROM RECYCLED MATERIALS OBTAINED FROM END-OF-LIFE TIRES

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Introduction

In the rubber industry, end-of-life tires (ELT) represent the most significant waste stream with approximately half of ELT designated for material recovery. Mechanical recycling of ELT generates rubber powder (particle size of 0.8 mm), which is used as a low-cost filler in various polymeric materials for low-performance applications such as shoe soles and playground surfaces. The main objective of this work was to utilize a high concentration of ELT powder as a secondary raw material to improve the sustainability of high-performance rubber compounds used in tire treads.

Methodology

To achieve this goal, it was essential to evaluate the influence of the ELT powder (ELTp) proportion in rubber compounds and the interaction between the rubber matrix and the incorporated ELTp. A virgin rubber compound was used with different amounts of ELTp to select the optimum quantity to incorporate. The optimum compound was then reformulated by incorporating a more vulcanisation system due to the higher concentration of rubber associated with the ELTp. In addition, it was carried out the devulcanization of ELTp and RAR-X (commercial mixture of ELTp and bitumen), using two different approaches: 1) a two-screw extruder; 2) a two-roller mixer. Subsequently, the samples were reformulated in the same way as the previous samples.

Results and conclusions

As the sulphur content increased, the modulus and hardness of the compounds were increased, but the elongation at break and tensile strength were decreased. The dynamomechanical properties of the reformulated compounds were slightly superior to the virgin rubber without ELTp, contrary to the mechanical properties. Furthermore, both properties were found to be inferior to those of an industrial commercial product used for tire tread formulations. The negative effect on the properties of the compounds was due to a poor interface interaction between the powder particles and the rubber matrix. This was evidenced by freezing-point DSC analysis, which showed that the particle is bigger than the polymer chains. Finally, an in-depth analysis of the constituents of the ELTp and RARX will be carried out with the aim of determine the present substances and their interaction with the rubber matrix.

Acknowledgments and References

The authors acknowledge the support given by Valora T Polímeros, SIGNUS and CIRTEC in providing the rubber product, the ELTp and RAR-X respectively. We also thank the financial support from Ministerio de Ciencia, innovación y universidades (PID2020-119047RB-I00, PLEC2021-007793). And finally, I would like to thank the JAE ICU scholarship for the funding of the first months of the thesis.

DEGRADABLE ALTERNATING COPOLYMERS BY RADICAL COPOLYMERIZATION OF 2-METHYLEN-1,3-DIOXEPANE AND CROTONATE, AND TERTPOLYMERIZATION WITH INDUSTRIAL MONOMERS.

Alice Marchand

Polymat, Donostia- San-Sebastian, España

Introduction

Polymer emulsion represents over 20 million (wet) tons per year of the global polymer production but only 0.4% are (bio)degradable.1 Waterborne polymer emulsion are usually performed on vinyl monomers using free Radical Polymerization. However, the polymer particles are mainly formed by C-C bonds that are non-degradable. Radical Ring Opening Polymerization (rROP) on Cyclic Ketene Acetals (CKAs) is an efficient way to introduce ester moieties in the polymer backbone to make them degradable. 2-methylene-1,3-dioxepane (MDO) is known for having good reactivity and ring opening among other CKAs.2 But its homogeneous incorporation during copolymerization is challenging because of its low reactivity ratio compared to other radical polymerization monomers.

Methodology

Crotonic acid derivative esters can be produced completely from biomass but they are difficult to (co)polymerize due to low propagation rates and unfavorable reactivity ratios. The surprisingly easy copolymerization between MDO and butyl crotonate (BCr), which shows the ability to form alternating copolymers will be presented. We will present as well how the crotonates can help the incorporation of the MDO's open form during a terpolymerization with common comonomers used in the industry for radical polymerization.

Results and conclusions

The alternating nature of the MDO-BCr copolymer was characterized by MALDI-TOF. The reactivity ratios were calculated experimentally (r_{MDO} =0.105 and r_{BCr} =0.017). The degradability was assesed under basic conditions Other crotonates were tested to extend the portfolio. Styrene was found not to be suitable for terpolymerization, as it just homopolymerized. With methyl methacrylate, the incorporation of MDO was substantially enhanced due to the presence of MDO, but the terpolymer was not homogeneous, and MDO was primarily incorporated in the closed form, which only partially enhanced the degradability. In the terpolymerization with ethyl acrylate high MDO incorporation is achieved and most of it was incorporated into the open formed. Therefore, the obtained terpolymer showed complete degradation in 28 days. Last, the terpolymerization of vinyl acetate was the most successful, as almost total conversion of all monomers was achieved in short times, including MDO. Furthermore, the obtained terpolymers were highly homogeneous and their complete degradation was achieved.

Acknowledgments and References

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DESIGN AND CHARACTERIZATION OF BIOBASED POLYMERS FROM VEGETAL PROTEINS

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Introduction

Most synthetic polymers, such as plastics that come from petroleum, cannot be attacked by any type of microorganism that exists in nature, so they are not biodegradable and this gives rise to a serious environmental problem. Currently, the need to create new bioplastics as an alternative to commonly used plastics from fossil sources is becoming increasingly important. In addition to the fact that their source is being depleted, the pollution they produce is very high. Through this work, the manufacture of new bioplastics that present biodegradability with characteristics similar to those of synthetic plastics is investigated. In this context, the obtaining of bioplastics from vegetable proteins has been studied, focusing the research on lentil protein, a legume that is grown in large quantities in the community of Castilla y León, where the climatic conditions allow adequate growth of the legume.

Methodology

In order to obtain bioplastics, it is necessary to mix proteins with plasticizers. Obtaining them from different plasticizers has required an analysis of the raw material and plasticizers for subsequent treatment with pressure and heat. The lentil protein was characterized by optical microscopy, thermogravimetric analysis and Fourier transform infrared spectroscopy. In addition, different protein:plasticizer formulations have been studied to analyze their properties. One of the most widely used plasticizers is water, which is introduced into the structure of proteins and interacts with their polar chains forming hydrogen bonds, enabling the plasticization. Another example is glycerin capable of interacting with the polar substituents of the protein and thus allowing the plasticization process.

Results and conclusions

Several aspects of the bioplastics obtained with water or glycerine have been evaluated, such as: visual homogeneity, consistency and its rigid or flexible behaviour. To this end, the thermo-plasticity of proteins and subsequently the processability of the biopolymer have been studied by extrusion process to obtain pellets and process them by injection moulding. Lentil protein with plasticizers needs the help of an additional polymer to be injected. In this study, we have chosen polycaprolactone (PCL). The best formulations of PCL:Protein:GLY:H_2O were selected to obtain injected samples. Finally, a mechanical characterization and an analysis of the general degradation methods in accordance with the UNE-EN ISO 14855 standard were carried out. The best properties of breaking strain of the samples were obtained by PCL:Protein:GLY:H_2O; 70:24:6:0.

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ESTUDIO DE FILMS BASADOS EN RESIDUOS DE FILAMENTOS DE POLI (ÁCIDO LÁCTICO) DE IMPRESORAS 3D CON NANOPARTÍCULAS DE COBRE

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Introducción

El trabajo forma parte de una línea de investigación sobre nuevos productos desarrollados a partir de la revalorización de residuos de filamentos de impresoras 3D [1], principalmente compuestos de poli(ácido láctico) (PLA), plástico biobasado y biodegradable. Se prepararon y caracterizaron films basados en residuos de filamentos comerciales de PLA cargado con nanopartículas de cobre (PLA-Cu), rechazados en el proceso de producción. Con la finalidad de introducir estos materiales en la Economía Circular y considerando que la Unión Europea establece que los productos de un sólo uso deben contener al menos un 30 % p/p de material reciclado, se prepararon formulaciones en las que se añadieron pequeñas cantidades de PLA-Cu reciclado (rPLA-Cu) para conseguir distintas proporciones de nanocargas de Cu. La revalorización de estos residuos resulta ventajosa ya que el Cu presenta un amplio espectro de actividad microbiana, inhibiendo el crecimiento de bacterias, hongos, virus y algas [2].

Metodología

Se utilizaron residuos de las partes inicial y final de procesos de producción de filamentos de impresión 3D (PLA-Cu), proporcionados por el fabricante Colfeed4print (Madrid, España). Estos se trituraron (molino 3Devo), se secaron a 80 ºC, y se mezclaron con rPLA para obtener composiciones de 0,10 % p/p y 0,05 % p/p de Cu, y un 70 % p/p de vPLA. Tras la extrusión (extrusora de filamento 3Devo) se obtuvieron nuevos pellets con esas formulaciones y, posteriormente, se fabricaron films mediante moldeo por compresión (prensa de platos calientes MrHide). Se determinaron propiedades ópticas, térmicas, mecánicas y estructurales de los films obtenidos, y su degradación en compostaje.

Resultados y Conclusiones

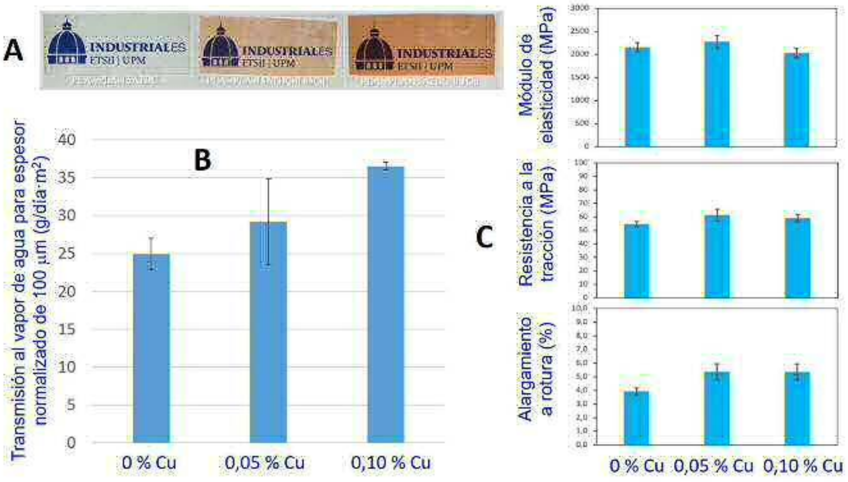

Fig. 1. (A) Films de PLA/Cu obtenidos y resultados de: (B) transmisión de vapor y (C) propiedades mecánicas.

Se obtuvieron films homogéneos y semitransparentes con dos composiciones de nanocargas de Cu. Los resultados mostraron que estos films poseen buenas propiedades mecánicas, similares a las del material sin carga. La adición de cantidades crecientes de Cu genera un aumento en la transmisión al vapor de agua (WVTR). Los materiales se desintegraron completamente en condiciones de compostaje a escala de laboratorio en menos de 1 mes. Los resultados sugieren potencial interés de los materiales obtenidos como films para la agricultura.

Agradecimientos

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FILMS TRICAPA SOSTENIBLES A BASE DE RPLA/CASEINATO/RPLA REFORZADOS CON CELULOSA BACTERIANA DE KOMBUCHA FERMENTADA EN RESIDUOS DE CAFÉ PARA ENVASE ACTIVO DE ALIMENTOS

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Introducción

El elevado uso de plásticos tradicionales derivados de la petroquímica ha provocado una gran acumulación de residuos, especialmente en aplicaciones de corta duración como el envasado de alimentos. Esto ha impulsado el desarrollo de materiales más sostenibles basados en materiales reciclados, biobasados y/o compostables [1]. En este trabajo, se desarrollaron sistemas tricapa basados en un film intermedio de caseinato sódico, y dos capas externas de poli(ácido láctico) (PLA) y PLA reprocesado (rPLA) Además, se ha cargado la capa interna con celulosa bacteriana obtenida de la fermentación de Kombucha (KC).

Metodología

La KC se fermentó en una infusión de residuos de posos de café obtenidos de la cafetería de la ETSII-UPM (KC) para obtener envases antioxidantes, ya que la KC absorbe polifenoles durante la fermentación [2]. Se desarrollaron películas tricapa, utilizando una película de caseinato sódico plastificado con glicerol al 35%p/p (SC-G) como capa intermedia, para mejorar la adherencia entre dos capas exteriores de PLA. Las capas de PLA se prepararon con un 70%p/p de PLA virgen y 30 %p/p de PLA reciclado mecánicamente (rPLA), plastificadas con un 15%p/p de acetil tributil citrato (ATBC). Además, la capa interna se cargó con 0.5%p/p y 1.0%p/p de KC. Las formulaciones obtenidas se caracterizaron determinando sus propiedades ópticas, térmicas, mecánicas, de barrera, antioxidantes y su degradabilidad en compostaje.

Resultados y Conclusiones

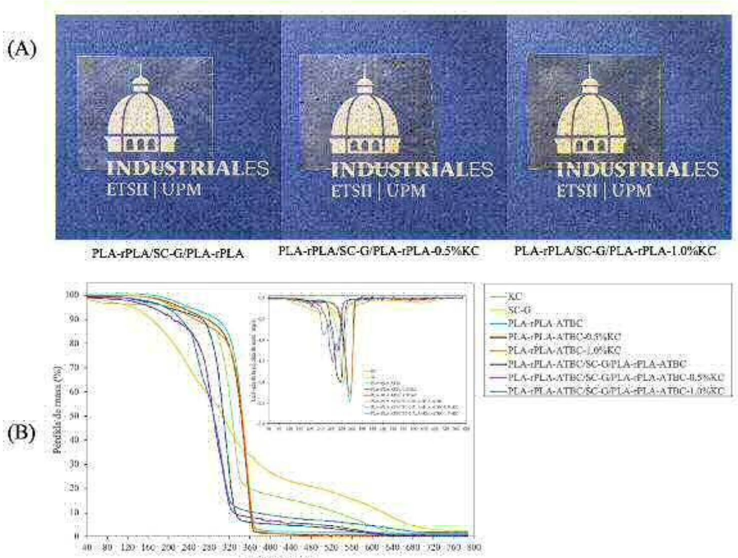

Figura 1. Resultados de (A) films de tricapa obtenidos y (B) termogramas TGA-DTGA de films mono y tricapa.

Se obtuvieron con éxito films tricapa transparentes y homogéneos. La a adición de KC no afectó significativamente las propiedades mecánicas y la incorporación del film de SC-G disminuye la resistencia. KC mejoró la resistencia térmica del PLA, protegiéndolo de la degradación durante el procesamiento y mejorando la estabilidad térmica del sistema tricapa. El comportamiento de todas estas propiedades se atribuyó a la buena adhesión entre las capas de PLA-rPLA y SC-G, atribuida a interacciones de enlace de hidrógeno. Los sistemas tricapa rPLA/SC-G/rPLA-KC1.0%KC y rPLA/SC-G/rPLA-0.5%KC demostraron su potencial como envases antioxidantes para alimentos sostenibles.

Agradecimientos

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A CLOSED-LOOP PROCESS TO TRANSFORM MIXED PLANT BIOMASS WASTE INTO CELLULOSE ACETATE BIOPLASTIC AS INNOVATIVE GROWING SUBSTRATES IN PLANT CULTIVATION

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Introduction

Annually, our planet produces approximately 140 gigatons of biomass waste (United Nations Environment Programme 2015). Due to its high carbon content and reliable accessibility, biomass waste exhibits potential as a cost-effective resource for the recovery of materials and energy. There are many sources of biomass waste including agriculture, forestry, and industry. Presently, biomass waste from industrial sources is being utilized more extensively compared to other sources, because industrial biomass waste tends to be more uniform and purified in quality, simplifying its handling and processing (Gupta et al. 2022). The majority of research studies focus on industrial biomass waste or single-source agricultural biomass waste. Garden waste, including grass clippings, leaves, branches, and plant trimmings, is a common source of mixed plant biomass waste and is usually not valorised due to its heterogeneous nature.

Methodology

The composition of several common garden waste was measured, consisting of wheat straw, tomato leaves and stalks, strawberry leaves and stalks, radish shoots, cucumber leaves and stalks, corn leaves and stalks, runner bean leaves and stalks and grass. A mixture of these garden residue was prepared and extracted for cellulose using alkaline hydrogen peroxide (AHP). The extracted cellulose was converted into cellulose acetate using a solventless method with iodine as the catalyst. The generated cellulose acetate was modified and 3D printed into porous structures for plant cultivation.

A closed-loop process to transform mixed plant biomass waste into cellulose acetate bioplastic as innovative growing substrates in plant cultivation

Results and conclusions

This research innovatively valorises mixed waste into biopolymers for sustainable plant cultivation, addressing waste management and enhancing agricultural sustainability. It presents a circular economy solution by converting biomass waste into valuable growing substrates, reducing environmental impacts and supporting food security. The approach also offers potential applications in space agriculture, demonstrating a significant stride towards resource efficiency and sustainability.

Acknowledgments

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TRANSFORMACIÓN DE LIGNINA EN FILTROS SOLARES FOTOADAPTATIVOS.

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Introducción

El uso de filtros solares es uno de los mecanismos más recomendados para evitar el cáncer de piel y otras enfermedades cutáneas derivadas de la exposición al sol. Roka Furadada comercializa desde 2022 la gama de activos ROKA Smart UV®. A diferencia de los filtros ultravioleta convencionales, estos activos se fotoactivan con la luz solar experimentando una transposición de tipo Photo-Fries, transformándose en nuevas moléculas que absorben a otras longitudes de onda y prolongando la capacidad de absorción de radiación de la molécula. Esta tecnología permite una protección fotoadaptativa que se ajusta a las condiciones atmosféricas y que se incrementa cuánta más radiación recibe. Con el fin de reducir el impacto medioambiental de sus productos y contribuir en la economía circular, se han llevado a cabo los primeros estudios exploratorios para sintetizar y producir protectores solares biobasados en lignina con la tecnología ROKA Smart UV®. La lignina es el segundo biopolímero más abundante de la tierra solo por detrás de la celulosa. No obstante, es considerada como un subproducto de bajo valor derivado de la producción del papel y del bioetanol. Sin embargo, la complejidad estructural y funcional de la lignina comporta una serie de retos que han debido ser superados mediante distintas estrategias a lo largo de este proyecto.

Metodología

La lignina se modificó químicamente con el objetivo de aumentar su funcionalidad para favorecer la posterior reacción de Photo-Fries. Se ensayaron dos estrategias: 1) reacción directa con los grupos fenólicos, o 2) preactivación química de la estructura de lignina para favorecer su foto reactividad.

Resultados y Conclusiones

La primera familia de productos obtenidos por funcionalización directa dio lugar a productos con escasa actividad. Sin embargo, tras realizar modificaciones previas en la estructura de la lignina, se obtuvieron productos que si presentan fototransformación cuando se irradian, aunque con conversiones relativamente bajas. Los resultados obtenidos permiten demostrar que se puede realizar la transformación Photo-Fries en la lignina. Estos resultados abren la puerta a potenciales activos ROKA Smart UV® derivados de lignina.

Agradecimientos

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VALORIZACIÓN DE RESIDUOS DE CORCHO EN POLÍMEROS: HACIA MATERIALES COMPUESTOS MÁS SOSTENIBLES

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Introducción

El corcho es un producto natural que se extrae de la corteza de los alcornoques. Posee múltiples propiedades únicas (aislante térmico y acústico, bajo coeficiente de Poisson…) que hacen que este material sea excelente en diversas aplicaciones, como en la fabricación de tapones y paneles aislantes. Sin embargo, alrededor del 30% del corcho de partida se pierde en el proceso de lijado y en el procesado. Este residuo generalmente se desecha, quemándose, en la mayoría de los casos para eliminarlo. Una de las estrategias que se plantea es la valorización de este residuo integrándolo en una matriz polimérica con el objetivo de fabricar materiales compuestos sostenibles [1,2].

Metodología

Se usaron residuos de corcho procedente del parque de los Alcornocales de Cádiz, tamizado en diferentes granulometrías, desde 63 µm a 1.8 mm. Este residuo se integró en matrices poliméricas de ASA (polímero de ingeniería) y nanoquitina (biopolímero) mediante solvent casting o extrusión de doble husillo, empleando un amplio rango de concentraciones de corcho. Una vez sintetizados los materiales compuestos, se fabricaron distintos objetos mediante fabricación aditiva y moldeo por compresión. Por último, se estudió la influencia del corcho en estos materiales compuestos mediante ensayos de tracción y de compresión.

Resultados y Conclusiones

En los materiales compuestos de ASA se estudió la cantidad máxima de corcho que se puede integrar en la matriz polimérica, permitiendo que el material sea procesable por fabricación aditiva de gran formato mediante fabricación de granza fundida (FGF). Se observó que se pudieron procesar correctamente materiales compuestos con hasta un 30%p de corcho con tamaños de partícula de hasta 1.8 mm. Aunque las propiedades mecánicas para este material compuesto disminuyeron al aumentar la cantidad de corcho, el material mostró unas propiedades mecánicas aceptables (resistencia a la tracción mayor de 20 MPa) al mismo tiempo que permitió reducir el porcentaje de plástico derivado del petróleo. En los materiales compuestos basados en nanoquitina se evaluó la posibilidad de emplear la nanoquitina como aglutinante en lugar de otros compuestos derivados del petróleo en la fabricación de tapones de corcho mediante moldeo por compresión. En este caso se obtuvo que el material compuesto con un 80%p de corcho permite obtener un compuesto totalmente biobasado con buenas propiedades mecánicas por compresión.

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DEPOLIMERIZACIÓN DEL POLIMETACRILATO DE METILO A TEMPERATURAS MODERADAS

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Introducción

El polimetacrilato de metilo (PMMA) es un polímero con una producción notable y alta demanda especialmente desde la pandemia debida al COVID para la fabricación de barreras transparentes de protección, entre otros productos. El PMMA se puede reciclar por tratamiento mecánico. Sin embargo, las propiedades mecánicas del producto tratado se ven seriamente afectadas. En 2019 la IUPAC estableció que la depolimerización de los plásticos se encuentra entre las 10 tecnologías emergentes más importantes en química. La pirólisis del PMMA permite la depolimerización cuantitativa hasta el monómero (MA) pero requiere condiciones energéticamente demasiado costosas. Recientemente se ha demostrado que se puede diseñar los polímeros de PMMA para conseguir su fácil depolimerización en condiciones más suaves de temperatura [1]. Esta estrategia se basa en introducir al final de la cadena de PMMA grupos funcionales clave que tengan una baja energía de enlace (halógeno o un grupo ditiocarbonato) En este trabajo se aborda el diseño de polímeros de PMMA con nuevas arquitecturas (preparados por polimerización controlada) y se muestran los resultados de su degradación térmica al monómero a temperaturas moderadas.

Metodología

La cinética de depolimerización se estudió en función del disolvente, temperatura, peso molecular y concentración de polímero por diferentes técnicas: SEC-MALS, 1H RMN y espectroscopía de absorción UV-vis

Resultados y Conclusiones

Los resultados sugieren que además de la temperatura, la elección del disolvente y la concentración del polímero son factores cruciales para el proceso de depolimerización. Se optimizaron las condiciones y se consiguió una alta eficiencia de depolimerización.

Agradecimientos

Ministerio de Ciencia e Innovación (Consolidación Investigadora 2022. Ref. CNS2022-135568).

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BIOCOMPOSITES BASED ON PHBV WITH PHA MICROPARTICLES AS FILLERS FOR PACKAGING APPLICATIONS

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Introduction

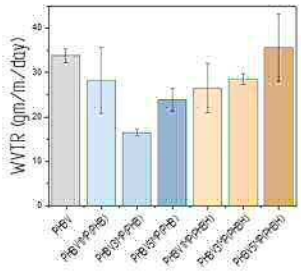
Polyhydroxyalkanoates are promising sustainable materials for packaging applications as they have similar characteristics to commercially available plastics [1]. In order to adapt their property profile to the requirements, they are often used as biocomposites. By using PHA microparticles as fillers in the PHBV matrix, it is possible to preserve the green character, modify the properties and maintain the chemical homogeneity. In this work, their suitability for packaging material is investigated by studying their mechanical and barrier properties along with their morphological and thermal properties.

Methodology

The biocomposites were produced with Poly-(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Goodfellow), Polyhydroxybutyrate PHB (Biomer), Polyhydroxybutyratehexanoate PHBH (Maip) were used. The PHB and PHBH microparticles were produced by miniemulsion-evaporation-technique. The biocomposites were produced by preindustrial melt processing via Haake miniextrusion and miniinjection. The produced biocomposites were tested by transmission electron microscopy (TEM), differential scanning calorimetry (DSC), tensile test and barrier properties.

Results and conclusions

The incorporation of all microparticles induced a heterogenous nucleation resulting in higher crystallization temperatures and increased crystallization in the biocomposites in comparison to the neat PHBV. This led to an embrittlement in the composites of their mechanical properties, especially by the PHB particles composites showed in a loss of the elongation and higher Youngs Modulus, thus showing a reinforcing effect of the particles in the matrix. Beside good mechanical properties, the barrier properties are crucial for their application as packaging material. Here the transmission rate of water vapor and oxygen was significantly reduced for the particle reinforced composites due to the higher crystallinity resulting in slower permeation of the gas molecules through the samples [2].



Gas barrier properties of the PHBV biocomposites against water vapor

Acknowledgments

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PREPARATION OF FILMS POTENTIALLY APPLIED TO AGROINDUSTRY FROM DISCARDED 3D PRINTING MATERIAL BASED ON POLY(LACTIC ACID) AND IRON PARTICLES.

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Introduction

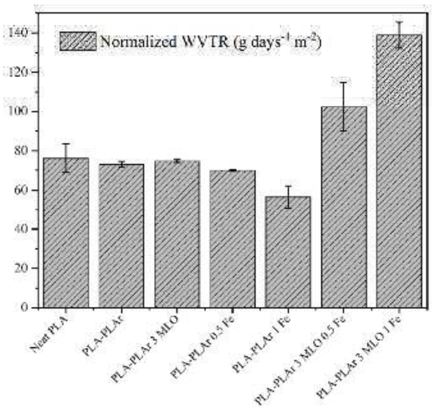
Polymer-based composites are gaining importance in the Fused Deposited Modeling (FDM). Specifically, metals and metal oxides are widely studied as reinforcement (highlighting the PLA composites) due to improvements in mechanical strength, more uniform biodegradability, or magnetic-controlled motion. This work uses the recovered material from a 3D printing filament production line, based on PLA and Fe particles, to produce translucent films. Generally, an amount of material from the beginning and end of the process is discarded to ensure a homogeneous distribution of particles. This material and other discarded parts have been homogenized and diluted with reprocessed PLA to obtain materials with two different concentrations of Fe (0.5 and 1 wt.%). To counteract the effect of reprocessing (rPLA), virgin PLA was added in a 30/70 proportion and plasticized at 3 wt.% with maleinized linseed oil (MLO). Fe particles were initially sieved under 25 microns.

Methodology

Due to the potential applicability of the films to the agroindustry, the water permeability and compostability have been studied. The water vapor transmission ratio (WVTR) was determined by gravimetric keeping the samples in a desiccator with a saturated KNO3 solution at 23 ± 1 ºC and 90 % RH. The degree of compostability was determined by following the ISO 20200 standard.

Results and conclusions

Obtained WVTR results show that in blending PLA with reprocessed PLA the permeability and compostability are not significantly affected, nevertheless, both are slightly higher for the PLA-PLAr, since reprocessing induces a decrease in the average molecular weight which facilitates the interaction with water molecules [1]. Lower WVTR values were obtained for the films produced from PLA with iron particles depending on the Fe content. However, this decreased permeability is noticeably counteracted with the addition of MLO. In addition, the plasticized accelerates the compostability since the matrix free-volume increment while the presence of Fe and the formation of oxides also increased the biodegradability compared to the PLA.



Acknowledgments

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SÍNTESIS DE POLIURETANOS SIN ISOCIANATO MEDIANTE FIJACIÓN DE CO2

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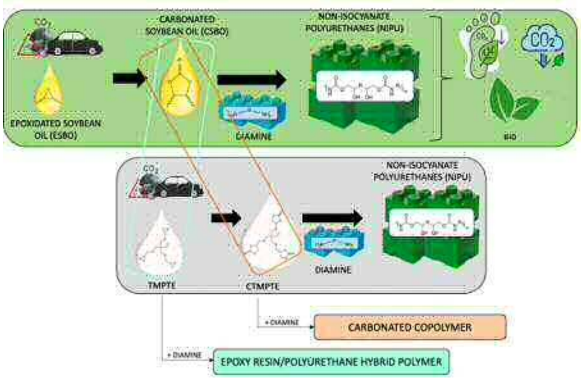
Introducción

El incremento de la concentración de CO2 en la atmósfera motivado por la actividad humana está acelerando el cambio climático. Por lo tanto, resulta importante desarrollar procesos para reducir la cantidad de CO2. Una de las vías para lograr este objetivo, utilizada en la obtención de poliuretanos, es el empleo de este gas como materia prima.

Metodología

Los poliuretanos convencionales se sintetizan utilizando isocianatos que son muy tóxicos. Sin embargo, su obtención por vías libres isocianato (NIPU, non-isocyanate polyurethanes) utilizando CO2 [1] además de reducir la cantidad de CO2, genera polímeros más verdes y sostenibles. Para sintetizar NIPUs sostenibles, en este trabajo se ha utilizado aceite de soja epoxidado (ESBO, epoxidated soybean oil) y CO2. Mediante fijación de CO2 y catálisis homogénea, se ha optimizado la producción del aceite de soja carbonatado (CSBO, carbonated soybean oil) [2]. Las variables analizadas para la optimización del proceso han sido la temperatura (100 -140 ºC), presión (10 – 30 bar) y porcentaje en peso de catalizador (0,5 –3,5%). Las conversiones obtenidas y el análisis estadístico con el sofware JMP Pro 1700, han permitido establecer las condiciones óptimas de reacción (140 ºC, 10 bar y 3,5% de catalizador). Además, también se ha llevado a cabo la síntesis de éter triglicidílico de trimetilolpropano carbonatado (CTMPTE), partiendo de éter triglicidílico de trimetilolpropano (TMPTE).



Resultados y Conclusiones

Una vez carbonatado el aceite de soja, se han obtenido NIPUs mediante la reacción de aminólisis entre el carbonato y las diaminas. El CSBO se ha mezclado con diferentes diaminas para establecer su influencia en la estructura y en las propiedades del NIPU. Por otro lado, la 1,4-butanodiamina se ha empleado para la obtención de una serie de polímeros híbridos (epoxi/uretano) a través de los monómeros CSBO y TMPTE, y copolímeros utilizando los monómeros CSBO y CTMPTE. Variando la concentración se han obtenido polímeros con diferentes propiedades mecánicas. Los resultados muestran que el CO2 puede ser utilizado para obtener NIPUs evitando el uso de los monómeros tóxicos isocianatos.

Agradecimientos

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PREPARATION AND CHARACTERIZATION OF BIOCOMPOSITES REINFORCED WITH NOVEL GREEN GRAPHENE

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Introduction

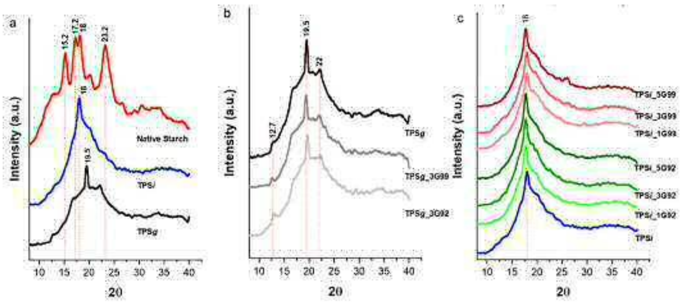
A major research focus on the search for alternative materials in the packaging industry to replace conventional petroleum-based polymers continues to this day, through the use of environmentally friendly materials with plastic-like properties, but which are biodegradable, non-toxic, naturally occurring and from renewable sources. One alternative that meets these characteristics are starch biopolymers, which have high availability, low cost and the possibility of obtaining them from various renewable sources. Although starch itself is not thermoplastic, it is possible to obtain thermoplastic starch (TPS) through the addition of a suitable plasticizing agent, as well as through shearing and temperature control processes. The main objective of this research is the development of starch-based biocomposites for implementation in food packaging.

Methodology

Plasticized corn starch comparing two different types of plasticizers (isosorbide and glycerol) was used for the preparation of new biocomposites, which were reinforced with two types of graphene fillers with different levels of oxidation at different concentrations. The prepared samples were characterized in aspects such as morphology, mechanical properties, thermal stability, crystallinity, water absorption and biodegradation.

Results and conclusions

The most important results include the use of isosorbide as a plasticizer, which prevented retrogradation of the material and thus maintained its properties for a long time. In addition, the biocomposite is 100% biodegradable. In conclusion, the use of isosorbide as a plasticizer and the reinforcement with "green" graphene increased thermal stability, avoided retrogradation over time, reduced water absorption and improved biodegradability



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MATRICES BIODEGRADABLES A PARTIR DE UN SUBPRODUCTO PROTEICO PARA LA LIBERACIÓN CONTROLADA DE NUTRIENTES Y AGUA A LOS CULTIVOS

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Introducción

El incremento en la producción hortícola ha llevado a una percepción renovada de la agricultura, fomentando el cultivo intensivo para satisfacer la creciente demanda. Este tipo de agricultura intensiva, junto con la mayor incidencia de plagas y el cambio climático, ha incrementado el uso de plásticos en este sector. Estos plásticos se utilizan para el suministro de agua y fertilizantes y para proteger los cultivos, pero su uso implica costos adicionales tanto por su adquisición como por su retirada para evitar la contaminación del suelo. En este contexto, los bioplásticos ofrecen una solución debido a su biodegradabilidad, eliminando la necesidad de retirarlos tras su uso. No obstante, se requiere más investigación para que los bioplásticos puedan competir y eventualmente reemplazar a los plásticos tradicionales. Optimizar el proceso de fabricación y desarrollar aplicaciones multifuncionales en un solo dispositivo son desafíos clave. El objetivo de este trabajo fue el desarrollo de matrices bioplásticas proteicas para la liberación controlada de micronutrientes y agua en cultivos.

Metodología

El aislado proteico de soja, un subproducto de la producción de aceite de soja, se seleccionó como materia prima para estas matrices, las cuales fueron procesadas mediante inyección. También se seleccionaron diferentes micronutrientes (zinc, hierro, manganeso y cobre) con la intención de evaluar su incorporación en las matrices y su efecto en las plantas (cinética de liberación, captación de agua, biodegradabilidad y crecimiento del cultivo).

Resultados y Conclusiones

Los resultados indicaron que el subproducto de soja es viable para el desarrollo de las matrices bioplásticas biodegradables con micronutriente incorporado, permitiendo su liberación controlada y la captación de agua. Los estudios con cultivos mostraron que las matrices mejoran la asimilación de nutrientes, resultando en plantas más grandes y fuertes, con frutos enriquecidos en micronutrientes y una menor necesidad de riego. Este trabajo demuestra un nuevo concepto de fertilización más eficiente y sostenible, alineado con la economía circular y los objetivos de la Agenda 2030. No obstante, es necesario seguir investigando en esta línea para conseguir un escalado industrial y la validación en campo abierto.

Agradecimientos

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FUNCTIONALIZED STARCH-BASED MATERIALS FOR FOOD PACKAGING APPLICATIONS

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Introduction

The research on bio-based plastics has to tackle several challenges for proposing reliable alternatives to current commodity plastics. The appeal of starch lies in its biodegradability and non-toxicity, being also an inexpensive and widely bioavailable material. Starch can be chemically modified relatively easily, commonly through hydroxyl substitutions in C6, C2, and/or C3, to change the structure of amylose and amylopectin [1]. This modification can increase the thermal stability, hydrophobicity, paste clarity, mechanical strength, freeze-thaw stability, and retrogradation resistances of starch [2]. In this study, we aim to develop active packaging materials from functionalized starch granules with antimicrobial agents.

Methodology

The modification of potato starch was carried out using a one-pot reaction. First,1,6-hexamethylene diisocyanate (HDMI) was linked in bulk to an antimicrobial agent, menthol or sulfobetaine. The isocyanate derivative then reacts with starch dispersed in methyl-THF at 70 ˚C, using K2CO3 as a base. FTIR, NMR, and TGA characterization were used to study the reaction evolution. Films were prepared from a solution of glycerol, water, and various ratios of neat/modified starch. The solutions were heated for 30 min at 80 ˚C, cast in PE petri dishes, and left to dry in an oven. The mechanical properties of the films were studied.

Results and conclusions

Menthol and sulfobetaine were linked to starch through the hydroxyl groups in the granules' surfaces, using HMDI as a connecting agent. With the successful completion of the chemical modification, up to 15 mol% of the antibacterial agent was anchored to the starch. As predicted, menthol-modified starch exhibited a stronger hydrophobic behavior with higher content, and greater than the sulfobetaine-modified granules. On the mechanical properties, this functionalization had little effect. The antibacterial behavior of these materials will be examined in the future. These bio-based materials will help develop active packaging that maintains food quality and safety.

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ANÁLISIS Y POLIMERIZABILIDAD DE MMA RECICLADO QUÍMICAMENTE.

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Introducción

El polimetilmetacrilato (PMMA) es un material cada vez más solicitado a nivel mundial debido a sus propiedades y su versatilidad. Es un polímero ligero, de elevada resistencia a la tracción y la flexión, transparente y con buena resistencia a los rayos UV que tiene múltiples aplicaciones. [1]

Actualmente, de las 300.000 toneladas de PMMA producidas anualmente en Europa, solo se reciclan mecánicamente 8.000 toneladas debido a que, mediante esta vía de reciclaje se obtiene un PMMA de baja calidad que no alcanza los requisitos de transparencia y resistencia al clima y, por tanto, su aplicación es limitada.

Por este motivo y por la previsión del aumento de volumen del mercado de PMMA, surge la necesidad de conseguir una transición hacia una economía circular encontrando alternativas de reciclaje de PMMA rentables y respetuosas con el medio ambiente como puede ser el reciclaje químico que permitiría la recuperación del material monomérico que podría utilizarse para un nuevo ciclo de vida. Sin embargo, es necesaria una mayor investigación para reducir entre otros el coste energético del proceso y mejorar la conversión del reciclado. [2]

Metodología

Se ha empleado para la pirólisis del polímero un reactor de lecho fluidizado TRL-5 a 450ºC. Para la repolimerización se ha empleado la polimerización radical iniciada térmicamente utilizando AIBN como iniciador. Los polímeros se han caracterizado mediante GPC, TGA y DSC y espectroscopia UV-vis.

Resultados y Conclusiones/Results and conclusions

El PMMA comercial es reciclado por despolimerización termoquímica cuando se calienta por encima de su temperatura techo, Tc, y se producen roturas de cadena que inician el unzipping. En este trabajo se presentan resultados de despolimerización por pirólisis de PMMA obtenido a partir de diversos materiales (planchas, granza, piezas defectuosas de automoción…) al final de su vida útil y posterior destilación del crudo.

El monómero obtenido de la pirólisis se caracteriza mediante diversas técnicas comparándolo con los resultados del monómero comercial. Además, se estudia su repolimerizabilidad analizando los polímeros obtenidos y comparando su reciclabilidad con respecto a los polímeros comerciales.

Agradecimientos

Esta contribución forma parte del proyecto TED2021-130093B-C22, financiado por MCIN/AEI/10.13039/501100011033 y por la Unión Europea «NextGenerationEU»/PRTR."

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ARE GREEN METHODS SUITABLE FOR CHITIN DEPROTEINIZATION?

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Introducción

Extraction of chitin from natural sources requires several independent processes, such as deproteinization. Conventional chemical deproteinization processes have several disadvantages, mainly related to environmental contamination derived from the production of corrosive waste, alongside high energy consumption. Therefore, green strategies must be introduced to diminish the environmental impact associated with the use of this natural polymer.

Besides the chemical deproteinization of chitin, this polymer can be processed through the use of Deep Eutectic Solvents. In this study, the chitin deproteinization efficacy of different DESs is evaluated. These results are compared with enzymatic-mediated deproteinization of chitin. Through this study, a novel and greener chitin deproteinization methodology will be established.

Metodología/Methodology

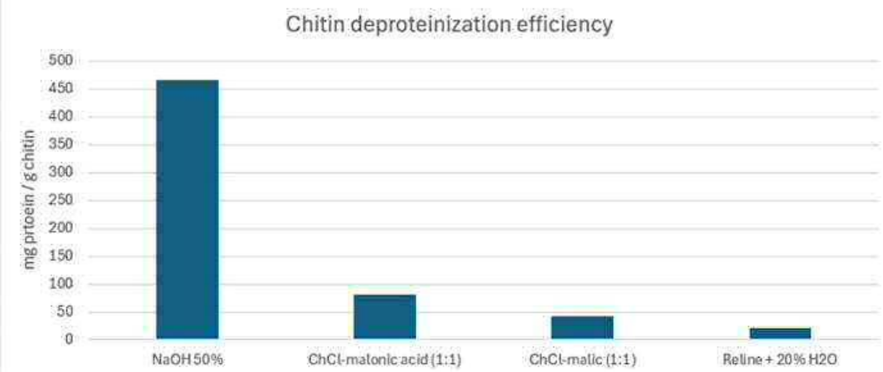
Squid pen chitin was exposed to NaOH, DES media, or aqueos enzyme media. After a given amount of time, chitin is washed with distilled water and a 1 mL aliquot is taken. The washing step is repeated until a neutral pH value is obtained. Once the neutral pH value is obtained, the protein concentration of each obtained aliquot is determined through the bicinchoninic acid (BCA) assay.

Samples were dried at 50ºC for 24 h and weighed. BCA assay was used to determine protein concentration in the supernatant of the reaction media and in the washings.

Resultados y Conclusiones/Results and conclusions

When it comes to enzymatic deproteinization efforts of squid pen chitin, Neutrase was the enzyme less effective to remove the proteins while alcalase 2,5 was the most efficient enzyme. In the first case 128 mg protein/g of polymer were removed while in the second one 363,8 mg/g of polymer were removed.

Basic DESs systems achieve a minimal deproteinization of chitin. On the other hand, acidic DESs systems have a higher deproteinization efficacy. Future studies will seek to optimize chitin deproteinization with this novel media.



Agradecimientos y Referencias/Acknowledgments and References

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SUSTAINABLE POLYMERS FOR A BETTER ENVIRONMENT: CHITOSAN-BASED COATINGS EMBEDDED WITH ACTIVATED CARBON FOR WATER REMEDIATION

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Introduction

Pesticide residues in the environment severely impact potable water. To remove them, adsorption is an effective means due to its ease of operation and efficiency,[1] with activated carbons (ACs) being the most important type.[2] However, its separation from treated water for recycling and reuse is prohibitively costly. To address this issue, integrating AC into a matrix offers a promising solution.

Chitosan (CH) an abundant biopolymer with an estimated annual global production of ~10^{11} tonnes (2021),[3] is inexpensive, non-toxic, biodegradable, and also contains many -NH_2 and -OH groups that aid polymer network swelling, improving contaminant molecule penetration. CH-based films embedded with adsorptive particles exhibit great adsorption capacity and rectify many of ACs limitations,[4] though are mechanically poor.

Herein we present robust CH/AC-textile supported systems and test them for herbicide adsorption (Fig. 1).

Methodology

CH was dissolved in dilute acetic acid and mixed with ACs to form a composite slurry. This slurry was cast on different textile types using a doctor blade, then neutralised and crosslinked to obtain supported CH/AC adsorbents. These were used for water remediation: removal of atrazine, one of the most problematic herbicides in groundwater on a global scale. Adsorption kinetics, isotherm and thermodynamics studies were conducted to understand the adsorption performance and mechanism.

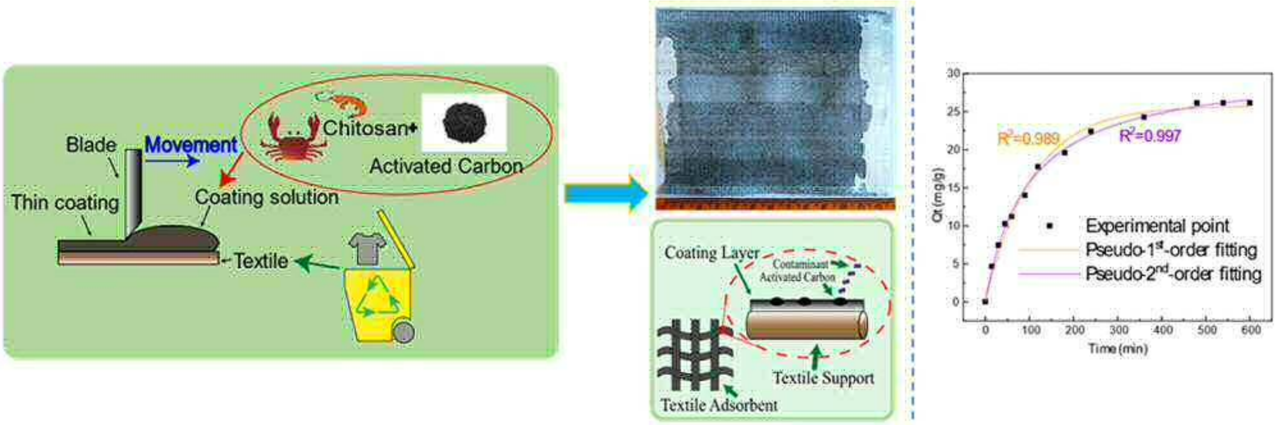

Figure 1. CH/AC textile coating preparation and its adsorption performance

Results and conclusions

The presentation will show how the composite slurry was optimised for casting by tuning both the CH molecular weight and the AC loading. The composite coating on the textiles was stable under pH conditions ranging from 3 to 11, suggesting its application potential under realistic conditions. The textile support improved mechanical strength of the coated films and also facilitated after use removal from aqueous media. The textile-based adsorbent shows a capacity of ~25mg/g towards the tested herbicide.

Acknowledgments

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PLA PLATFORM MEMBRANES FOR APPLICATIONS AS 3D SLIPS

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Introduction

Many industrial processes related to species separation and transport rely on membrane technology due to its advantages in selectivity, processability, cost-effectiveness, and operational simplicity. However, this technology commonly involves the use of non-renewable polymers and toxic and polluting organic solvents.Currently, in PoEMA Project, the research is focused on the replacement of polymers which pose environmental issues, by greener ones, biobased and/or biodegradable, bringing the membranes closer to the new model of circular economy where sustainable materials are demanded.From a sustainable perspective, platform membranes for 3D SLIPS (Slippery Liquid Infused Porous Surfaces) will be developed, inspired by the structure of the liquid-infiltrated porous and rough peristome of the Nephentes Pitcher Plant. These membranes will create a smooth surface liquid layer, additionally storing lubricant throughout the entire volume.

Methodology

Membranes were prepared using the Non-Solvent Induced Phase Separation Method (NIPS), incorporating a crystallinity induction step to texture the surface. Polylactic acid (PLA) and green solvents, Cyrene and γ-Valerolactone, were utilized instead the commonly used DMF or NMP. After optimizing the membrane formation and the texturization process, a set of membranes were prepared with PLA, and their morphology (SEM and optical profilometry), crystallinity (DSC, IR and XRD), thermal stability (TGA), and wettability properties (Contact Angles and hysteresis) were studied. According to morphology and performance, the best membranes are selected for 3D SLIPS applications, where various lubricants are infiltrated to assess sliding speed and lubricant stability.

Results and conclusions

PLA3052 at 200µm, with γ-Valerolactone as the solvent and ethanol as the coagulant, were utilized for the membrane preparation. Texturization with acetone increased membrane roughness, resulting in altered profilometer parameters and a superhydrophobic character. The acetone-treated membranes were then infiltrated with castor and silicone oils, the most successful being the former with a sliding speed of 0.10 mm/s.

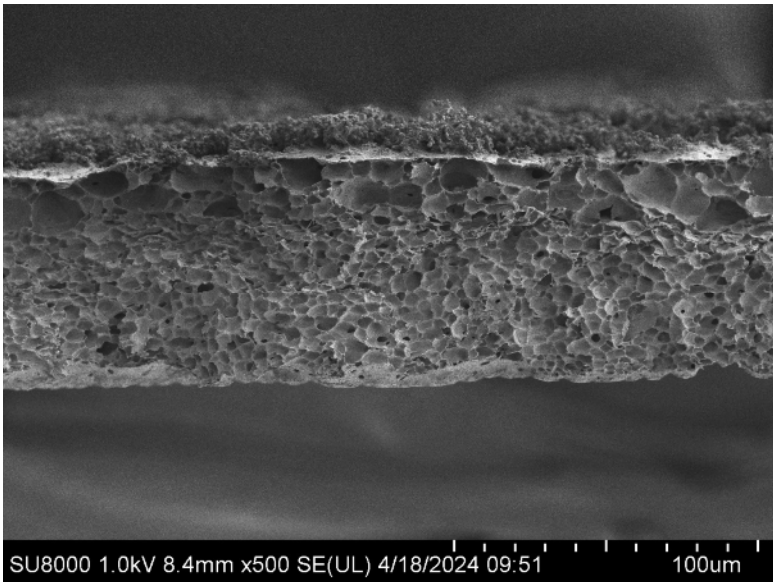

Figure 1. SEM image of the cross section of a porous membrane prepared.

To conclude, the first 3D SLIPS of the group have been achieved, employing biodegradable PLA and green solvents in the processing.

Acknowledgments

The authors would like to acknowledge to the Spanish Ministry of Science, Innovation and Universities for funding Project PoEMA (PID2022-143310OB-I00).

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RECYCLED VS VIRGIN PET: DISTINCT FEATURES AND PROPERTIES

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Introduction

The transition to a Circular Economy Model must be guided by legislation. Thus, the Directive (EU) 2019/904 of the European Parliament on the reduction of the impact of certain plastic products on the environment imposes to each Member State to ensure that from 2025, beverage bottles manufactured from polyethylene terephthalate (PET) as the major component contain at least 25 % recycled plastic, and from 2030, PET bottles must contain 30% recycled plastic. This regulation published on June, 12th 2019 was an inflection point for the plastics manufacture industry and led to a substantial increase in recycled PET pellets price and suppliers. Although, the chemical recycling is nowadays trending topic, the mechanical procedure is that generally used for most applications. However, the mechanical recycling has an impact on the final properties of PET, mainly on rheology, mechanical performance and transparency that negatively affect to the quality of the finished goods produced.

This work focuses on the characterization of several samples of recycled and virgin PET in the search of particular features to understand the distinct behaviour. This will ultimately allow to optimize the processing conditions to minimize the effect of recycled PET addition on the final properties of the finished product.

Methodology

A combination of characterization techniques such as DSC, FTIR, AFM, SEM, XRD, TGA, and viscosity measurements was used to get a deep knowledge on the chemical structure and crystal morphology of a set of recycled and virgin PET samples from different suppliers. Chemically and mechanically commercial recycled samples are also compared.

Results and conclusions

The mechanical recycling alters the crystallinity content and morphology which is clearly observed by the characterization protocol applied in this study. DSC is the most useful technique to show the particular thermal behaviour of the recycled samples compared to the virgin PET.

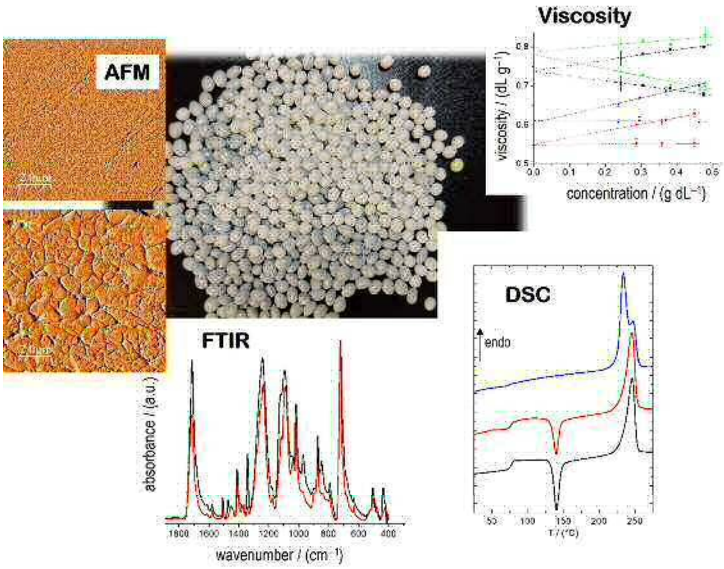

Figure 1. Some useful techniques used for characterization of recycled and virgin PET samples.

Recycled and virgin PET samples are compared in terms of chemical and physical properties. The mechanical recycling diminishes the polymer molecular weight which influences the crystallization ability and crystal morphology and, therefore, the final mechanical and optical performance.

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CHARACTERIZATION AND BIOMEDICAL APPLICATIONS OF ELECTROSPUN PHBV SCAFFOLDS DERIVED FROM ORGANIC RESIDUES.

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Introduction

The growing environmental concerns and the necessity for sustainable development have driven significant interest in the production of biodegradable bioplastics from renewable resources. This study explores the potential of using organic waste residues, specifically milk and molasses, as feedstock for the production of polyhydroxyalkanoates (PHAs), a class of biodegradable bioplastics.

Methodology

By utilizing these agricultural by-products, we aim to demonstrate a cost-effective and environmentally friendly approach to bioplastic production that aligns with the principles of a circular economy. Furthermore, the feasibility of employing PHA samples in biomedical applications was explored through the fabrication of nanofibrous scaffolds via electrospinning.

Results and conclusions

The resulting scaffolds were evaluated for their fiber morphology using Scanning Electron Microscopy (SEM), thermal behavior with DSC, polymer degradation using Gel Permeation Chromatography (GPC), and biocompatibility through cytotoxicity tests. Additionally, in vitro drug release and antibacterial activity assays were conducted to assess the potential of these scaffolds for drug delivery applications.

The integration of PHBV production from renewable resources with advanced electrospinning techniques exemplifies an innovative approach to developing environmentally sustainable materials for diverse applications.

RESINAS DE POLIURETANO SOSTENIBLES A PARTIR DE RECURSOS NATURALES: SÍNTESIS Y APLICACIONES

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Introducción/

Los poliuretanos (PUs) son polímeros muy versátiles, que presentan alta resistencia mecánica y al impacto, empleados en distintas aplicaciones como espumas rígidas o flexibles, elastómeros, materiales compuestos, pinturas, recubrimientos o adhesivos.

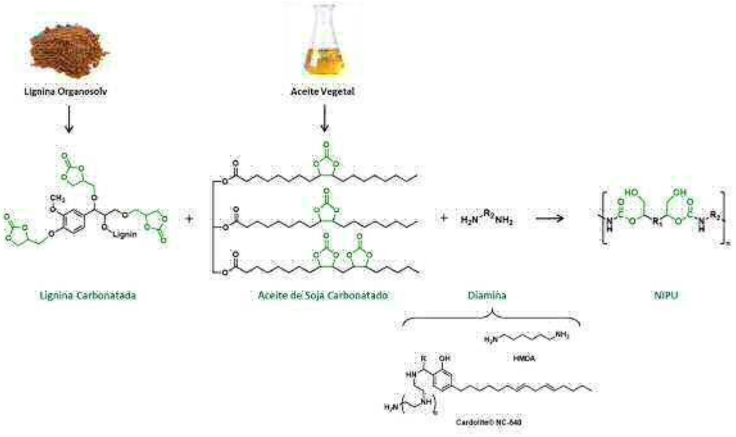
Debido a sus diversas opciones de formulación, los PU son la opción preferida cuando se trata de formular revestimientos o adhesivos de alta calidad. [2] La mayoría de los PU aplicados industrialmente se basan en materias primas no sostenibles, como el petróleo y el gas. Por ello, existe un impulso para sustituir los recursos fósiles por otros renovables con el fin de avanzar hacia una industria más sostenible [3] y emplear rutas más seguras que limiten el uso de isocianatos tóxicos. Así, en la última década, los NIPUs (poliuretanos sin isocianato) han surgido como alternativa a los PU convencionales.

Metodología

Los NIPUs se han sintetizado a partir de intermedios bio-basados derivados de residuos naturales (aceites vegetales, lignina o vanilina) en dos pasos que implican la cicloadición de CO2 al intermedio de base biológica en presencia de un catalizador y la reacción de los carbonatos cíclicos obtenidos con una diamina como hexametliendiamina (HMDA) o una dimaina bio-basada como Cardolite NC-540 (NH/CC = 1, 1,5, 2, 4) y DBU como catalizador. Los componentes se mezclaron y después de 30 min a vacío se transfirieron a un molde de teflón y se curaron a 100ºC durante 12h.

Resultados y Conclusiones

Los NIPUs basados en derivados de aceite vegetal (AV-NIPUs), mostraron buena capacidad de formación de películas en general, siendo estas bastante flexibles. Sin embargo, en las mismas condiciones de reacción, debido a la estructura química de la lignina, las películas obtenidas a partir de los LIG-NIPUs eran bastante rígidas. Se estudió la combinación de carbonato de aceite vegetal y carbonato de lignina, para ajustar las propiedades mecánicas. A medida que el contenido de lignina aumentaba del 30 al 100 %, los NIPUs se hacían progresivamente más rígidos. Los materiales mostraron buenas propiedades térmicas, siendo estables hasta 300ºC. Las propiedades térmicas de los NIPUs sintetizados con diamina Cardolite, mostraron una mejora significativa en comparación con los sintetizados con HMDA y alcanzaron valores de Tmax superiores a 350°C.



Conclusiones Se ha demostrado la posibilidad de producir poliuretanos 100% de origen biológico con buenas propiedades mecánicas, lo que supone un avance significativo hacia el desarrollo de materiales sostenibles con potencial para ser aplicado como adehsivos o recubrimientos. Agradecimientos Se agradece la financiación al proyecto FRACTION (GA nº101023202) del programa Horizon 2020 de la Unión Europea y al proyecto RECIPOL del programa RED CERVERA del CDTI.

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EXPLORING THE EXCEPTIONAL VITRIMERIC PERFORMANCE OF POLY(DITHIOURETHANES): AN IN-DEPTH STUDY OF DYNAMIC CHARACTERISTICS

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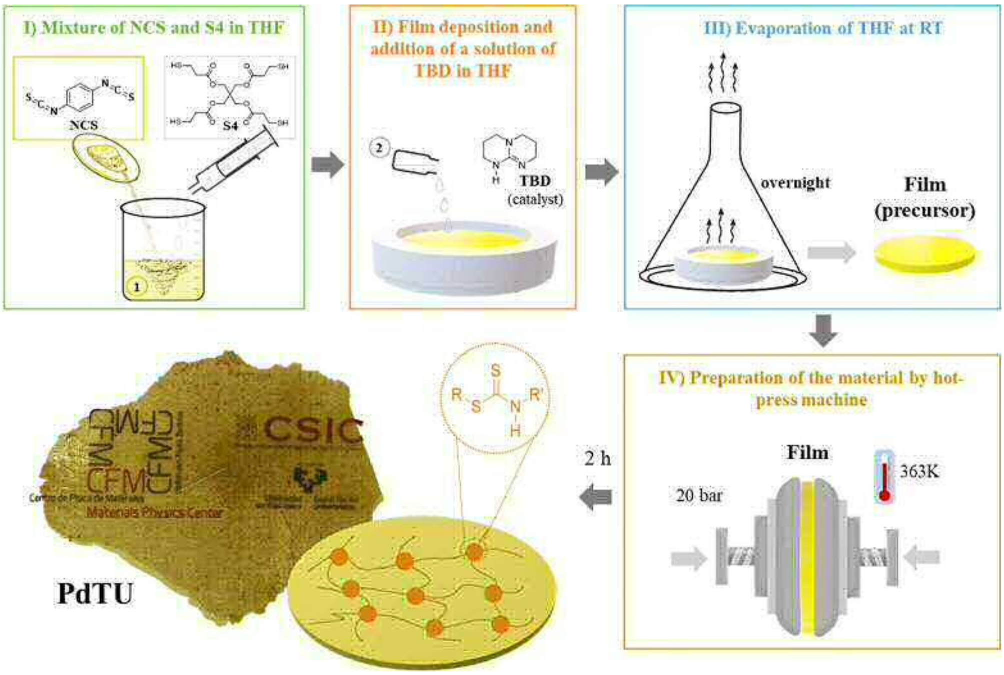
Introduction

Contrary to thermoplastics, thermosets encounter numerous challenges in recycling. Integrating dynamic covalent bonds into their structure represents a perceptive approach in the quest for extending the lifespan of these materials [1]. Over the last decade, researchers have investigated various dynamic bonds including esters, urethanes, disulfides, imines, silyl ethers, among others [2]. This study delves into the incorporation of dithiourethane bonds into cross-linked structures for the first time, leveraging their previously reported dynamic behavior in thermoplastics [3].

Methodology

Poly(dithiourethanes) (PdTUs) covalent adaptable networks (CANs) were synthesized from readily available monomers (thiol and isothiocyanate), as depicted in the Figure 1. A comprehensive investigation was conducted to analyze the thermal, thermomechanical, vitrimeric, and dielectric properties using techniques such as TGA, DSC, DMTA, FTIR, Raman, and BDS. Mechanical recycling of the materials was performed, followed by the assessment of mechanical properties through tensile testing. BDS experiments provided insights into distinguishing the glass transition temperature (Tg) and the topological freezing transition (Tv).



General scheme of poly(dithiourethane) covalent adaptable networks preparation

Results and conclusions

The materials exhibit relatively low thermal stability, with a maximum characterization temperature of 363 K. Despite this, DMTA tests revealed rapid stress relaxation occurring even close to the Tg (tanδ at 347 K), with a relaxation time of 0.7 minutes and complete relaxation within 7.2 minutes at 363 K for the 1% TBD sample. Analysis of the DMTA data revealed an Arrhenius relationship between viscosity and temperature. However, solubility tests indicated partial solubilization of the materials at 363 K, suggesting a vitrimer-like behavior characterized by a dissociative exchange mechanism with a high association constant. In order to investigate both transition processes characteristic of vitrimer and vitrimer-like materials (Tg and Tv), BDS experiments were conducted, yielding similar results to the DMTA tests. A mechanical recycling process was undertaken under mild conditions (363 K) and within a short duration (15 minutes). Remarkably, the recycled material exhibited no discernible differences in its properties compared to the original material.

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4D PRINTABLE ELECTROACTIVE AND BIODEGRADABLE PEDOT:κ-CARRAGEENAN INKS FOR (BIO)ELECTRONICS

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Introduction

In the last decade, conducting polymers (CPs) have been widely employed as electroactive inks for the additive manufacturing of (bio)electronic devices through 3D printing technologies, where light-based printing techniques, i.e., digital light processing (DLP) and two-photon polymerization (2PP), are gaining increasing attention due to their high-resolution printing. PEDOT, the gold of CPs for (bio)electronics due to its biocompatibility and conductivity, is usually coupled with non-fully degradable polystyrene sulfonate (PSS) leading to PEDOT:PSS dispersions that also need to be mixed with photocurable polymers to be processed through light-based 3D printing. Thus, the development of conducting polymer-based inks with high electronic conductivity for printing disposable devices presents difficulties in terms of degradability and sustainability. Therefore, the replacement of PSS with biopolymers to act as dopants of PEDOT represents an interesting approach to obtaining biodegradable electroactive inks.

Methodology

We have synthesized PEDOT:biopolymer dispersions by chemical oxidative polymerization of EDOT in the presence of biopolymers, κ-carrageenan (CAR), alginate, or inulin with different anionic groups (sulfate, carboxylic, and hydroxyl respectively). Furthermore, CAR was partially modified with methacrylate (MA) moieties to obtain photopolymerizable PEDOT:CAR-MA inks with the capability to be printed via DLP to obtain 3D conductive scaffolds also, the stability of these printed scaffolds were tested in PBS buffer (pH= 7.4).

Results and conclusions

Among the synthesized PEDOT:biopolymer dispersions, PEDOT:CAR dispersion showed the highest conductivity (0.1 S/cm). The photocrosslinkalbe inks with PEDOT:CAR were found to be resulting in shape-defined hydrogels with response to electrical stimuli. The 4D printed PEDOT:CAR-MA hydrogels exhibited good electrical conductivity, swelling/deswelling shape memory, and degradability. The printed hydrogels were found be stable in PBS buffer with only 10-20% of weight loss. These conductive 4D-printed hydrogels could be used as sustainable disposable wearable sensors to detect physical movements and bioelectrodes to record physiological signals such as electrocardiograms (ECG) and electromyograms (EMG).

Acknowledgments References

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VEGETABLE OIL-BASED INKS FOR 3D PRINTING USING A THIOL—MICHAEL—EPOXY DUAL-CURING STRATEGY

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Introduction

Additive manufacturing (AM) allows the construction of a 3D object by a layer-by-layer process under computer control, allowing on-demand fabrication of complex geometries. Different polymer-based AM technologies can be found, althought this work focuses on vat photopolymerization, which consists on the irradiation of a patterned light in a liquid resin to achieve photopolymerization. However, the sustainability of commercially available inks for light-based AM is rather limited, as they are generally (meth)acrylate- or epoxide-based derived from non-renewable fossil feedstocks. Vegetable oils present as an attractive option to prepare sustainable inks due to their easy functionalization with their double bonds. Here, vegetable oil-based photocurable inks for digital light processing (DLP) 3D printing using a dual curing of a thiol—Michael—epoxy system were developed with the aim of synthesizing novel sustainable inks combining the speed of thiol—Michael reaction and properties of thiol—epoxy materials.

Methodology

Linseed oil was functionalized with acrylate and epoxy groups to increase the reactivity of the system and enable printability. Inks with different acrylate and epoxide content were studied and characterized using NMR and FTIR spectroscopy. The curing performance of the inks was described by the Jacobs' working curve and the printing parameters were adjusted to optimize their printing. For the dual-curing process, the suitability of the photobase generators and the appropiate conditions were determined using Raman spectroscopy to follow thiol—Michael—epoxy reactions. DMA measurments were performed to analyze the thermomechanical properties of the structures.

Results and conclusions

In this work, vegetable oil-based photocurable inks using the dual-curing of a thiol—epoxy—Michael system were developed with the aim of developing new sustainable materials for 3D printing. Linseed oil was modified to increase the reactivity of the system with acrylate and epoxy groups. Inks with different content of epoxides and acrylates were prepared and tested. A tetraphenylborate salt was selected as the most suitable catalyst for the light activated thiol—Michael and the thermal activated thiol—epoxy curing, following a dual-curing strategy. Overall, this system proved to have the potential to be a competitive candidate in the field of DLP printing.

Acknowledgments

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RHEOLOGICAL AND TRIBOLOGICAL BEHAVIOUR OF GREEN LUBRICATING GREASES BASED ON CELLULOSE ACETATE/SILICA NANOCOMPOSITES

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Introduction

Green chemistry is increasingly drawing the attention of society as a consequence, among other factors, of a greater awareness of the adverse effects that petroleum-based products may exert on the environment. This fact, in combination with the limited availability and/or high costs associated with those products, is challenging the industry to produce greener products with cleaner processes. Specifically, the industry of lubricants aims to develop environmentally friendly and efficient formulations, while preserving or improving the lubrication performance, i.e. reducing friction and wear [1]. Both phenomena are related to energy losses and machinery failures, which underline the crucial role of lubricants in terms of cost-effectiveness and energy efficiency [2]. The present study deals with the development of electrospun cellulose acetate/silica nanocomposites which are proposed as novel multifunctional ingredients in green lubricating grease formulations. Combining the benefits of both the cellulose acetate, to impart thickening properties, and the silica, conferring additional anti-friction and anti-wear functions.

Methodology

Cellulose acetate/silica (CA/Si) nanocomposites were prepared by electrospinning from solutions of CA/Si, with different concentrations and CA:Si weight ratios, in a 2:1 (wt./wt.) Ac:DMAc binary solvent. CA/Si solutions were physicochemically characterized (electrical conductivity, surface tension, and dynamic viscosity). Electrospun CA/Si nanostructures obtained were analyzed in a scanning electron microscope. Finally, the electrospun nanostructures were dispersed in castor oil in concentrations ranging from 5 to 12.5 wt.%. The resulting oleo-dispersions were rheologically and tribologically characterized.

Results and conclusions

The fine dispersions of electrospun CA/Si nanocomposites in castor oil exhibit gel-like rheological responses and the values of the linear viscoelastic functions increased by several orders of magnitude with spinning solution concentration and CA:Si weight ratio. However, the rheological response is essentially dependent on the morphology of the nanofiber mat obtained. On the contrary, anti-friction and anti-wear properties are significantly improved by increasing the silica content in the nanocomposites as well as by forming nanofibers-dominated structures by electrospinning. The adequate multifunctional activity of CA/SIL nanocomposites is the result of a balance between silica incorporation and nanofiber-dominated structures. Overall, the oleo-dispersions of electrospun CA/Si nanocomposites, formulated with a very reduced number of components, can be proposed as efficient environmentally friendly replacements for traditional lubricating greases.

Acknowledgments

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INFLUENCE OF THE TYPE OF CLAY ON THE OIL STRUCTURING PROPERTIES OF ELECTROSPUN CELLULOSE/CLAY NANOCOMPOSITES

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Introduction

Ceramic materials have been used since ancient times for their utility in different fields. Nowadays, progress in nanotechnology has led to a significant transformation in the way these materials are used [1]. Clay or silica-based materials have been used as innovative reinforcements in the matrix of composite materials with the aim of improving different properties such as thermal resistance and mechanical behavior [2]. Within the lubricant industry, the incorporation of clay materials into lubricant formulations aims to impart thickening properties and reduce friction and wear, acting as multifunctional agents [3]. In this work, different kinds of silica and clays have been incorporated to cellulose acetate to form nanocomposites by electrospinning and these nanocomposites were further dispersed in castor oil to explore different functionalities in semi-solid lubricant formulations, such as rheological and tribological properties.

Methodology

Nanocomposites of cellulose acetate (CA) combined with several silicas (SIL) or clays (CL), with different hydrophilic or hydrophobic nature, were produced by electrospinning using 15 wt.% feeding solutions with 10:1 (wt./wt.) CA:SIL or CA:CL ratios. The cellulose acetate together with the silica or clay was dispersed in a binary mixture of organic solvents: acetone (Ac) and dimethylacetamide (DMAc) in a 2:1 (wt./wt.) ratio. The electrospun nanostructures obtained were analyzed by scanning electron microscope and then dispersed in castor oil at a 7.5 wt.%. concentration. The resulting oleo-dispersions were rheologically and tribologically characterized.

Results and conclusions

Electrospun nanostructures produced from CA:CL solutions showed a predominance of nanofibers, which results in oleo-dispersions with higher values of the viscoelastic moduli, as well as better tribological performance than those composed of CA:SIL. Furthermore, among all the silicas and clays studied, the ones that impart higher values of viscoelastic moduli to the oleo-dispersions were those of hydrophobically modified, despite the fact that they all exhibited similar nanoarchitectures. Overall, the rheological and tribological response is greatly influenced by the kind of clay or silica employed to produce the nanocomposite. The oleo-dispersions obtained can be proposed as an environmentally friendly alternative to traditional lubricating greases

Acknowledgments

This study has been carried out in the framework of the Research Project PID2021-125637OB-I00, funded by MCIN/AEI/10.13039/ 501100011033 and by ERDF “A way of making Europe”

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FABRICACIÓN DE VITRÍMEROS CON PROPIEDADES MECÁNICAS VARIABLES Y EVALUACIÓN DE LA REPROCESABILIDAD MEDIANTE LA ACTIVACIÓN DE REACCIONES DE TRANSESTERIFICACIÓN

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Introducción

Los polímeros termoestables son redes poliméricas tridimensionales en las que las cadenas poliméricas están entrecruzadas covalentemente. Este entrecruzamiento confiere a estos materiales excelentes propiedades mecánicas, estabilidad dimensional, resistencia química y a altas temperaturas. No obstante, estos polímeros son difíciles de reciclar, siendo un reto actualmente por la gran cantidad de residuos que generan.

Para tratar de mejorar estas limitaciones en los últimos años se han desarrollado las redes covalentes dinámicas (RCDs), que son materiales entrecruzados donde los puentes de unión entre las cadenas se pueden generar y romper de forma reversible. Estas redes se reorganizan mediante reacciones de intercambio reversibles al aplicar un estímulo externo, lo que permite el reprocesado de dichos materiales. Dependiendo del mecanismo de reacción de intercambio reversible, se distinguen dos tipos de RCDs: las disociativas y las asociativas o vitrímeros.

En este trabajo, nos hemos centrado en el diseño y la preparación de vitrímeros mediante fotopolimerización utilizando una cámara de fotocurado o mediante impresión 3D, con el objetivo de que estos materiales sean reprocesados mediante la activación de reacciones de transesterificación.

Metodología

El diseño de los vitrímeros se ha realizado con monómeros acrilato o metacrilato, entrecruzantes diacrilato con distinta longitud de cadena y un fotoiniciador. La fabricación se lleva a cabo mediante fotopolimerización en una cámara UV (modelo BLX-365) o mediante impresión 3D por DLP (Creality LD-002H).

Los materiales se han caracterizado mediante ATR-FTIR, DSC, TGA y mediante ensayos de tracción. Posteriormente, se ha evaluado la reprocesabilidad de los materiales, utilizando una prensa y aplicando las condiciones de temperatura y presión requeridas para activar las reacciones reversibles de transesterificación.

Resultados y Conclusiones

Las RCDs se prepararon mediante fotopolimerización y se caracterizaron utilizado ATR-FTIR para confirmar la desaparición de la señal correspondiente al C=C del grupo vinilo durante la polimerización. Así, se ha conseguido optimizar el diseño de estos materiales para asegurar la formación de la red. Se han caracterizado las propiedades térmicas y mecánicas de los vitrímeros, confirmando que pueden ser controladas variando la composición química de la red. La temperatura máxima para realizar el reprocesado de estos materiales se determina mediante TGA, donde se observa que la $T_{5\%}$, es mayor a 200ºC. Además, se ha confirmado la reprocesabilidad, que permitirá, a diferencia de los materiales termoestables tradicionales, reciclar y reprocesar el material.

Agradecimientos

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POSTER PRESENTATIONS SESSION 2

(September 17th)

TIRE FILLING: FROM DESIGN TO ADVANCED CHARACTERIZATION BY LOW-FIELD NMR

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Introduction

Polyurethanes are synthesized by polycondensation of isocyanate groups with alcohol moieties. All industries in the sector incorporate more ingredients in their formulations, adding a degree of complexity when obtaining materials with different morphologies, properties and applications, as is the case of a recent and innovative one: tire filling. Tire filling is presented as a solution to the problem of punctures [1,2], which cuts across sectors. The situation is particularly acute in the civil engineering sector where operational downtime causes big economic losses, and in the military sector where safety is compromised. In addition, replacing large, punctured tires requires specialized infrastructure and qualified personnel.

Methodology

The preparation of the polyurethanes was conducted by mixing stoichiometric quantities of isocyanate, polyol, plasticizer and catalyst. Several series were synthesized, in which catalyst loading, distribution of plasticiser and excess isocyanate were modified. Their effects were evaluated by compression experiments and hardness tests. The molecular structure and dynamics of all the polyurethanes were determined by low-field time-domain Nuclear Magnetic Resonance (MQ-NMR).

Results and conclusions

The amount of catalyst affected the reaction rate as expected, so the gel time decreased with the increase of catalyst content. The different plasticizer distribution showed correlation between the degree of polymerization and reaction rate due to the increased viscosity. The excess isocyanate also had an impact on the viscosity because of the stoichiometric imbalance and its effect on the delay of the polymerization reaction. The main takeaway of the 1H MQ-NMR experiments allowed for the correlation of the obtained data, the residual dipolar coupling constant (Dres), with the crosslink density [3], which was significant in the case of the excess isocyanate series. A storage problem in the isocyanate fraction was detected, hindering the preparation of the polymers. To overcome it, new formulations were proposed in which the plasticiser was substituted. The difficulty of preserving these materials on an industrial scale could be solved without affecting the performance of the final polyurethanes. The polyurethanes were characterized by compression and hardness experiments to estimate their behaviour. The final materials had the added value of providing comfort to the driver, and this outcome tied with industrial requirements.

Acknowledgments

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DISEÑO DE ESTRUCTURAS POLIMÉRICAS BIOBASADAS CON CAPACIDAD ANTIMICROBIANA Y ANTIOXIDANTE

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Introducción

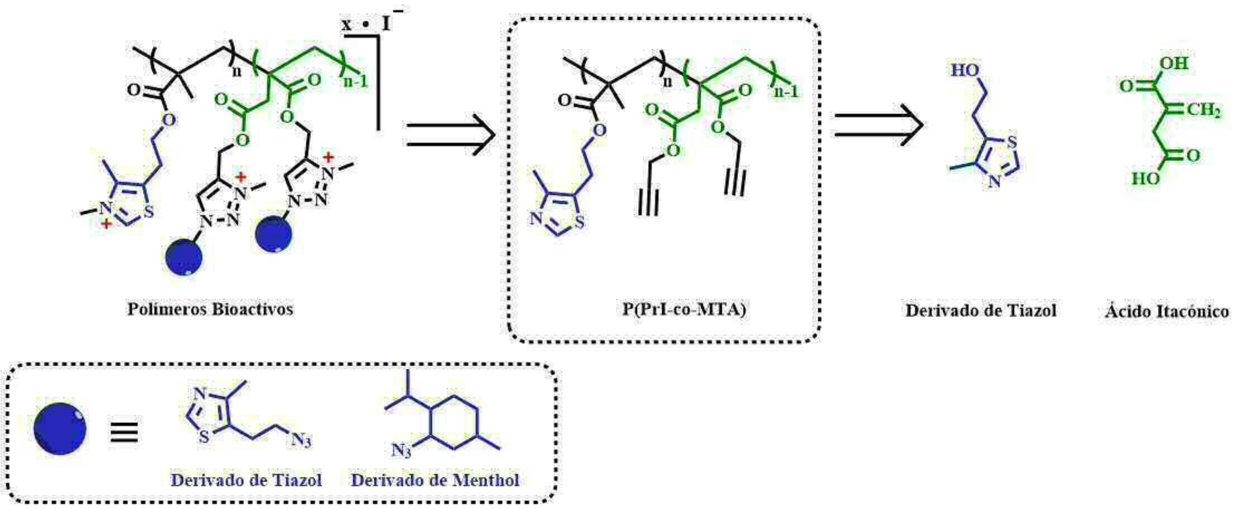
Actualmente, hay un interés creciente en crear materiales de fuentes renovables para reducir la dependencia de los plásticos de petróleo y afrontar los desafíos de desarrollo sostenible. A su vez, la escasez de monómeros biobasados que permitan la polimerización por radicales supone un reto sintético con el fin de conseguir nuevos sistemas que puedan funcionalizarse para incorporar las propiedades deseadas.[1] En este estudio, hemos desarrollado nuevos polímeros mediante la copolimerización de dos monómeros: MTA [2], monómero metacrílico obtenido por síntesis enzimática con un componente de la vitamina B1, y PrI, un derivado del ácido itacónico de origen natural.[1] La versatilidad química del ácido itacónico nos ha permitido añadir grupos susceptibles a la química click (cicloadición azida-alquino) para incorporar moléculas bioactivas, dotando al polímero de propiedades antibacterianas y antioxidantes. Además, es posible post-funcionalizar los polímeros preparados mediante reacciones de cuaternización (n-alquilación) en los nitrógenos susceptibles, introduciendo cargas positivas en la estructura para potenciar la actividad biocida.[3,4]

Metodología

Se preparan dos monómeros biobasadados para su copolimerización radicálica y posterior post-funcionalización. En primer lugar, se prepara el derivado de ácido itacónico, a partir su esterificación con alcohol propargílico. Por otro lado, el monómero MTA se prepara enzimáticamente con vinil metacrilato y 5-(2-hidroxietil)-4-metiltiazol. Finalmente, la copolimerización radical de ambos monómeros permite obtener polímeros aptos a post-funcionalización mediante química click o cuaternización. La caracterización estructural de los compuestos sintetizados se llevó a cabo mediante las técnicas habituales: RMN, FTIR, EM, GPC, además del estudio de sus propiedades antibacterianas, antioxidantes y de potencial zeta.

Resultados y Conclusiones

A partir de los dos monómeros empleados se ha preparado un copolímero biobasado de partida, del que se han diseñado distintos materiales variando la disposición y número de cargas en la estructura, así como la molécula bioactiva introducida. Finalmente se obtienen materiales respetuosos con el medio ambiente con potente actividad antimicrobiana y antioxidante.



Análisis retro-sintético de los polímeros bioactivos preparados

Agradecimientos y Referencias

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EFFICIENT SYNTHETIC ROUTE FOR CYANO-BASED POLYMERS FROM THE BULK THERMAL POLYMERIZATION OF AMINOMALONONITRILE

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Introduction

Aminomalononitrile (AMN) polymerises spontaneously under slight alkaline aqueous conditions to generate films, which could be applied in biomedicine [1]. Moreover, pure AMN is a yellow oil that evolves quickly into a dark-brown tarry mass [2]. Therefore, it is generally commercialized as its stable tosylate salt, aminomalononitrile p-toluenesulfonate (AMNS). In this communication is described the thermal stability of AMNS using several thermo-analytical techniques to gather more information about the reactivity of this cyano compound with recent interest in polymeric materials science [3].

Methodology

DSC measurements of AMNS were carried out at different heating rates (2.5-25 °C/min) from room temperature to 250 °C, under nitrogen atmosphere. Complementary, TGA and DTA studies were performed, and a coupled TG-MS system was employed to analyse the main volatiles evolved during the heating of the AMNS samples. A structural characterization by FTIR spectroscopy was also conducted.

Results and conclusions

DSC under non-isothermal conditions from AMNS has revealed the AMN thermal induced polymerization with the proven generation of polymeric conjugated structures plus unmodified p-toluensulfonic acid. Moreover, these measurements demonstrated that the bulk AMNS polymerization is notably easy and reproducible, and it can be considered a very fast reactive system; and the first systematic kinetics approach has been described. With the application of different iso-conversional methods, the variation in the activation energy at different conversion degrees showed a transition from a kinetic- to a diffusion-controlled regime. Polymerization kinetic was consistent with an apparent self-acceleration model, $d\alpha/dt = k\ \alpha m\ (1-\alpha)n$ with a autocatalytic order $m \approx 1$ and n dependent on the heating rate. All these results suggest that complex mechanism involving multiple stages could be considered. By means of TG-MS analysis were observed deamination and dehydrocyanation processes, which were directly related with the weight loss detected during the thermal polymerization of AMNS. These results could shed light on the mechanism of polymerization of this reactive molecule with potential applications as advanced multifunctional systems.

Acknowledgments

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SÍNTESIS Y FUNCIONALIZACIÓN DE BIOPOLIÉSTERES HIPERRAMIFICADOS SOPORTADOS EN CELULOSA MICROCRISTALINA

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Universitat Jaume I, Castellón, España

Introducción

Los biopoliésteres representan una alternativa sostenible a los polímeros convencionales debido a su biodegradabilidad y menor impacto ambiental. Sin embargo, la aplicación industrial de muchos de ellos, como es el caso de algunos polihidroxialcanoatos (PHA), se ve comprometida por su baja tenacidad. En las últimas décadas, los polímeros dendríticos, incluyendo los polímeros hiperramificados, han destacado en la investigación debido a sus arquitecturas altamente ramificadas y propiedades físicas y químicas únicas. Estos materiales ofrecen ventajas económicas y de síntesis en comparación con los dendrímeros arquitectónicamente perfectos, lo que los hace atractivos para aplicaciones industriales en recubrimientos y resinas, bio aplicaciones o como aditivos en polímeros lineales [1,2]. Este trabajo se enfoca en la síntesis y funcionalización de biopoliésteres hiperramificados (HBBPE) soportados sobre celulosa microcristalina (MCC) para utilizarlos como aditivos que mejoren la tenacidad de los biopoliésteres sin comprometer su biodegradabilidad.

Metodología

La síntesis de HBBPE soportados en MCC se realizó mediante la reacción de ácido 2,2-bis(metilol)propiónico y MCC en presencia de p-TSA como catalizador. La reacción se llevó a cabo en fundido a 140 ºC bajo atmósfera inerte y vacío. Posteriormente, se añadió DMF como dispersante, y la reacción continuó durante 24 horas con agitación continua, seguida de centrifugación, filtración, lavado con cloroformo y secado. Los HBBPE sintetizados se funcionalizaron mediante la adición de diferentes cadenas terminales para aumentar la longitud de las cadenas ramificadas y modificar su arquitectura. Los polímeros obtenidos se caracterizaron mediante FTIR, RMN, DSC, TGA y análisis elemental.

Resultados y Conclusiones

Los análisis de 1H-RMN y FTIR confirmaron la síntesis de los HBBPE soportados sobre MCC. Los estudios térmicos (DSC y TGA) y el análisis elemental permitieron evaluar la estabilidad térmica de los polímeros sintetizados y las modificaciones en su estructura. Los resultados preliminares sugieren que la incorporación de HBBPE soportados en MCC como aditivo tiene un gran potencial como estrategia para mejorar las propiedades mecánicas de biopoliésteres sin comprometer su biodegradabilidad.

Agradecimientos

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HIGHLY EFFICIENT GRAFTING OF HETERO-COMPLEMENTARY AMIDINIUM AND CARBOXYLATE HYDROGEN-BONDING/IONIC PAIRS ONTO POLYMER SURFACES

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Introduction

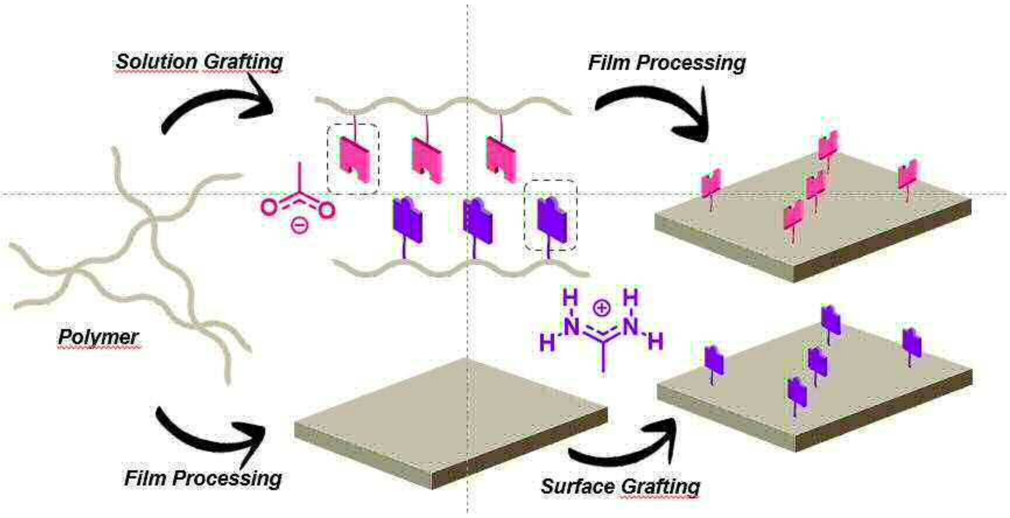
Self-assembly and molecular recognition phenomena are ubiquitous in natural systems and, in some cases, adhesion is the resulting property. In a bioinspired fashion, the development of synthetic adhesive materials using the tools and concepts of supramolecular chemistry is becoming an excellent approach to target unprecedented properties that rely on the versatile, reversible, dynamic, and selective nature of non-covalent interactions.[1]

Methodology

Here, we describe a method to efficiently incorporate highly polar, ionizable, hetero-complementary hydrogen-bonding carboxylate and amidinium groups into polymer materials.

Results and conclusions

We optimized a grafting reaction between thiols containing the "sticky" carboxylate and amidinium functions, and pendant pentafluorophenyl groups present in poly(n-alkyl acrylate-co-pentafluorostyrene) copolymers. Interestingly, the procedure affords excellent grafting yields when carried out both with the dissolved polymer and directly onto polymer surfaces, with the aim to produce materials showing hetero-complementary adhesion.[2]



Polymer materials endowed with hetero-complementary carboxylate and amidinium supramolecular functions can be generated either by solution or by surface grafting

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STUDY OF THE SELF-HEALING CAPACITY OF A MODIFIED PLA WITH A COUMARIN METHACRYLATE

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Introduction

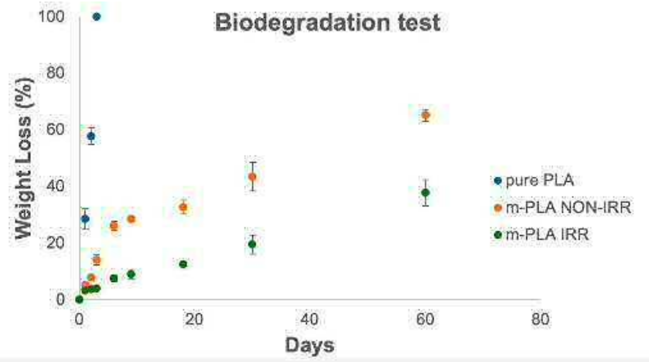
In this work, a study of the applicability of a modified PLA polymer matrix grafted with a methacrylic derivative of coumarin (7-hydroxycoumarin-yl methacrylate) as a self-healing material has been carried out. Coumarin derivatives experiment photodimerization under UV irradiation at 300-350 nm forming a cyclobutane ring due to a [2π+2π] cycloaddition (1). After grafting to PLA, it is expected that this reaction between the coumarin units allow the crosslinking between PLA chains (2).

Methodology

This modified polymer matrix, produced by reactive processing in a previous work, is transformed into thermoconformed films up to 200 μm of thickness and later exposed at 311nm under optimized conditions. The films, irradiated and non-irradiated, have been characterised from different points of view to determine the effect of the incorporation of the coumarin derivative to the polymer matrix. Firstly, non-irradiated samples were damaged with a razor and later irradiated at different times to determine the self-healing capacity of the material. Optical microscopy was used to monitor the self-healing process on uncovered and covered parts from the same sample.

Results and conclusions

It has been observed that there are two curing processes performed at the same time: one induced by UV radiation (uncovered) and other, with lower efficiency induced by temperature (covered). On average, the defect of uncovered face was healed two hours faster than covered one. The presence of grafted coumarin units, in conjuction with a specific temperature, accelerates the repairment of a superficial physical damage. Parallelly, a biodegradation test of the films was conducted using an enzymatic degradation medium (proteinase K in an aqueous medium) at 37ºC, evaluating the weight loss with immersion time. In contrast to non-irradiated modified PLA, photocrosslinked PLA exhibited a one-month delay in biodegradability owing to the increased molecular weight of macromolecules due to crosslinking (Figure 1). DSC and TGA were conducted to determine the effect of crosslinking on glass transition, cold crystallization, melting and maximum degradation temperatures. Finally, the effect on mechanical performance was evaluated under dynamomechanical analysis (DMA). DMA tests were conducted isothermally at 20ºC subjecting the samples to a frequency range of 0.05-100 Hz. Storage modulus of irradiated samples increased around 23% regarding non-irradiated ones.



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AROMATIC POLYMERS HAVING HIGH FRACTIONAL FREE VOLUME AND LARGE THERMAL AND CHEMICAL STABILITY FOR ENERGY-SAVING APPLICATIONS

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Introduction

It is imperative to search for novel materials that markedly enhance the efficiency of industrial operations. In this context, there is a high demand to promote the industrial use of aromatic polymeric materials, which have high chemical and thermal stability, for energy-efficient applications such as gas separation and flow batteries.

Some of these aromatic polymers are materials obtained through Klump-Zolotukhin (K-Z) type reactions; i.e., electrophilic aromatic substitution (SEAr) reactions between aromatic difunctional monomers (e.g. biphenyls, terphenyls, and others) and ketones possessing electron-withdrawing groups (EWG) (e.g. isatin, trifluoracetophenone, and others). When the ketone is well selected (e.g., isatin), further modification is feasible, which can result in the creation of highly specific functional materials. However, except for a few select cases, these K-Z polymers do not possess high fractional free volume (FFV).

Triptycene represents a molecular template with an intrinsic FFV. However, concerning the K-Z reaction, this monomer is trifunctional resulting in the formation of polymeric networks that cannot be processed as films. In this study, we present an effective method for converting triptycene into a bifunctional monomer, which has enabled the synthesis of soluble polymers producing homogeneous films with excellent mechanical properties. This methodology involved the selective incorporation of an electron acceptor group into one of the three aromatic rings of the triptycene.

Methodology

The methodology employed to obtain the triptycene-derived difunctional monomer, as well as the optimization of polymer synthesis, characterization, and preliminary evaluation as separation membranes and flow batteries, will be presented in detail during the congress.

Acknowledgments

Financial support from the Agencia Estatal de Investigación (AEI) AEI/PID2023-149594OB-C22 and PID2021-123753NB-C31 AEI/10.13039/501100011033 and the Junta de Castilla y León (INVESTUN/22/VA/0001) are greatly acknowledged.

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NANOMECHANICAL PROPERTIES OF SOLID AND FOAMED PCL-SEPIOLITE ELECTROSPUN FIBERS.

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Introduction

The mechanical properties of polymeric membranes are crucial due to their wide range of applications in industries such as water treatment, biomedical engineering, and gas separation, as they determine their effectiveness and durability under real operational conditions. Fibrous polymeric membranes exhibit enhanced mechanical properties compared to their solid counterparts due to their small cross-section and high aspect ratio. In this area, the electrospinning technique is noted for its cost-effectiveness and large-scale production capability, producing fibers with a large specific surface area and abundant microstructures. In this work, solid and foamed PCL-sepiolite nanocomposite electrospinning fibers are produced, and their mechanical properties are characterized using bimodal AFM.

Methodology

PCL electrospun nanofibers were obtained from the polymeric solution of PCL in clorophorm by adding quaternary amonium salt modified sepiolite (QAS-SE) at different concentrations. Gas-disolution foaming process was performed imbibing the fibers in PVOH and then performing the gass-dissolution foaming process using pressurized CO2 at 30 MPa and then RT for 24 hours. Solid and foamed fibers were characterized by thermal (TGA, DSC), morphological (SEM) and nanomechanical (bimodal-AFM) analyses.

Results and conclusions

SEM analysis showed that all the mats exhibited a Gaussian or near-Gaussian fiber diameter distribution. It was demonstrated that the mean diameter decreases as the sepiolite content increases, with a minimum average diameter of 476 ± 58 nm achieved for 8SE-10PCL. This reduction in fiber diameter, driven by higher nanoparticle content, enhances the contact area for filtration processes, enhancing the nanoparticles' role as active agents in adsorption. Additionally, foamed fibers were successfully produced. Bimodal-AFM measurements of the fiber surfaces revealed an increasing trend in Young's modulus with higher sepiolite content in solid fibers, indicating effective transfer of mechanical properties between the nanoparticles and the polymeric matrix. Foaming shows an increase in the Young's modulus compared to their solid counterparts.

Acknowledgments and References

This work has been financially supported by Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04) and the EU NextGenerationEU/ PRTR program (PLEC2021-007705). This work has been achieved in collaboration with ForceTool Group from Instituto de Ciencia de Materiales de Madrid (icmm).

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CARACTERIZACIÓN TÉRMICA Y VISCOELÁSTICA DE PLÁSTICOS COMERCIALES PARA ORTODONCIA INVISIBLE

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Introducción

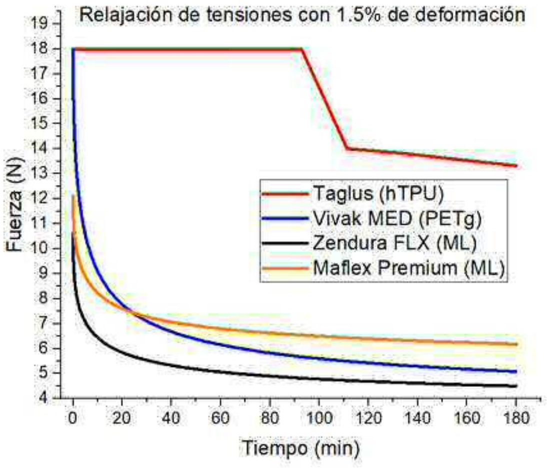
La ortodoncia invisible es un novedoso tratamiento ortodóntico que se está expandiendo con rapidez por todo el mundo gracias a sus ventajas estética, de confortabilidad e higiene. Este tratamiento se basa en un termoplástico termoformado que recubre completamente la superficie del diente, por lo que consigue distribuir la fuerza en una mayor área, consiguiendo mover todos los dientes de manera armónica. [1], [2]

Metodología

En este trabajo se han caracterizado los materiales más utilizados en el mercado para lograr discernir que tienen en común y las diferencias que presentan. La naturaleza química de cada material se ha analizado por FTIR-ATR junto con DSC . Las propiedades viscoelásticas de los materiales se testaron por DMTA a tracción. En el mismo equipo se realizaron ensayos de relajación de tensiones a 37 ºC en algunos materiales seleccionados. Dichas pruebas se basan en deformar el material en tensión hasta un porcentaje dado, y mantener dicha deformación por 3 h mientras se monitoriza la fuerza, tras lo cual se lleva la fuerza a cero y se monitoriza la deformación por 5 minutos.

Resultados y Conclusión

Se encontró que el material más utilizado es el tereftalato de PETG al que siguen el TPU duro (hTPU) y finalmente multicapas de distintos materiales. Las pruebas de DMTA arrojaron que el módulo de carga en monocapas es alrededor del doble del recomendad [3] y que la Tg en estos materiales está relativamente cercana a la temperatura oral (75-90 ºC). Las multicapas en cambio arrojan valores más cercanos al módulo recomendado, y una Tg mayor (120 ºC). Esto se traduce en que las multicapas son capaces de mantener fuerzas iniciales y finales bajas y similares independientemente del nivel de deformación, y unas deformaciones remanentes relativamente bajas, lo que no ocurre en monocapas.



Agradecimientos

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DESARROLLO DE FIBRAS POLIMÉRICAS BASADAS EN CELULOSA Y POLI(ÁCIDO LÁCTICO) MEDIANTE ELECTROHILADO EN FUNDIDO PARA APLICACIONES BIOMÉDICAS.

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Introducción

La celulosa (CE) es el polímero natural más abundante en la Tierra, no proviene del petróleo y tiene propiedades muy atractivas que han generado gran interés en los últimos años, tales como su biodegradabilidad y biocompatibilidad. Además, se ha empleado como refuerzo en distintos sistemas poliméricos1. Las aplicaciones de este polisacárido están muy condicionadas por su estructura química, ya que sus abundantes grupos hidroxilo ofrecen diversas oportunidades para sintetizar derivados de CE con diferentes propiedades. Por su parte, el poli(ácido láctico) (PLA) es un polímero biobasado, biodegradable y biocompatible, muy atractivo en la industria del envasado, biomédica o textil, pero con propiedades mecánicas reducidas, por lo que se emplean tanto plastificantes como refuerzos para mejorar dichas propiedades.

Metodología

En este trabajo se propone la funcionalización de la CE microcristalina por el grupo hidroxilo del carbono 6, para introducirle una capacidad antimicrobiana y posteriormente conseguir un tejido con fibras altamente orientadas por electrohilado en fundido utilizando como matriz otro de los biopolímeros más estudiados en la actualidad, el ácido poliláctico (PLA). Para la funcionalización de la celulosa se utilizó un ácido sintetizado previamente por el grupo de investigación compuesto por anhídrido succínico y 4-metil-5-tiazoletanol, el cual se cuaternizó con yoduro de metilo, para obtener un compuesto cargados positivamente2. La mezcla de PLA con CE se realizó mediante disolución y posterior evaporación. Se introdujeron distintas concentraciones (1%, 3% y 5%) de CE previamente modificada y sin modificar. Después se prepararon fibras por electrohilado en fundido.

Resultados y Conclusiones

La síntesis del ácido y su posterior cuaternización se confirmó por H-RMN en DMSO-d6. La modificación de CE con el ácido se evaluó por FTIR, donde se comprobó la aparición de una nueva banda a 1720 cm-1 correspondiente al grupo carbonilo. Asimismo, se realizó un análisis de resonancia de carbono en estado sólido para confirmar dicha modificación. Se hicieron mezclas de PLA con distintas composiciones de CE modificada y sin modificar. Dichas mezclas se incorporaron al equipo de electrohilado en fundido para la obtención de las correspondientes fibras. Se llevó a cabo tanto la caracterización físico-química como la microbiológica, analizando el tamaño, la cristalinidad y las propiedades mecánicas de las fibras, así como su respuesta frente a bacterias gram-positivas y gran-negativas.

Agradecimientos

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MODULACIÓN DE LA BIODEGRADABILIDAD DE POLIURETANOS PARA APLICACIONES BIOMÉDICAS

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Introducción

Los implantes poliméricos del sector biomédico pueden ser reabsorbidos por el cuerpo humano a lo largo del tiempo. Este proceso de absorción está íntimamente relacionado con la biodegradabilidad de los materiales poliméricos. Una forma de modular esta biodegradabilidad está relacionada con la naturaleza química de los materiales de partida. Los poliuretanos más empleados en este sector están basados en poli(e-caprolactona) (PCL), gracias a su alta biocompatibilidad. Sin embargo, estos poliuretanos muestran perfiles de biodegradación muy lentos, lo que descarta su uso en aplicaciones que requieran tiempos cortos de degradación. Esto es debido principalmente a la hidrofobicidad de la cadena de PCL. Una estrategia de modular la biodegradabilidad de estos materiales sería empleando nuevos materiales basados en PCL con unidades de láctida y otros monómeros biodegradables. En el presente trabajo se aborda el estudio sistemático de la degradabilidad de poliuretanos basados en PCL con unidades de lactida. También se aborda la inserción de otros monómeros degradables como alternativa al sistema clásico 1,4-butanodiol (BD). Finalmente, se ha estudiado la citotoxicidad y proliferación celular sobre estos poliuretanos.

Metodología

Para la preparación de los poliuretanos se han empleado derivados de poli(e-caprolactona) con diferente contenido de lactida (43%-15%) variando también el peso molecular (1000, 2000, 3000 g/mol). Como alternativa al BD, se ha estudiado la influencia del monómero biodegradable EDA-2CL.

Resultados y Conclusión

Se han preparado poliuretanos de alto peso molecular funcionalizados con derivados de poli(e-caprolactona) portando diferentes contenidos de lactida. Los contenidos de este co-monómero variaron entre el 43 y 15%, lo que permitió conocer la influencia de este éster sobre la degradación de los materiales finales. Los resultados demostraron que a medida que el contenido de lactida aumentaba, la degradación del poliuretano era más favorable. Del mismo modo, se demostró que la inserción del monómero EDA-2CL favoreció la degradación del poliuretano. Esto es debido a que la introducción de lactida dentro de las cadenas de PCL fue aleatoria, las cadenas de este polímero mostraron mayores dificultades para cristalizar. Por lo que la degradación de los materiales está más favorecida. Los estudios biológicos indicaron que estos poliuretanos fueron no tóxicos después de 28 días, además de mostrar una buena adhesión celular y citotoxicidad. Por tanto, estos nuevos poliuretanos se presentaron como materiales atractivos para aplicaciones biomédicas con altas velocidades de degradación.

Agradecimeintos

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HIDROGELES CONDUCTORES EN BASE A COLÁGENO COMO APÓSITOS PARA HERIDAS

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Introducción

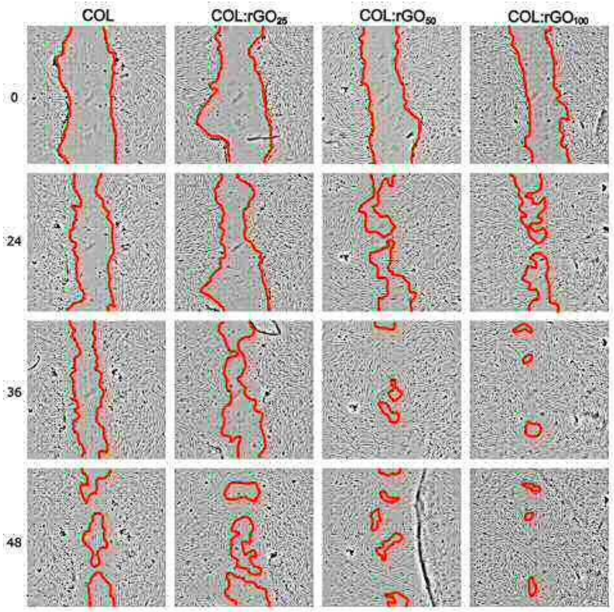
Las heridas en la piel alteran su integridad estructural y provocan un cortocircuito debajo de la epidermis. Cuando esto se produce comienza el proceso de regeneración tisular, donde una serie de mediadores celulares (plaquetas, células inflamatorias, citocinas y factores de crecimiento) se dirigen a la lesión tisular para favorecer el proceso de cicatrización. Diferentes estudios han demostrado que restablecer la conductividad de la piel en la zona dañada produce una migración celular ordenada. Por tanto, una estrategia para promover la cicatrización de heridas es reestablecer la conductividad de la piel utilizando apósitos conductores.

Metodología

En este estudio, se sintetizaron hidrogeles conductores utilizando colágeno bovino tipo 1 (COL) y óxido de grafeno reducido (rGO), polimerizados con dopamina y reticulados enzimáticamente con peroxidasa de rábano picante (HRP) para ser utilizados como apósitos para heridas. Se utilizó como medio de disolución ácido acético al 5% y se mantuvo a 40°C durante 14 horas para favorecer la reticulación de la peroxidasa. La conductividad eléctrica se determinó por el método de las 4 puntas. La biodegradación in vitro se evaluó utilizando colagenasa I en una solución salina tamponada con fosfato (PBS). Los hidrogeles se validaron in vitro en Fibroblastos Dérmicos Humanos (FDH).

Resultados y Conclusión

La conductividad de los hidrogeles oscila entre 20,02 y 39,76 mS/m, incrementándose con el aumento de la concentración de rGO, lo que puede atribuirse a la creación de un campo eléctrico adicional. También se observa una mayor estructuración con el aumento de las interacciones entre COL y rGO que conduce a una menor tasa de biodegradación con el aumento y mayor estabilidad. La biocompatibilidad de todos los materiales sintetizados exhibió una tasa superior al 80% y esto evidencia que la incorporación de rGO no tuvo un efecto tóxico frente a FDH. La migración de los FDH fue más pronunciada después de las 48 horas, lo cual se debió a la elevada densidad de cargas negativas en la superficie del material. También se observó una mayor tasa de cierre de la herida con el aumento de la concentración de rGO. Los resultados evidencian que es posible desarrollar hidrogeles entrecruzados de COL con la incorporación de rGO como apósitos de heridas que mejoran la migración celular y la cicatrización.



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PHOTOCROSSLINKED HYDROGEL DERIVED FROM AN UNSATURATED POLY(ESTER AMIDE)

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Introduction

Tissue engineering pursues to heal damaged or diseased tissues by developing biomaterials into structural scaffolds that emulate the extracellular matrix of cells and offer support for cell proliferation and tissue regeneration [1]. With this aim, interest in the development of hydrogels is growing because these materials provide an ideal framework for cell adhesion and proliferation [2]. Hydrogels can be made from amino acid containing poly(ester amide)s (PEAs), that provide consistent physical and chemical characteristics, which are crucial in scaffolds used in tissue engineering [3]. Moreover, their degradation products are harmless and easily absorbed by the body [4]. In this work, we describe the preparation of a water-soluble amino acid-containing PEA which was converted into hydrogel through photoinitiated crosslinking.

Methodology

The unsaturated PEA (PEA10A5K), was synthetized by solution polymerization (Fig. 1a). After purification by recrystallization and dialysis, the polymer was analyzed by FTIR and NMR, DSC and TGA tests. The hydrogel was made by adding Irgacure (0.4%) to a 5% w/v solution of PEA10A5K in PBS and then irradiating it at 365 nm. Measurements of the mass swelling ratio (MSR), gel (GC) and equilibrium water content (EWC) were employed to characterize the hydrogel. Compression, SEM and FTIR tests were also performed.

Results and conclusions

FTIR and NMR spectra confirmed the expected chemical structure of PEA10A5K. The melting and crystallization temperature values were 49 and 32°C, respectively and the thermal degradation started at 350 °C. Fig. 1b depicts the hydrogel after the crosslinking procedure; MSR, GC, and EWC were 36, 85, and 95%, respectively. SEM (Fig. 1c) revealed that the structure exhibits good porosity. The elastic modulus (E) was found to be 30 KPa based on the compression test results (Fig. 1d). Because of all these properties, it can be concluded that the hydrogel described in this work has potential applications in tissue engineering.

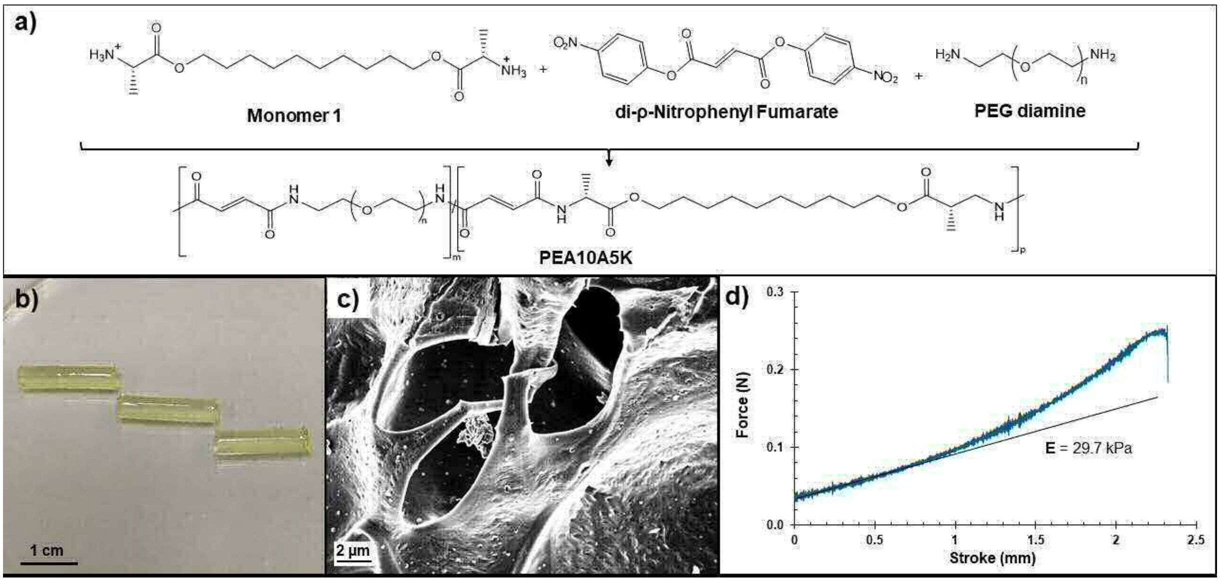

Fig. 1 a) Synthesis of PEA10A5K. b) Representative images of the hydrogel after removal from the mold. c) SEM micrograph of transversal section. d) Compression test

Acknowledgments

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AMPHIPHILIC PSEUDO-PROTEINS VIA MICHAEL PEGYLATION AND THEIR APPLICATION FOR FABRICATING CORE-SHELL PARTICLES.

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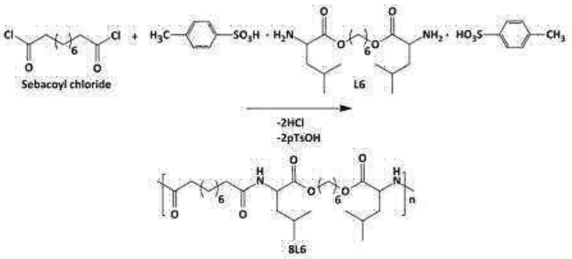
Introduction

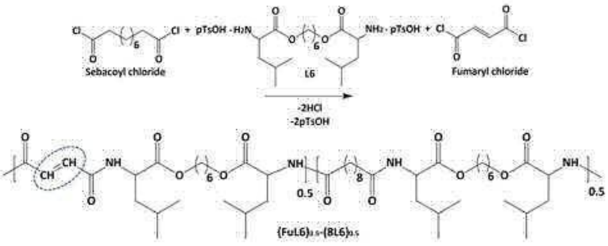
The present study deals with the application of amino acid-based biodegradable polymers - pseudo-proteins (PPs) [1] acting as both PEGylating surfactants and key polymers for nanoparticle preparation. The PEG-coated NPs were studied using TEM and Synchrotron-radiation FTIR microscopy. In parallel, we fulfilled the study of the kinetics (using 1H-NMR) of conjugating heterobifunctional PEG molecules to unsaturated PP, resulting in amphiphilic PPs.

Methodology

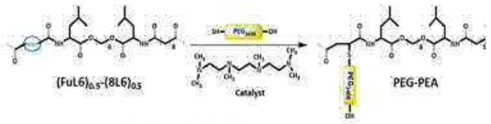
The key polymer labeled as 8L6 is composed of sebacic acid (8), L-leucine (L), and 1,6-hexanediol (6) units. The unsaturated PP (FuL6)0.5-(8L6)0.5 is composed of fumaric (Fu) and sebacic acids, L-leucine and 1,6-hexanediol units. Both PPs were synthesized by interfacial polycondensation of corresponding diacyl chlorides with di-p-toluene-sulfonic acid salt of bis(L-leucine)-1,6-hexylene diester monomer, labeled as L6. PEGylating surfactants - PEG-PPs were synthesized Michael conjugation of heterobifinctional PEGs - SH-PEG-OH (3,4kDa) and H2N-PEG-OH (3.4 kDa) with (FuL6)0.5-(8L6)0.5 catalyzed by various tertiary amines, both mono and polyamines. Nanoparticles of PP 8L6 were prepared according to the nanoprecipitation method reported in Ref. [2] using a SH-PEG-PP as a surfactant.



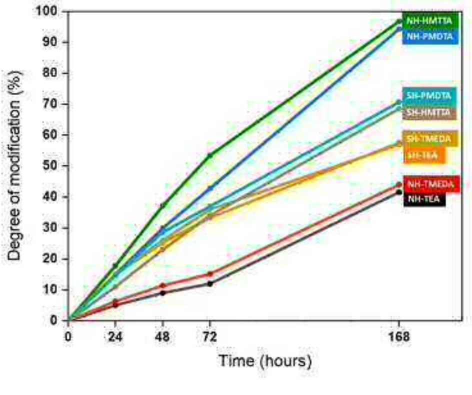
Synthesis of polymer 8L6



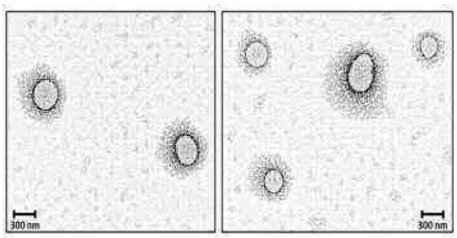
Synthesis of the $(FuL6)_{0.5}$-$(8L6)_{0.5}$ co-poly(ester amide)



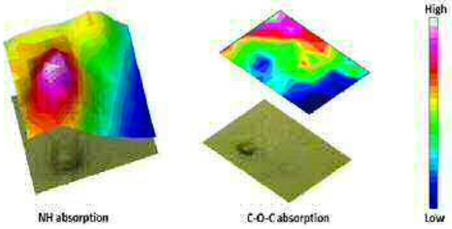
Thiol-Michael addition reaction



Reaction kinetics



TEM IMAGES



FTIR MICROGRAPHS

Results and conclusions

FTIR micrographs show the intensity of the NH band is stronger in the center of the particle and decreases around it. Conversely, the intensity of the C-O-C band (PEG shell) is extremely low in the core and increased significantly in the peripheral area. TEM images show the core-shell structure and PEG chains densely cover the nanoparticle core. The study of the kinetics of the conjugation of functionalized PEGs with the unsaturated PP demonstrated that the nitrogen content of the catalyst significantly influences the catalytic activity. The higher the number of nitrogen atoms within the catalyst the higher the reaction rate.

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ESTUDIOS DE LA FORMULACIÓN DE HIDROGELES APLICADOS A LA BIOIMPRESIÓN DE IMPLANTES

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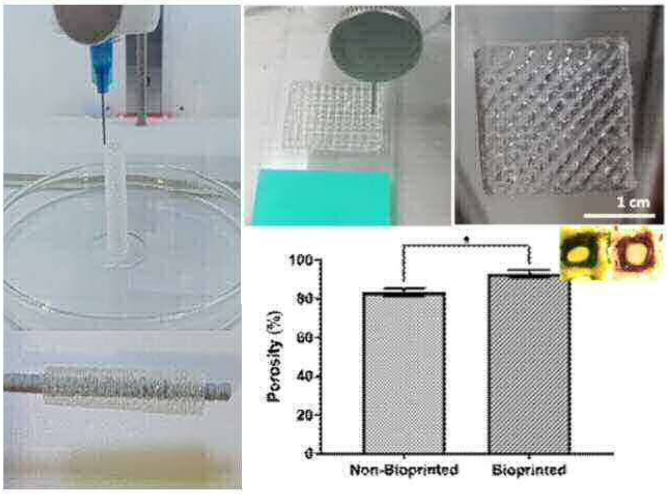
Introducción

La bioimpresión es una de las principales líneas de estudio en el desarrollo de la medicina regenerativa personalizada, en especial para el desarrollo sustratos implantables (injertos) con los que potenciar la regeneración tisular, con función mecánico-física y terapéutica. El injerto tiene varios requisitos a nivel celular, reológico, mecánico, etc., de acuerdo con la actividad del tejido y condiciones de manufactura. Una amplia parte de estos requisitos están predeterminados por las formulaciones para la bioimpresión, que en gran medida tiene base acuosa (hidrogeles). Por eso y con el objetivo de evaluar la implantación de la bioimpresión en diferentes campos de la medicina regenerativa personalizada, estamos estudiando las formulaciones de los hidrogeles basados en los compuestos más referenciados (alginato, konjac, fibroina, PVDF, PP, etc.).

Metodología

Nuestros estudios son una evaluación semi-cuantitativa de propiedades tanto técnicas del proceso de bioimpresión (imprimibilidad, estabilidad estructural, etc.) como de funcionalidad (mecánica, degradabilidad, etc.), así como de compatibilidad celular (adhesión, proliferación, etc.) como tisular (inflamación, integración, etc.). El estudio se ha basado en la caracterización por microscopia de las dimensiones de los modelos impresos frente al modelo informático. La cuantificación de la supervivencia celular se realizó tanto en superficie como en la matriz del material, antes y después del proceso de impresión (análisis de live-dead) y por último el grado de implantación (estudios de histopatología). Los modelos impresos en formato de parche poroso como de vaso, se obtuvieron con una impresora Cellink BioX y como referencia se han usado muestras obtenidas por electrospinning.



Impresión de los modelos de injertos en formato de vaso y en forma de parche y estudios de porosidad de los parches

Resultados y Conclusión

En los estudios histopatológicos se ha podido observar la formación de las estructuras que forman los tejidos (sistema vascular), lo que es indicativo de la adecuada integración. Del trabajo in-vitro sobre viabilidad celular se ha podido ver que una vez parametrizado el proceso de impresión, la producción de injertos con potencial de ser aplicados es alta, siendo el aspecto más crítico y a mejorar la supervivencia celular a la bioimpresión, mientras que como sustrato de cultivo han demostrado resultados prometedores. Podemos concluir, que si bien la bioimpresión sistemática de injertos está muy desarrollada, el mayor reto sigue siendo la supervivencia celular al proceso. También, hemos observado que la integración con el tejido es prometedora, ya que hemos observado, estructuras tisulares similares a los del tejido sano, con menores signos de inflamación.

Agradecimientos

Esta investigación ha sido financiada por el proyecto BIOIMP_ACE_MAS_6_E, cofinanciado por la Unión Europea a través del Programa Interreg VI-A España-Portugal (POCTEP) 2021-2027.

DEVELOPMENT OF CHEMICALLY CROSSLINKED PECTIN AND HYALURONIC ACID HYDROGELS WITH HIGH STABILITY AND PH RESPONSE FOR 3D EXTRUSION PRINTING

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Introduction

Hydrogels obtained from natural polymers, polysaccharides and proteins, are widely employed as biomaterial inks in 3D extrusion (bio)printing, an additive manufacturing technique which holds significant potential in the biomedical field for applications such as drug delivery or tissue engineering among others[1]. As most of the hydrogel-based biomaterial inks are physical gels, one of the main challenges is the optimization of their rheological properties for printing and their final mechanical stability[2],[3].

Methodology

In this study, we propose an innovative approach based on 3D extrusion printing of chemical crosslinked hydrogels obtained from natural polymers aimed to increase mechanical and stability properties of the resulting hydrogels. To this aim, high molecular weight pectin and hyaluronic acid were chemically modified with bis(3-aminopropyl) amine (APA) and subsequently crosslinked with genipin.

Results and conclusions

The resulting hydrogels were fully characterized as to their viscoelastic properties, stability, and weight variation. Biphasic hydrogels were formulated following a procedure reported by our group[4] and successfully manufactured through 3D extrusion printing into polymer scaffolds with high hydrolytic stability and pH response which are currently being evaluated for drug release applications.

Acknowledgments

This research was funded by the project PID2020-113045GB-C22 funded by MCIN/ AEI /10.13039/501100011033 and the call ‘Doctorados Industriales’ (DIN2019- 010868). We acknowledge the financial support from the Molecular Design of Polymers for Biomedical Applications (MEDIPOL) project.; this project has received funding from the European Union's Horizon 2020 Research and Innovation Programme. H2020-MSCA-RISE-2019.Grant agreement ID: 871650

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MICHAEL ADDITIONS TO ACTIVATED ALKYNES FOR THE PREPARATION OF PH-RESPONSIVE HYDROGELS

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Introduction

Hydrogels are polymeric networks with high water uptake capacity and excellent candidates for biomedical applications. Their preparation can be afforded by activated alkyne-based Michael additions due to their high reactivity and compatibility with aqueous media [1]. Among all possibilities, amino-yne click chemistry highlights because of the pH-responsiveness of the resultant β-aminoacrylate bond, which enables the recovery of the initially conjugated amine (Figure 1A) [2]. Here, we investigate the stimuli-responsive characteristics of hydrogels with β-aminoacrylate crosslinks. We study the effect of acidifying the pH of the media, combining amines and thiols. We examine the consequences of an internal pH switch by the encapsulation of a merocyanine-based photoacid into the hydrogel network.

Methodology

PEGalk and merocyanine-based photoacids were synthetized [2,3]. FESEM analysis was performed on a FEG INSPECT-F50. Responsiveness of hydrogels to environmental pH was examined through gravimetric analysis. A He-Cd laser (KIMMON IK4171L-G) of 441.6 nm (380 mW/cm2) was used for light-induced pH switch.

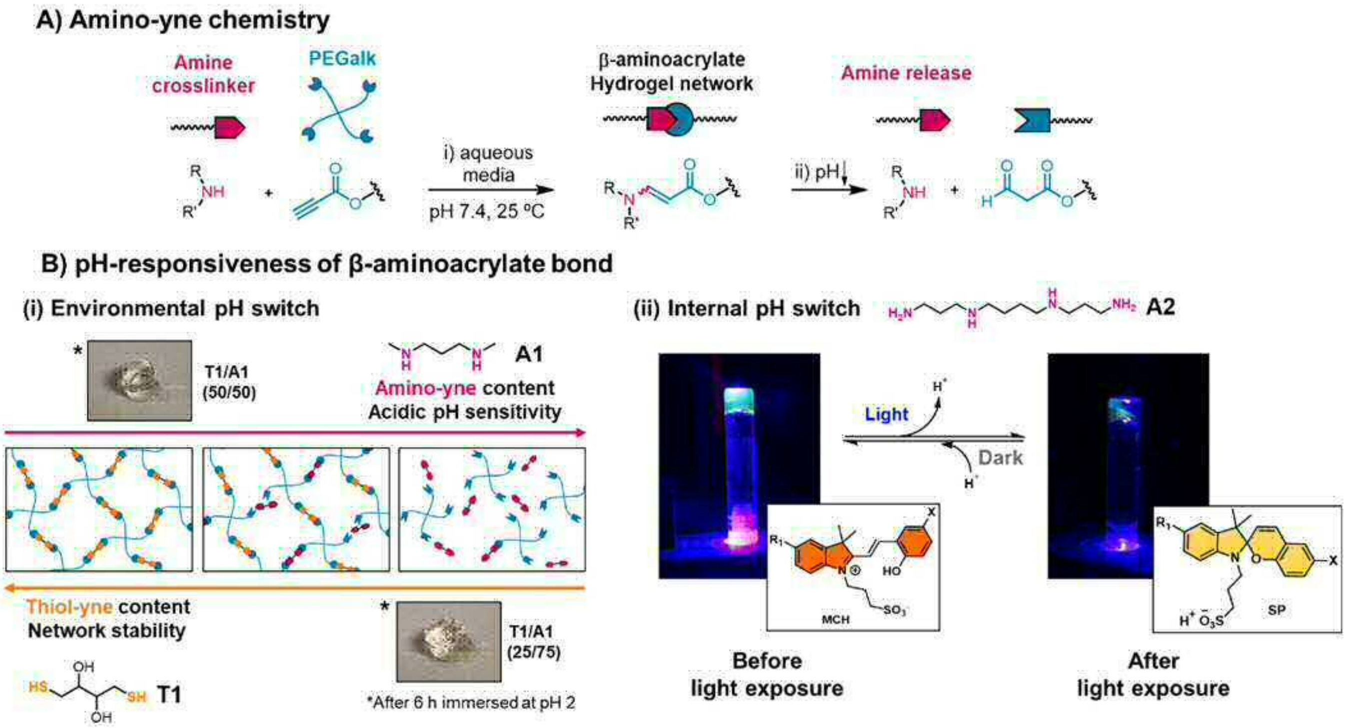

Figure 1. A) Scheme of ß-aminoacrylate formation and cleavage by amino-yne chemistry and B) pH-responsiveness of the bond by environmental pH switch (i) and light-induced internal pH switch (ii).

Results and conclusions

PEGalk was synthesized from 4-armed PEG and propiolic acid. Amines A1 and A2, and thiol T1 were used as crosslinkers of PEGalk for hydrogel formation at pH=7.4 and 25 ºC. Crosslinking was a consequence of the formation of β-thio/aminoacrylate bonds. The characterization of their morphology by FESEM revealed a highly porous structure. For the PEGalk-A1 hydrogel, it was observed that degradation was accelerated by decreasing the pH of the media. Moreover, higher stability of the network was observed as T1/A1 ratio increased, while maintaining the release of the amine (Figure 1B.i). PEGalkA2 hydrogel was synthetized in presence of a merocyanine-based photoacid, using different pH=7.4 buffer/DMSO ratios and polymer concentrations. Under light illumination, proton release successfully mediated the cleavage of the bond, resulting in sol formation (Figure 1B.ii). β-aminoacrylate based crosslinks are outstanding candidates for the preparation of pH-responsive hydrogels. Combination of thiol and amino-yne chemistries have been used as a useful tool for controlling degradation rate against external changes of pH. Encapsulated merocyanine-based photoacids are able to induce β-aminoacrylate cleavage under light illumination

Acknowledgments

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SISTEMAS PIEZOELÉCTRICOS BASADOS EN POLILACTIDA CON ESTABILIDAD TÉRMICA MEJORADA Y PROPIEDADES MECÁNICAS AJUSTABLES

Asier Panfilo Elechiguerra[1,2], Richard Schönlein [1,2], Paula Sofía Maroto Herrera[1], Amaia Montilla Allende[1], Aitor Larrañaga Espartero[1,2], Jone Muñoz Ugartemendia[1,2]

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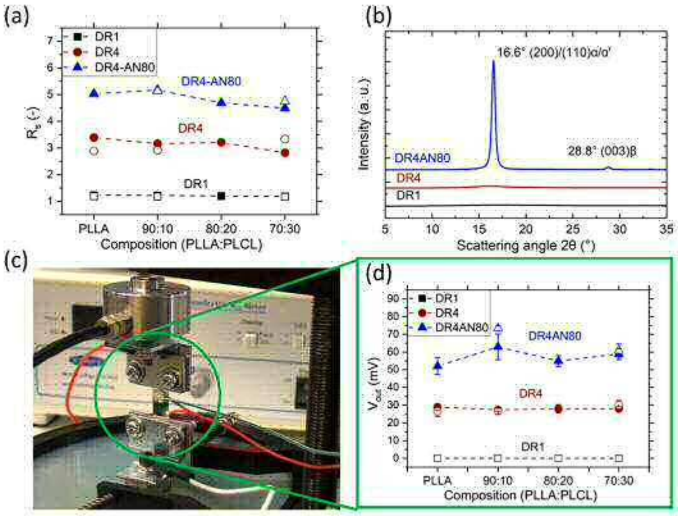
Introducción

Los soportes celulares electroactivos capaces de mimetizar los coeficientes piezoeléctricos fisiológicos han adquirido un creciente interés en diversas aplicaciones biomédicas [1]. Estos son capaces de convertir estímulos mecánicos derivados del movimiento dinámico fisiológico o de estímulos no invasivos (p.ej.: ultrasonidos) en señales eléctricas, que pueden ser utilizadas para modular la respuesta celular y mejorar la estrategia terapéutica [2]. La poli(L-lactida) (PLLA) presenta respuesta piezoeléctrica cuando su estructura macromolecular está alineada y soporta tensiones de cizalla, y se puede modular controlando el alineamiento de las cadenas durante el proceso de estirado y el grado de cristalinidad inducida en el post-procesado. Sin embargo, el PLLA presenta dos principales inconvenientes: i) su inherente fragilidad y ii) su baja estabilidad térmica que dificultaría su procesado mediante técnicas de fabricación avanzada [3]. Para superar estos inconvenientes, se propone aquí formular nuevos sistemas piezoeléctricos basados en mezclas miscibles de PLLA con poli(L-lactida-co-caprolactona) (PLCL), un copolímero termoplástico elastomérico, que mezclado con el PLLA permitiría modular las propiedades mecánicas y mejorar su estabilidad térmica [4].

Metodología

En este trabajo se ha analizado el comportamiento piezoeléctrico de tres composiciones concretas de mezclas PLLA:PLCL (90:10, 80:20 y 70:30 en peso) en tres estados diferentes y se han comparado con el PLLA puro: 1) Filmes amorfos sin estirar (DR1), 2) filmes estirados un 400%, produciendo cadenas orientadas con bajo grado de cristalinidad (DR4), y 3) filmes estirados un 400% y recocidos a 80 grados (DR4AN80), produciendo cristales orientados. Además, se ha analizado el cambio en la respuesta piezoeléctrica después de un mes en condiciones fisiológicas.



(a) Factores de orientación de los sistemas PLLA:PLCL*. (b) Medidas XRD que muestran la fase cristalina del PLLA en función de parámetros de procesado y post-procesado. (c) Stand para medir la piezoelectricidad de los sensores bajo tensión que provoca esfuerzo de cizalla en las cadenas alineadas a 45º. (d) Respuesta piezoeléctrica de los sistemas PLLA:PLCL*.
*Símbolos sin relleno: 30 días en condiciones fisiológicas.

Resultados y Conclusión

Los resultados han demostrado que se puede modular el coeficiente piezoeléctrico ajustando los niveles de orientación (figura a) y cristalinidad (figura b) inducidos durante el procesado y post-procesado. Por otro lado, se ha demostrado que los sistemas investigados son piezoeléctricos y que la señal eléctrica que emiten se mantiene constante durante un mes en condiciones fisiológicas (figura d). Los resultados obtenidos refuerzan el potencial que pueden tener los sistemas piezoeléctricos PLLA:PLCL en ingeniería de tejidos.

Agradecimientos

Agradecimientos al proyecto PID2022-139821OB-I00 financiado por MCIN/AEI/10.13039/501100011033/, FEDER, Una manera de hacer Europa y Gobierno Vasco (IT1766-22), concesor de la beca predoctoral (0101706).

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LINEAR DENDRITIC BLOCK COPOLYMERS AS THERMORESPONSIVE NANOCARRIERS IN AQUEOUS MEDIA

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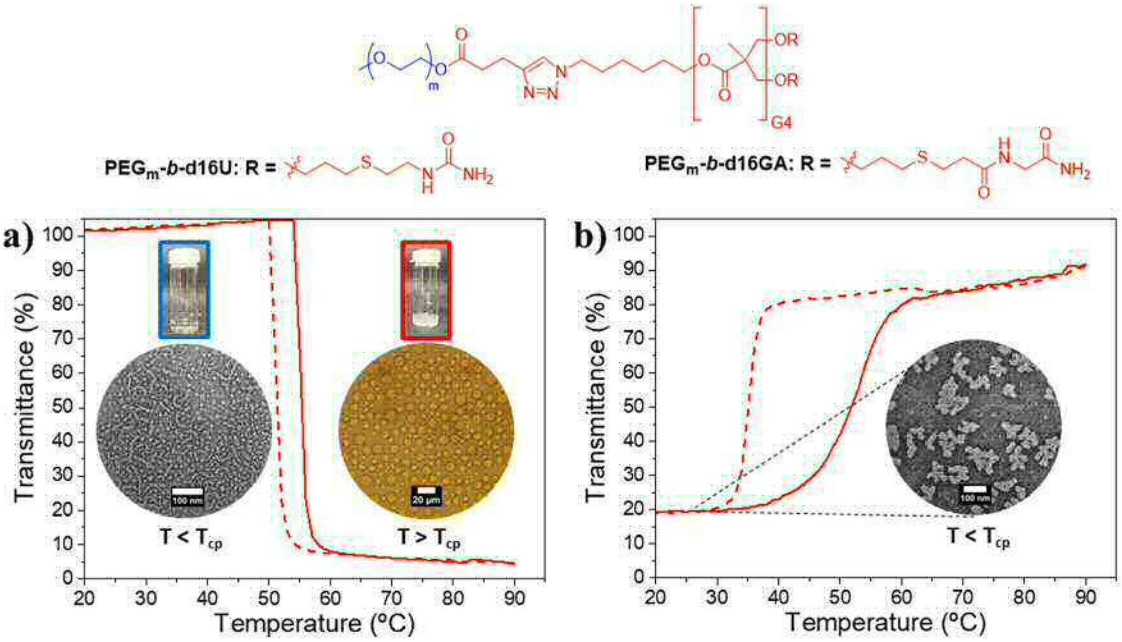
Introduction

Amphiphilic thermoresponsive block copolymers have extensively been investigated to develop new drug delivery systems which enable their controlled release with the temperature.[1] Those with an upper critical solution temperature (UCST) are soluble above a certain temperature (Tcp) and insoluble below it. For drug delivery applications, the UCST nanocarriers based on hydrogen bonding are reliable because they are hardly sensitive to pH and ionic strength.[2] Herein, we report new amphiphilic linear-dendritic block copolymers (LDBCs) featuring a permanently hydrophilic block and a UCST dendron block. When compared to linear counterparts, thermoresponsive dendritic structures are expected to have more reproducible thermoresponsiveness. This is due to their monodispersity, which allows for precise control over the number of peripheral groups.

Methodology

Amphiphilic LDBCs consisting of a poly(ethylene glycol) (PEG) segment and a 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) based dendron with 16 peripheral ureido (PEGm-b-d16U) or glycinamide groups (PEGm-b-d16GA) were prepared by click coupling of preformed blocks. The complete peripheral functionalization was verified by IR, mass and RMN spectroscopy. Self-assemblies were formed by nanoprecipitation and characterised by DLS, TEM and fluorescence spectroscopy. The thermoresponse was evaluated by optical microscopy, DLS, TEM, and UV-Vis and NMR spectroscopy. Besides, the ability of drug loading and release has been evaluated by UV-vis spectroscopy.



Amphiphilic LDBCs with UCST thermoresponse. Transmittance curves of (a) PEGm-b-d16U and (b) PEGm-b-d16GA at 1.0 mg/mL in water (solid curves are heating process and dashed curves are cooling process)

Results and conclusions

Ureido BC PEGm-b-d16U formed stable small micelles. In contrast, due to their higher crystallinity, the glycinamide counterparts PEGm-b-d16GA self-assembled in different morphologies with a lower stability. The thermoresponse was also dependent on the UCST promoting peripheral group. Thereby, PEGm-b-d16U micelles did not dissolve, instead they swell and collapse forming a coacervate phase above 50 ºC. Conversely, PEGm-b-d16GA self-assemblies show a typical UCST response as they were dissolved on heating above 50 ºC. Besides, their Tcp was increased between 31 to 46 ºC by decreasing the length of PEG block. Drug models, curcumin and dexamethasone, were encapsulated inside of these self-assemblies and their release was evaluated with the temperature. The synthesis of LDBCs with a controlled number of appropriate thermoresponsive promoting groups allows the preparation of UCST macromolecules with a reproducible Tcp close to physiological temperature and making them suitable to use in controlled drug delivery.

Acknowledgments

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NUEVOS BIOMATERIALES BASADOS EN COPOLÍMEROS DE GELMA PARA REGENERACIÓN ÓSEA

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Introducción

En la actualidad es de gran interés el diseño de biomateriales en forma de estructuras porosas 3D para aplicación en ingeniería de tejidos óseo. Estos biomateriales deben ser capaces de imitar las características biológicas y estructurales de la matriz extracelular (MEC), que permitan a las células proliferar y diferenciarse para regenerar el tejido dañado. En particular, se busca una matriz versátil que permita mejorar las propiedades mecánicas o degradación incontrolada y permita la adhesión, proliferación y diferenciación celular, esencial para el inicio del proceso de remodelación ósea. Una estrategia ampliamente utilizada es el uso de mezclas de polímeros biodegradables, sintéticos o naturales, para obtener hidrogeles híbridos cuyas propiedades puedan diseñarse a medida. El objetivo es obtener estructuras 3D porosas similares a la MEC, que favorece un intercambio eficiente de nutrientes, la adsorción de macromoléculas implicadas en la adhesión celular y la vascularización del andamio; además de un marcado carácter hidrofílico, que permite el hinchamiento en medios acuosos sin disolverse [1].

Metodología

En este trabajo, presentamos nuevos andamios porosos 3D basados en copolímeros ternarios de GelMa [2], vinilpirrolidona (VP) y 2-hidroxietilmetacrilato (HEMA). Los biopolímeros se caracterizan mediante espectroscopia infrarroja (FTIR) y análisis termogravimétrico (TGA); por microscopía electrónica de barrido (SEM) se estudia la presencia de la porosidad creada por liofilización; y se analiza la variación de su grado de hinchamiento y degradación enzimática in vitro, junto con sus propiedades mecánicas, en función de las diferentes composiciones. Además, se evalúan varios parámetros biológicos como la viabilidad y diferenciación celular con la línea celular preosteoblástica MC3T3-E1.

Resultados y Conclusión

Los sistemas ternarios de copolímeros H-GelMa / L-GelMA, presentan una clara mejora en sus propiedades mecánicas, en términos de incremento en valor del módulo de almacenamiento (G'). Se observa un perfil de degradación enzimática mucho más lento y sostenido, manteniendo un nivel de hidrofilicidad similar respecto a los homopolímeros GelMa. Finalmente, tras los ensayos de biocompatibilidad, se observa como los materiales basados en copolímeros con VP y/o HEMA son citocompatibles frente a células preosteoblásticas, permitiendo su diferenciación a osteoblastos maduros.

Agradecimientos

MICINN (PID2021-124926NB-I00), ISCIII (PI20/01384), Unión Europea FEDER y Consejo Investigación Europeo, Advanced Grant Verdi-Proposal No. 694160 (ERC-2015-AdG).

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THERMO-RESPONSIVE NANOVECTORS FROM SELF-ASSEMBLED AMPHIPHILIC DEGRADABLE BLOCK COPOLYMERS

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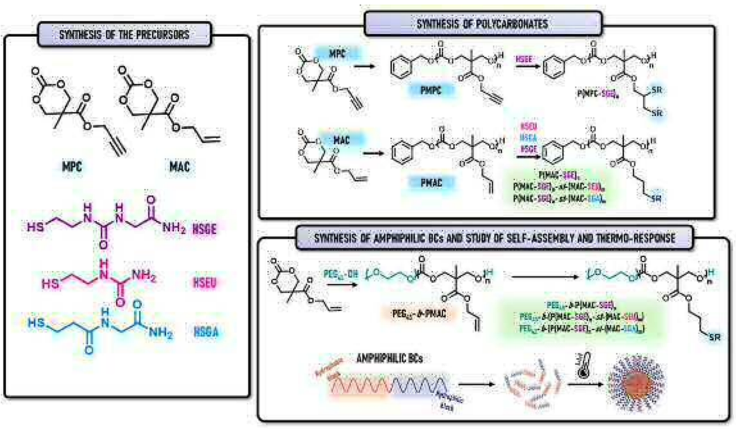
Introduction

Polymeric nanocarriers based on amphiphilic block copolymers (ABCs) self-assemble in water forming aggregates capable of encapsulating drugs.1 ABCs with aliphatic polycarbonates (APCs) as hydrophobic block synthesized via ring-opening polymerization (ROP) of 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) using polyethylene glycol (PEG) as initiator, are notable for their biocompatibility and the ease of incorporating moieties through click chemistry, enabling stimuli-responsiveness.2,3 Thermo-responsive polymers undergo conformational changes in response to temperature. UCTS (Upper Critical Solution Temperature) polymers are insoluble below a certain temperature and soluble above it, allowing for the release of molecular cargo. For non-ionic compounds, UCST behavior relies on the formation of hydrogen bonds, commonly between ureido or glycinamide groups.4 The objective of this work was to synthetize and characterize non-ionic thermo-responsive polycarbonates and ABCs with different UCST promoting units (ureido (SEU), glycinamide (SGE) and ureido-acetamide (SGE)) to evaluate their thermo-responsiveness and self-assembly in water.

Methodology

Polymers were prepared by combining ROP with post-polymerization functionalization via photoinduced thiol-ene/yne reactions using 365 nm light. Bis-MPA based monomers, 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC) and 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (MPC), were polymerized using either benzyl alcohol (for polycarbonates) or PEG (for ABCs). Polycarbonates were functionalized with thiols (HSGE, HSEU and HSGA) to afford a series of polymers with thermo-responsive units. ABCs were obtained under the same approach.



Results and conclusions

Polycarbonates and ABCs with pendant moieties were efficiently prepared. One of the polycarbonates shows thermo-response at a very low temperature, while the other polycarbonates do not. ABCs functionalized with stimuli-responsive moieties self-assemble in water forming spherical micelles, and one of them forms stable aggregates with thermo-responsive properties, showing a UCST type behavior with a transition temperature of 55ºC.

Acknowledgments

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CHARACTERIZATION OF THE ISOTHERMAL CRYSTALLIZATION OF POLY(VINYLIDENE FLUORIDE) BLENDED WITH THE IONIC LIQUID [EMIM]2[CO(SCN)4]

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Introduction

Smart materials are applied in different fields of knowledge, including biomedicine. The combination of poly(vinylidene fluoride) (PVDF) with ionic liquids (ILs) is being studied for the development of smart materials.. Thus, the isothermal crystallization of PVDF incorporating different contents of the magnetic ionic liquid bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate ([Emim]2[Co(SCN)4]) is characterized in this work.

Methodology

Fourier transform infrared spectroscopy (FTIR) spectra were obtained in the attenuated reflection mode using a Nicolet 6700 spectrometer. FTIR spectra were also acquired using a Spectrum 100, PerkinElmer, in attenuated total reflection mode over a range of 4000 to 400 cm-1. Differential scanning calorimetry (DSC) were carried out with a DSC 8000 from PerkinElmer to scan the crystallization and melting regions, in both cases under a flowing nitrogen (N2) atmosphere of 20 ml/min.

Results and conclusions

Although α, β and γ crystalline phases were present in all samples, their relative percentages varied greatly with the amount of IL present, demonstrating that [Emim]2[Co(SCN)4] is a strong inductor of the electroactive (EA) phases of PVDF. By evaluating both FTIR and DSC data, this effect has been ascribed to the higher melting temperatures (Tm) of the EA structures whose formation is favoured at higher crystallization temperatures. The Tm of the β phase is higher than that of the α phase, whereas Tm for the γ phase is higher than for α and β phases. Thus, together with the functional properties provided by the IL, such as magnetic response and ionic conductivity, the addition of [Emim]2[Co(SCN)4] strongly influences PVDF's crystallization kinetics, proving to be a simple and very effective way to nucleate specific phases of PVDF, according also to the specific processing conditions. Conclusions: The presence of [Emim]2[Co(SCN)4] enhances the nucleation of PVDF in the electroactive phases. Higher percentage of [Emim]2[Co(SCN)4] correlates to higher percentage of electroactive β and γ structures. The melting temperature of the γ phase is higher than that of the β phase and higher than that of the α phase for the same temperature of crystallization. This leads to an increase in the crystallization temperature observed in cooling scans with increasing e IL content, on the contrary to what one might expect due to the freezing point depression.

Acknowledgments

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ELASTOMERIC PROTEIN-BASED BIOACTIVE EUTECTOGEL FOR DRUG DELIVERY ON THE SKIN

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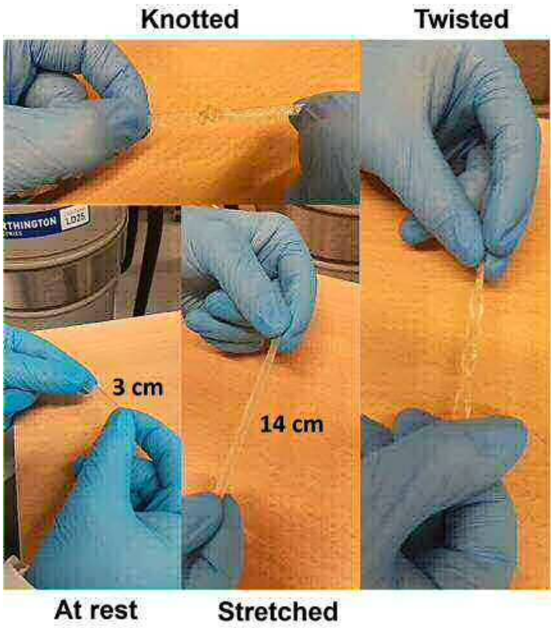
Introduction

Deep eutectic solvents (DES), particularly therapeutic mixtures (THEDES), are gaining traction for drug delivery due to their biocompatibility and ability to deliver drugs without harsh solvents. Choline and geranic acid (CAGE) is a particularly promising THEDES, effective for skin delivery and various other applications. However, its low viscosity limits its usefulness. Researchers have addressed this by creating a new type of material: protein elastomer therapeutic eutectogels. These gels combine CAGE with a protein scaffold and a natural compound (tannic acid) to create a strong, elastic material. This design solves the challenge of using protein gels with CAGE and offers exciting possibilities for innovative drug delivery materials made from natural components. This study explores a novel class of biocompatible materials termed "eutectogels." Eutectogels are constructed by incorporating therapeutic deep eutectic solvents (THEDES) with skin permeation capabilities within a dynamically crosslinked protein scaffold using natural polyphenols. This research unveils a surprising gelation mechanism within the ionic eutectic, distinct from traditional hydrogels. Interestingly, polyphenols modulate protein conformation, enabling the network's mechanical and viscoelastic properties to be precisely tailored, ranging from elastic to hyperelastic behavior. The resulting eutectogels exhibit strain-hardening characteristics, a reversible gel-to-sol transition upon heating, and exceptional adhesive properties.



Methodology

The protein eutectogels were created using a straightforward three-step process: First, a high concentration (20% w/v) of gelatin was dissolved in the CAGE solution at room temperature (25°C). Next, the mixture was heated to 70°C, followed by the addition of tannic acid (a natural compound). The mixture was then stirred for 45 minutes. Finally, the warm mixture was poured into silicone molds and cooled at 4°C for 24 hours. This cooling step allows the gel to form and the protein chains to become entangled, strengthening the material. Notably, the gelatin concentration was chosen specifically at 20% w/v based on previous research to achieve the best balance between elasticity and flow properties (viscoelasticity and viscosity).

Results and conclusions

This research unveils a revolutionary material: protein eutectogels. Imagine a material crafted from gelatin, a common protein, that can transform into a gel using a special solvent (CAGE) capable of delivering drugs deep into the skin. Unlike traditional gelatin gels, these eutectogels don't require the protein to adopt specific shapes, offering a simpler and potentially more versatile approach. To further enhance their strength and elasticity, a natural compound called tannic acid is incorporated, resulting in a remarkably stretchy material

Acknowledgments

The University of the Basque Country

PLA ELECTROSPUN FIBERS REINFORCED WITH YERBA MATE NANOPARTICLES AND VEGETABLE OILS AS PLASTICIZERS

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Introduction

Electrospinning is a novel technique widely used in the processing of polymeric matrixes for its use in diverse applications, such as biomedical or industrial applications.

Only soluble and fusible melt polymers are suitable for electrospinning processing. Among these, in the last years, one of the most used polymers through electrospinning processing is poly(lactic acid) (PLA). This is due to its biodegradability and biocompatibility. This polymer is an ideal choice for fabricating tissue engineering materials such as scaffolds, implantable devices, and drug delivery systems [1].

However, its thermal and mechanical properties need to be improved. PLA shows good stiffness and strength but its brittleness needs to be improved. In order to solve these drawbacks, enhanced PLA can be obtained through melt-spinning or electrospinning, being the most simple and effective way to obtain these enhanced nanofibers [2].

In this work, we have studied the effect of the addition of vegetable oils as plasticizers as well as the addition of nanoreinforcements extracted from yerba mate waste, from a circular economy point of view. In particular, woven no-woven PLA electrospun fiber mats are reinforced with yerba mate nanoparticles extracted from yerba mate waste and plasticized with maleinized corn oil and maleinized linseed oil.

Methodology

Different PLA electrospun mats have been produced by adding 1 wt% of lignocellulosic nanoparticles, as well as 5 wt% of both oils as plasticizers. Mats were obtained in an Electrospinner Y-flow 2.2D-XXX (Y-Flow, Malaga, Spain), using a voltage of 20kV a flow rate of 0.5 ml/h for the solvent mixture ($CHCl_3$/DMF 4/1) and 3.5 mL/h for the polymeric suspension and a distance with needle-collector of 14cm.

Results and conclusions

Different PLA electrospun mats reinforced with lignocellulosic nanoparticles extracted from yerba mate waste and both oils as plasticizers, have been successfully processed, being visible the change in the color of the mats, due to the starting materials. The effect of the addition of both nanoparticles and plasticizers on the diameter distribution of the electrospun fibers is obtained, as well as their thermal and mechanical characterization.

Acknowledgments and References

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HIDROGELES TERMOSENSIBLES PERSONALIZADOS PARA APLICACIONES EN BIOMEDICINA Y MEDICINA REGENERATIVA

Ana García-Crespo [1,2], Pedro Liz-Basteiro [1,2], Rubén García-Sobrino [1,2], Juan Rodríguez-Hernández [1], Helmut Reinecke [1], Alberto Gallardo [1], Carlos Elvira [1], Enrique Martínez-Campos [1,2]

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Introducción

Los retos en biomedicina requieren soluciones innovadoras debido a la complejidad de las enfermedades y la limitación de los tratamientos convencionales. Los hidrogeles que facilitan el crecimiento y mejoran la supervivencia de las células representan una solución innovadora para abordar complejos problemas de salud, así los hidrogeles de poli-vinilcaprolactama (PVCL) proporcionan un entorno bidimensional biocompatible y personalizable para el cultivo celular, basado en una superficie termosensible que facilita tanto el proceso de cultivo como el despegue celular no agresivo.

Metodología

Los hidrogeles se sintetizaron mediante fotopolimerización radical, las nanopartículas de PVCL cargadas con fármacos se obtuvieron mediante Tecnología SAS de CO_2 supercrítico, y las líneas empleadas para evaluación biológica fueron C166-GFP, C2C12 y MC3T3-E1.

Resultados y Conclusiones

Estos hidrogeles se aplican como membranas libres (hidrogeles no soportados) o como recubrimientos sobre placas multipocillo. Esta tecnología resulta versátil y ofrece la posibilidad de ser personalizada siendo posible controlar su topografía y morfología, regulando la actividad celular y la creación de estructuras tubulares[1]. También se ha propuesto la producción de hidrogeles mediante impresión 3D por fotopolimerización dado que ofrece mayor precisión, complejidad geométrica y capacidad de fabricación escalable.

Además, se pueden llevar a cabo modificaciones químicas de su superficie incorporando distintos grupos iónicos[2], péptidos o proteínas. Debido a su espesor en escala macroscópica, los hidrogeles permiten la modificación biológica mediante la carga de compuestos bioactivos, factores de diferenciación/regeneración celular, agentes antimicrobianos o ácidos nucleicos para terapia génica.

Actualmente, esta tecnología se enfoca en el desarrollo de superficies termosensibles funcionalizadas para controlar la actividad celular en regeneración ósea y cartilaginosa. Estas superficies incorporan nanopartículas de PVCL que encapsulan fármacos destinados a inducir la diferenciación ósea y secreción de matriz extracelular.

El objetivo es optimizar la formulación de los hidrogeles creando un producto personalizado que permita su aplicación en tratamientos de medicina regenerativa y terapia celular, pudiendo conseguir una recuperación más eficaz y controlada en pacientes con lesiones de cartílago, quemaduras cutáneas o degeneración ocular.

Agradecimientos y Referencias

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DEVELOPMENT OF REABSORBABLE BASEMENT MEMBRANE EQUIVALENT BASED ON BIOACTIVE, RECOMBINANT ELASTIN-LIKE POLYMERS FOR WOUND HEALING APPLICATIONS

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Introduction

The skin is the largest organ in the body, and any damage can result in a significant imbalance in its function, disability, or even death. The treatment of these injuries remains costly and can result in physical, mental, and emotional disabilities [1].

An ideal skin implant would be able to stop the invasion of the epidermal area by fibroblasts, induce regeneration, present adequate mechanical properties, and degrade progressively. It must also be antimicrobial and prevent the loss of fluids.

The objective is to obtain a membrane that achieves all ideal implant properties. The initial stages involve selecting appropriate Elastin-like recombinamers (ELRs) to develop membranes based on biocompatible hydrogels obtained via click chemistry. ELRs are a type of protein biopolymer based on the repetition of natural elastin sequences, L-Val-L-Pro-Gly-X-Gly [2].

Methodology

In previous studies, membranes with tunable properties were developed by covalently cross-linking two ELRs at the interface of two immiscible liquids using click chemistry (Figure 1). These membranes demonstrated successful biocompatibility with adjustable physicochemical properties, including shape, thickness, porosity, and diffusion coefficient. Additionally, membranes are non-cytotoxic, maintained the viability of skin cells, and showed better results than controls in tests with healthy animal models.

Results and conclusions

In this study, we included adhesion sequences in membranes, such as RGD, and degradative sequences that have also demonstrated their ability to induce regeneration and angiogenesis. Different techniques were used to characterize membranes and determine their properties. Subsequently, the ability to support the viability of skin cells was determined *in vitro* using primary human foreskin fibroblasts (HFF1). Cytotoxicity of the new membranes was evaluated with an LDH assay. *In vivo* assessment was performed by implanting the membranes subcutaneously in the dorsal area of diabetic mice [3].

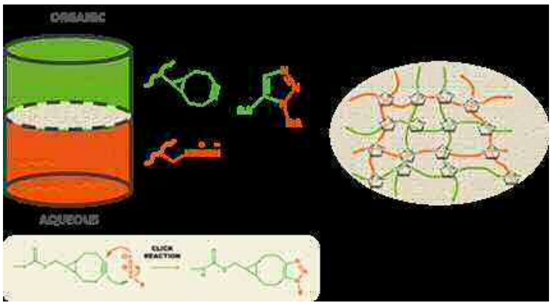

Figure 1. ELR-based catalyst-free click membrane formation: scheme of the design to obtain an ELR membrane where two immiscible phases are formed with ELR-cyclooctyne in an organic phase, and ELR-azide, in an aqueous phase.

To conclude, these membranes are biocompatible, and we can regulate their shape, thickness, porosity, and diffusion coefficient. The membranes are easy to produce and modify and have robust mechanical properties suitable for handling. The results of cell proliferation and cytotoxicity are ideal for wound healing. Additionally, the in vivo assays demonstrated the ability to regenerate the wound in diabetic models compared to controls.

Acknowledgments

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STUDY OF THE EFFECT OF THE ADDITION OF INORGANIC NANOPARTICLES ON BIODEGRADABLE-POLYMERIC ELECTROSPUN NANOFIBERS

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Introduction

Thermoplastic polymers can be processed with several techniques to obtain different morphologies, with the electrospinning is possible to obtain electrospun fibers mats with high surface area and porosity. These materials can find application in several fields as agriculture, membranes, packaging, wound dressing and tissue engineering [1]. Different polymers are suitable for these purposes, in particular biocompatible and biobased polymers as polylactic acid (PLA) and polycaprolactone (PCL) are one the main used. However, they present poor mechanical properties, low degradation rate and bioactivity and high hydrophobicity. In order to overcome these issues and to improve or provide new properties, neat polymeric matrices can be reinforced with either organic or inorganic nanoparticles (NPs) [2].

Methodology

Neat polymeric matrices (PLA and PCL) have been reinforced with both organic and inorganic NPs at different percentages between 0.5 and 20 wt% with respect the polymeric matrix. Electrospun fibers were prepared with an a Electrospinner Yflow 2.2.D-XXX (Nanotechnology Solutions) and the electrospinning parameters were set as following: voltage of 20 kV, flow rate of the polymeric solutions of 3.5, 2 and 1 ml h^{-1} depending on the system and distance between needle and collector of 14 cm.

Results and conclusions

The average diameter of fibers, which is a balance between the viscosity and electrical conductivity of the solution, strongly depends on NPs. The same type of NPs may have opposite effect with different polymeric matrices, for example Mg-based NPs are able to increase the main diameter of PCL-based nanofibers and decrease that one of PLA-reinforced nanofiber. Moreover, NPs can modulate the mechanical properties of polymeric matrix, indeed the effect of inorganic NPs, as Mg-based NPs and ZnO or organic NPs as lignin-based NPs have been studying. Furthermore, NPs have an accelerating effect on the hydrolytic degradation of polymers, and reinforcements as Mg-based NPs can improve the bioactivity of the materials, or ZnO may have an effect on the piezoelectric properties of the polymeric matrix. Hence, through the introduction of these kind of NPs it is possible to tailor the general properties of neat polymeric matrices but also improve properties as bioactivity and piezoelectricity.

Acknowledgments

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ELR-BASED HYDROGEL LOADED WITH PLASMA-TREATED PLA MICROPARTICLES AS AN EFFICIENT SYSTEM FOR CONTROLLED RELEASE OF LACTIC ACID

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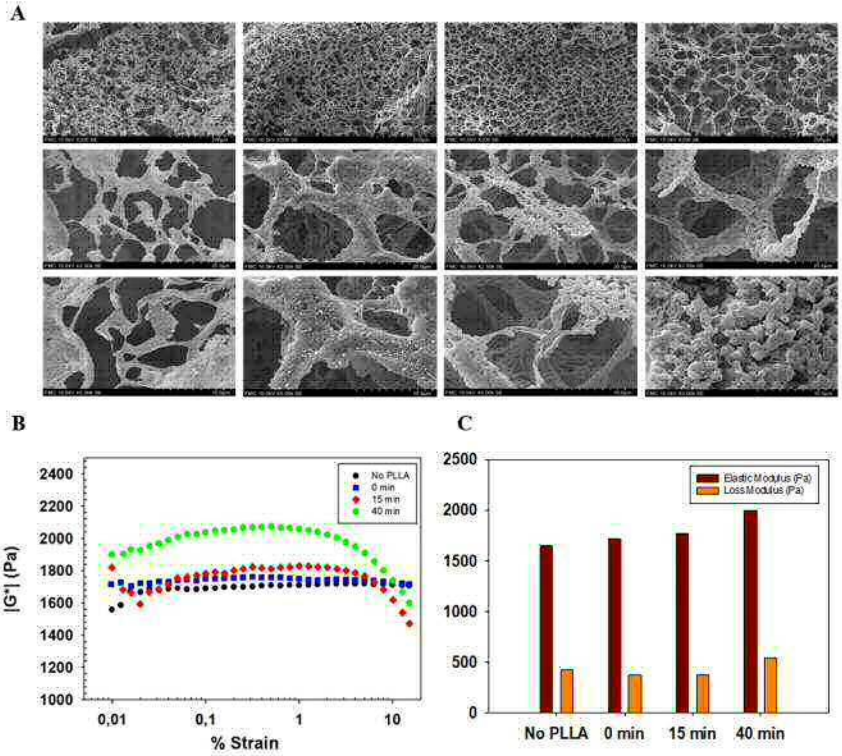
Introduction

The development of composite hydrogels represents the forefront of research with significant biomedical applications[1], including regenerative medicine, tissue engineering, and drug delivery. Recent studies have focused on developing drug delivery systems, with composite hydrogels being employed for the controlled release of various pharmaceuticals[2]. We report herein a new delivery system for early, controlled, and sustained lactic acid release based on a microcomposite hydrogel of recombinant elastin-like recombinamers (ELRs), with plasma-treated partially degraded PLLA embedded within it.

Methodology

In this study, we developed a microcomposite hydrogel designed for lactate release. The hydrogel is based on a biocompatible and biodegradable matrix composed of elastin-like recombinamers cross-linked via click chemistry. ELRs derive from the repetition of the L-Val-L-Pro-Gly-X-Gly [3] domain found in natural elastin. To reinforce the hydrogel, we incorporated poly-L-lactic acid (PLA) particles that had been partially degraded to lactic acid and various oligomers using oxygen plasma treatment. Consequently, we optimized the treatment times for the PLA degradation process, monitoring it through FTIR, UV, and NMR spectroscopy. Furthermore, the distribution of the particles within the hydrogel was monitored by scanning electron microscopy, and their mechanical properties were studied using rheological techniques.

Results and conclusions



Once the morphology and rheological properties of the hydrogel microcomposite were characterized (Figure 1), we obtained the lactic acid release curves of the microcomposite over time and modeled its release kinetics according to several models from which we deduced the dominant mechanisms in the release at each time frame. In the first 48 hours, early release of lactic acid produced by the degradation of PLA by oxygen plasma is observed, and at longer times, a sustained release of lactic acid produced by the hydrolytic degradation of PLA under physiological conditions takes place

A novel system has been developed that regulates lactic acid dosing by encapsulating plasma-treatment poly-L-lactic acid within chemical hydrogels. The hydrogels, which are designed to mimic the extracellular matrix (ECM), deliver lactic acid through PLA degradation by oxygen plasma treatment and hydrolysis. This process results in a system capable of controlled dosing of lactic acid both in an early and sustained manner over time. These achievements predict future applications in tissue engineering.

Acknowledgments

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BIOMINERALIZATION ASSISTED BY PEPTIDE SELF-ASSEMBLY

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Introduction

Bone regeneration is an intrinsic physiological process where the bone is repaired, and new bone is produced to replace damaged ones. However, this process can be prolonged, ranging from a few weeks to several months, depending on the severity of the damage. Existing methods, such as autografts, allografts, and bioactive molecules, are often time-consuming and have inherent limitations. Consequently, there is a need for efficient and accelerated bone regeneration strategies.

Methodology

Here, we study bone regeneration using peptide-induced self-assembly forming hydrogels comprised of peptide polymers (Fmoc-FFRRR1 and Fmoc-FFpY2), which allows the encapsulation of Calcium phosphate (CaP) particles, one of the major components of the bone by different technics to characterize the formation of composite hydrogels by inverted tube test and fluorimetry, the secondary structure by Circular Dichroism, InfraRed spectroscopy, and its morphology by optical and confocal microscopy. We also determined the mineralization occurrence by microscopy and the Von Kossa test.

Results and conclusions

We proposed that template-assisted peptide self-assembly can accelerate biomineralization. Specifically, the peptides FmocFFRRR and FmocFFpY function as hydrogelators, forming templates that can facilitate CaP mineralization. For the peptide FmocFFRRR, an additional phosphate source is supplied, which acts as a physical crosslinker to wave the nanofilaments into the fibrous network and form a phosphate template. Then, after adding calcium ions, the phosphate-rich template can capture calcium ions, thereby promoting CaP mineralization. Conversely, FmocFFpY inherently contains a phosphate source capable of capturing calcium ions within the fibrous network. By exploiting the distinct properties of FmocFFRRR and FmocFFpY, their combined application results in a hydrogel that enhances and accelerates the mineralization process. Our preliminary study showed the probable presence of CaP in the self-assembly, which has been analyzed by several methods. Under optimized conditions, the mineralized scaffold demonstrated promising properties, indicating its potential as a substitute for bone fracture repair.

Acknowledgments

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TUNING THE UNDERWATER ADHESIVENESS OF ANTIBACTERIAL POLYSACCHARIDES COMPLEX COACERVATES

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Introduction

Adjusting the water content and mechanical properties of polyelectrolyte coacervates for optimal underwater adhesion requires simultaneous control of the macromolecular design and the type and concentration of the salt used. Using synthetic or bio-inspired polymers to make coacervates often involves complicated chemistries and large variations in salt concentration.[1] The underwater adhesiveness of simple, bio-sourced coacervates can be tuned with relatively small variations in salt concentration. Bio-sourced polymers can also impart beneficial biological activities to the final material.

Methodology

We made complex coacervates from charged chitosan (CHI) and hyaluronic acid (HA) with NaCl as the salt. Their water content and viscoelastic properties were investigated to identify the formulation with optimal underwater adhesion in physiological conditions. The coacervates were also studied in antibacterial and cytotoxicity experiments

Results and conclusions

As predicted by linear rheology, the CHI-HA coacervates at 0.1 and 0.2 M NaCl had the highest pull-off adhesion strengths of 44.4 and 40.3 kPa in their respective supernatants. In-situ physical hardening of the 0.2 M coacervate upon a salt switch in 0.1 M NaCl resulted in a pull-off adhesion strength of 62.9 kPa. This material maintained its adhesive properties in physiological conditions. Finally, the optimal adhesive was found to be non-cytotoxic and inherently antimicrobial through a chitosan release-killing mechanism.[2] Our group is currently investigating the effects of polymer molecular weight and CHI degree of deacetylation on the complexation behavior and the mechanical properties of CHI-HA complex coacervates.

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CHITOSAN-NLCS LIPO-HYDROGELS AS CARRIERS IN WOUND HEALING.

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Introduction

Chitin, a natural polymer made of *N*-acetylglucosamine (GlcNAc) units linked by covalent β (1→4) bonds, found in the exoskeletons is the second most abundant biopolymer on Earth after cellulose[1]. Chitosan (mainly made of glucosamine (GlcN) also linked by covalent β (1→4) bonds) is the deacetylated derivative of chitin, is less common in nature and is primarily produced from the chemical deacetylation of chitin from crustacean sources[2]. Chitosan and chitosan-derived biomaterials (CDBs) are envisioned as a unique therapeutic strategy for treating various diseases, tissue engineering and drug delivery[3-5].

CDBs have a great applicability in inflammatory processes and wound healing[6]. In fact, ulcers of the skin involve a compromise in skin integrity, affecting at least the dermis, and are induced by a pathological process. Colloidal systems as Nanostructured Lipid Carriers (NLCs) crafted from polymers are utilised to shield the drug and facilitate controlled release, thereby reducing application frequency.

NLCs are composed of solid (palmitic acid) and liquid (oleic acid) physiological lipids, with no organic solvents employed in their preparation. Lipo-Hydrogels are hybrid assemblies composed of a lipid core (NLC) surrounded by a polymer layer.

The general objective is to develop lipo-hydrogels composed of NLCs coated with chitosan.

Methodology

NLCs are prepared by high shear homogenization and ultrasound method. Briefly, palmitic acid and oleic acid are heated to the fusion point of palmitic acid and then this lipid phase is mixed by high shear homogenization with a hot surfactant solution consisting in water and different concentrations of Pluronic 68, Tween 80 and chitosan. Then the NLC size is decreased by ultrasonication. Size and its distribution will be measured by DLS (Dynamic Light Scattering) and the surface charge by Zeta Potential.

Results and conclusions

The obtained Lipo-Hydrogels had a diameter lower than 500 nm with a polydispersity index of 0.2 and a Zeta Potential of -30 mV. One month after the synthesis of the NLCs coated with chitosan, no difference was seen in size or surface charge.

We managed to develop a method to synthesize Lipo-hydrogels of palmitic acid, oleic acid and chitosan. The obtained material showed good colloidal and long term stability since the production and up to one month.

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POSTER PRESENTATIONS SESSION 3

(September 18th)

VALORIZATION OF FORESTRY DERIVATIVES INTO FUNCTIONAL ACRYLIC POLYMERS FOR SPECIFIC APPLICATIONS.

Alba Tirado , Adrian Moreno , Gerard Lligadas , Marina Galià , Juan Carlos Ronda

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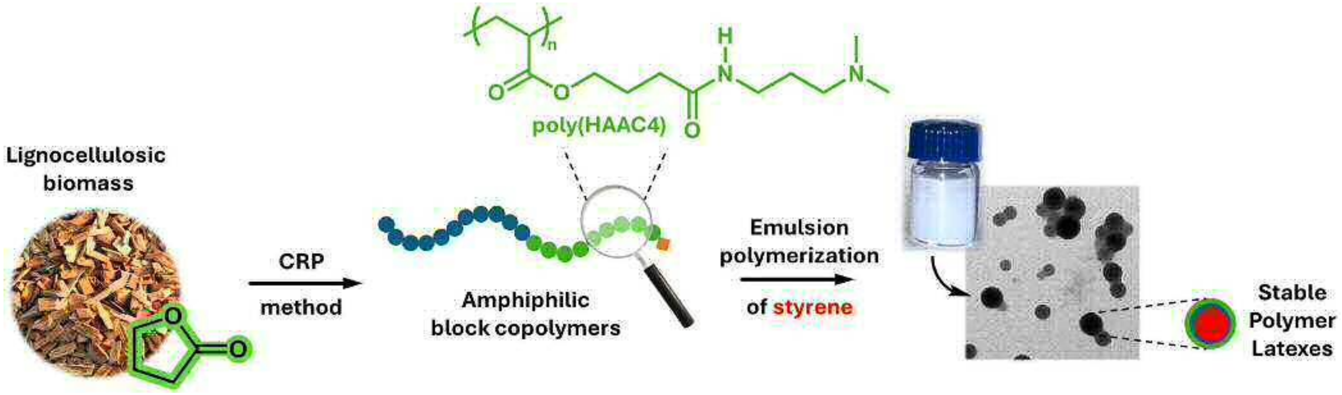
Introduction

Growing concerns about fossil resource depletion and environmental impact has led to the increase in 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 from forestry biomass or carbohydrates, being the last recently exploited in our group from solvents derived from lactic acid. 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 reduce the reliance on toxic reagents and solvents during their preparation. Towards this end, biobased water-soluble acrylates HAAC4 were synthesized from biomass-derived precursors and utilized as a key component in the preparation of sequential well-defined block copolymers composed of poly(butyl acrylate) poly(BA) and poly(HAAC4) segments, as hydrophobic and hydrophilic building blocks respectively. The amphiphilic poly(BA-b-HAAC4) obtained in this study showed potential as polymeric surfactants in the aqueous emulsion polymerization of relevant industrial hydrophobic monomers, providing a method for the preparation of stable latex dispersions.

Methodology

Biobased acrylates HAAC4 were synthesized following a ring opening aminolysis (ROA) of cyclic lactone γ-butyrolactone and a subsequent enzyme-catalyzed transesterification from biomass-derived precursors. Homopolymers poly(HAAC4) and poly(BA-b-HAAC4) were obtained through single electron transfer-living radical polymerization (SET-LRP) methodology. Characterization was performed using both 1H and 13C NMR spectroscopy. DLS and TEM analysis from latex solutions were conducted on diluted solutions by a factor of 100.



General overview of the use of biomass-derived copolymers for aqueous emulsion radical polymerization of styrene.

Results and conclusions

Amphiphilic poly(BA-b-HAAC4) copolymers demonstrated the ability to self-assemble in aqueous solutions, forming large compound micelles (LCMs) which have the potential to serve as surfactant stabilizers in emulsion polymerization, facilitating the preparation of stable latex dispersions. Notably, poly(BA-b-HAAC4) successfully stabilized relevant industrial hydrophobic monomers, such as styrene (S), demonstrating their practical significance for technological applications.

Acknowledgments

This work was supported by MCIN/ AEI /10.13039/501100011033 through project PID2020-114098RB-I00 (to G.L. and M.G.). The authors thank the "Ramón y Cajal" contract (RYC2022-035322-I) funded by MICIU/AEI/ 10.13039/501100011033 and ESF+ (A. M).

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RAFT-PHOTOPISA POLYMERIC NANO-OBJECTS FOR FUNCTIONALIZED LUMINESCENT COPPER NANOCLUSTERS (CUNCS) AND ITS APPLICATION AS SELECTIVE HG2+ SENSORS.

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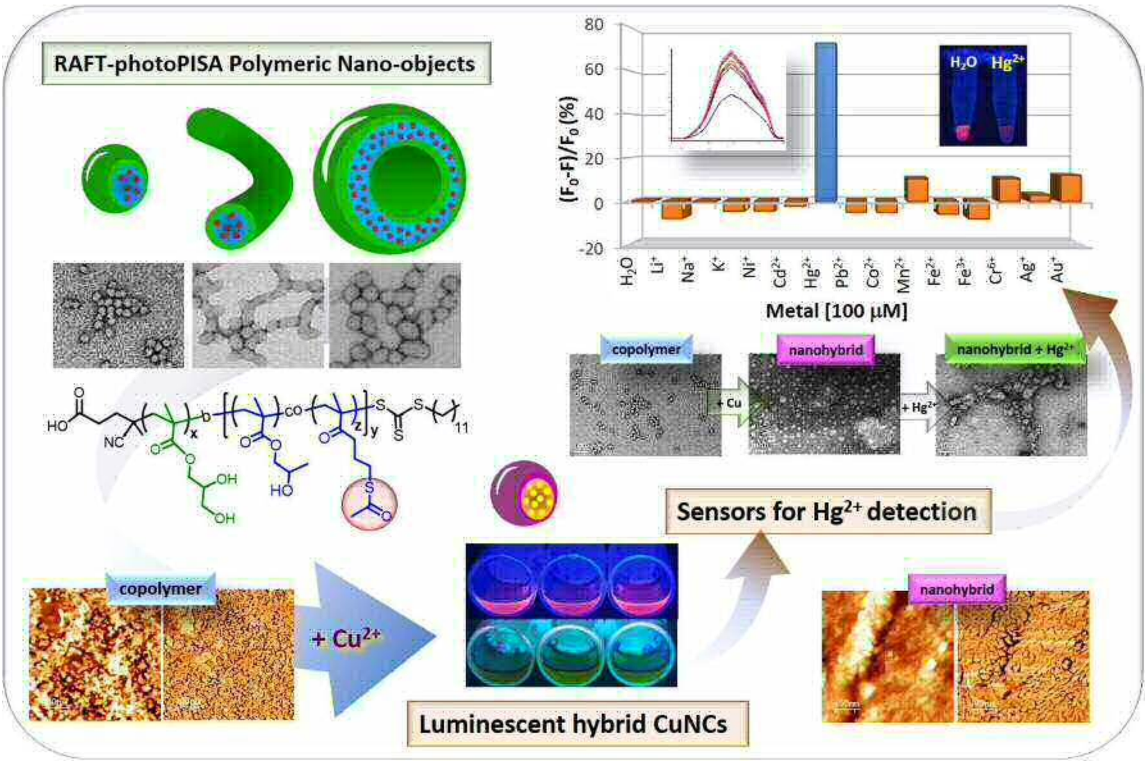
Introduction

In recent years, polymerization-induced self-assembly (PISA) has emerged as a versatile method for obtaining polymeric nano-objects with different morphologies, such as spheres, worms or vesicles. This technique enables relatively simple production with high solids content and a wide range of different monomers, making it a powerful approach for practical implementation [1,2].

Methodology

Herein, to widespread the applications of PISA, we have modified one of the most prototypical copolymers derived from RAFT-mediated PISA, namely poly(glycerol methacrylate)-b-poly(hydroxypropyl methacrylate) (PGMA-b-PHPMA), by incorporating a comonomer featuring a protected thiol group, 2-(acetylthio)ethyl methacrylate (AcSEMA), into the hydrophobic block. This functionalized monomer with protected thiol groups was developed by our Research Group. HPMA exhibits high aqueous solubility whereas AcSEMA is non-soluble in water, for this reason, the use of ethanol as co-solvent has been explored to increase the solubility of AcSEMA and prevent the phases separation during the photopolymerization process. Thus, this minor adjustment yielded diverse morphologies such as spheres, worms, and vesicles, influenced by the ratio between hydrophilic and hydrophobic blocks, as well as the AcSEMA content. Furthermore, the effects of various experimental variables on the synthesis and properties of the nanomaterials have been meticulously examined, as these parameters significantly influence the characteristics of the final hybrid material (nanostructure, size and morphology, dispersion, composition, coalescence, and final properties).



Results and conclusions

Finally, considering the strong affinity of thiol groups with metals, the incorporation of AcSEMA in self-assembled nanostructures paves the way for synthesizing novel hybrids with applications in biomedicine, sensing, catalysis, or water purification [3,4]. As demonstrated in this work, post-hydrolysis of the thioacetate group allowed for the utilization of thiolated polymeric nano-objects as templates to synthesize luminescent copper nanoclusters (CuNCs). Additionally, we demonstrated the potential use of the newly synthesized nanohybrids as fluorescent sensors for the selective detection of mercury. Our findings indicate that these cutting-edge polymeric copper nanohybrids could be effective tools for the simple, rapid, and economical detection of Hg2+ ions with high selectivity. These advancements could provide significant advantages over traditional methods of mercury detection and has potential implications for environmental monitoring and analytical chemistry.

Acknowledgments

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ON THE USE OF DEEP EUTECTIC SOLVENTS TO IMPROVE THE MECHANICAL PROPERTIES OF ELECTROSPUN POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE) FIBER MATS

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Introduction

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biobased polyester produced by microorganisms and is considered one of the most promising substitutes for conventional petrochemical-based polymers. However, the application of PHBV is highly limited, mainly due to its excessive stiffness. Deep eutectic solvents (DES) are emerging solvents with unique and tunable properties, such as high solubilization capacity, low cost, biodegradability, biocompatibility, the ability to liquefy compounds, and the ability to modify mechanical performance of polymeric systems. The present study demonstrates, for the first time, the potential of DES to balance the mechanical properties of electrospun PHBV fiber mats. Additionally, this study aims to demonstrate the effect of individual DES components, highlighting the importance of their selection.

Methodology

Choline chloride (ChCl):Urea:Water, ChCl:Glycerol (Gly), and Gly:Sodium Citrate (NaCitrate) were utilized as DES, while pure glycerol and acetyl tributyl citrate (ATBC) served as traditional plasticizers for comparison purposes. PHBV-based fiber mats containing 10 wt.% additives were produced via the electrospinning technique in a Fluidnatek LE-500 (Bioinicia S.L.). The mats were characterized by SEM, DSC, TGA, ATR-FTIR, simultaneous Synchrotron WAXS and SAXS, and mechanical properties over a 7-day aging period.

Results and conclusions

All samples produced macroscopically consistent, self-supporting, and handleable non-woven material sheets. The DES-containing PHBV showed thinner, bead-free but with a rugose surface morphology. DSC results indicated that glycerol, ATBC, and Gly:NaCitrate (DES) exhibited the highest reduction in melting temperatures, with a notable 5.6 °C decrease for the mat containing Gly:NaCitrate. Interestingly, DES containing electrospun PHBV fibers revealed a larger quantity of ß-form planar zigzag chain conformations, so-called ß-form crystals. Tensile test results revealed that depending on the additive formulation, the mechanical performance of the samples was fundamentally different from each other. Among DES, PHBV fiber mats with ChCl-based DES were excessively brittle. Surprisingly and interestingly, Gly:NaCitrate containing PHBV fiber mats exhibited an unreported significant increase in all mechanical properties, including modulus, elongation at break and toughness. Overall, the study highlights the potential of DES as unique additives to tailor the mechanical properties of electrospun PHBV materials.

Acknowledgments

This research was funded by the Spanish Ministry of Science and Innovation (MICI) (project PID2021-128749OB-C31). The authors would like to acknowledge the Polymer Technology joint unit UJI-IATA-CSIC, ALBA project. Mr. Basar would like to also acknowledge the MICI for his Grisolía Grant (GRISOLIA/2020/019).

GENERATION OF POLYMER BLENDS CASTED FROM POLY(STYRENE-CO-ACRYLONITRILE) CORE/ ACRYLIC SHELL LATEXES

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Introduction

The use of paper instead of plastic has received renewed interest in packaging field. Acrylic latexes offer an easy solution to modify paper surface to improve its properties. A suitable method to tailor them is by controlling the particle composition and morphology. This study focuses on the synthesis and characterization of core-shell latexes composed of a poly(styrene-co-acrylonitrile) (SAN) core and an acrylic shell, produced via seeded semi-batch emulsion polymerization. Due to the high glass transition temperature of SAN, its particles remain unmodified and dispersed within the coalesced acrylic matrix after water evaporation. To optimize these latexes, we synthesized various core-to-shell ratios, ranging from 35% to 65% by weight of the core, and modified the shell with different amounts of butyl acrylate.

Methodology

Characterization of the core, core-shell particles, and final polymer blends was conducted using dynamic light scattering (DLS), infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and electron microscopy (TEM and SEM). Mechanical properties were evaluated through tensile strength testing, while permeability was measured using a water vapor transmission rate tester.

Results and conclusions

Core and core-shell latexes were obtained with a high yield (> 98%). Core particles, analysed either by TEM and SEM, exhibited a spherical and uniform shape. In contrast, core-shell particles showed a lobed structure, attributed to the hydrophilicity difference between the two phases [1]. Increasing the amount of butyl acrylate in the shell phase enabled the production of homogeneous coatings at lower temperature [2]. The increased concentration of core in the final polymer blend made them more rigid, increasing Young's modulus, ultimate tensile strength and decreasing the elongation at break. TGA analysis revealed a slight increase in thermal stability with an increased ratio of core particles. Cross-section SEM micrograph of coated paper with this core-shell latexes showed the dispersion of core within the acrylic matrix (Figure 1).

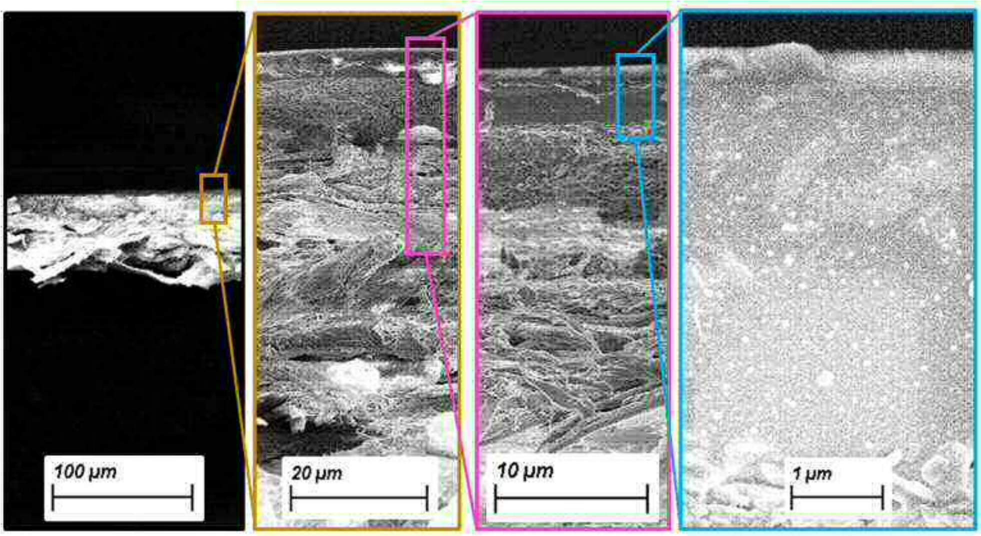

Figure 1: Cross-section SEM micrograph of coated paper with core-shell latex, where core particles remain dispersed within the acrylic phase.

The findings from this analysis offer valuable insights into the relationship between core-shell structure and polymer blend properties, potentially advancing high-performance acrylic latexes for coatings.

Acknowledgments

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EXPLOITING THE BASE-TRIGGERED THIOL/VINYL-ETHER ADDITION TO PREPARE WELL-DEFINED NANOPHASE SEPARATED THERMO-SWITCHABLE ADHESIVES

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Introduction

Pressure-sensitive adhesives with reversible activation via stimuli are crucial, but their production faces challenges due to complex chemical processes. This study reveals that vinyl ethers can react with thiols in the presence of a catalytic base, allowing the creation of adhesives with controlled properties. The base-catalyzed thiol-acrylate and thiol-vinyl ether reactions are highly orthogonal, with the acrylate reaction being faster. Thiols and acrylates are used to prevent disulfide formation, then polymerized with vinyl ethers to form a network with superior adhesive properties. These adhesives are thermo-switchable and resistant, with significant industrial potential.

Methodology

In this study, we explore 3 different systems, Thiol-ene/FRP, Thiol-Michael/FRP and Thiol-Michael/-ene. The first system was developed using a mixture of diacrylates and dithiols, that were photocured to obtain a crosslinked network. The second formulation was developed using a two-step polymerization, being the first one a base catalyzed Thiol-Michael reaction between diacrylates and dithiols, followed by a photocuring with a triacrylate corsslinker. The last system was performed by a sequential base catalyzed Thiol-Michael reaction between diacrylates/divinyl ethers and dithiols mixture, followed by a photocuring of the therminal divinyl ethers with trithiols, obtaining a corsslinked network. Thermal properties, phase separation behaviour, adhesion properties and dynamicity were studied for these systems.

Results and conclusions

Thiol-ene chemistry often faces issues with side reactions under uncontrolled conditions. This article elucidates a base-triggered room temperature Thiol-Michael reaction between acrylates and thiols, allowing high spatial and temporal control. It demonstrates slower vinyl-ether reactions compared to acrylates, leading to a well defined microstructure. The Thiol-Michael/-ene strategy achieves low crosslinking density, better phase separation, and higher stability, enabling scalable, industrially viable production without any protection. These adhesives also are thermally reversible, due to the thiol-acrylate bonds, allowing a better adhesion upon a previous annhealing.

Acknowledgments

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ENHANCED PHOTOCATALYTIC NOX REMOVAL USING CELLULOSE PAPER FILLED WITH ZINC OXIDE AND CALCIUM CARBONATE

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2. *IVL Swedish Environmental Research Institute, Stockholm, Sweden*
3. *RISE, Research Institute of Swede, Kista, Sweden*

Introduction

This innovative technique utilizes filled paper infused with basic ($CaCO_3$) and catalytic zinc oxide (ZnO) particles to clean indoor air. Using low-cost LED lamps emitting UV-B light at 365 nm, nitrogen dioxide (NO_2) can be converted into nitric acid (HNO_3), which then reacts with calcium carbonate to form nonpoisonous calcium nitrate. Integrating these LED lamps and filled papers into room lamps and curtains offers an aesthetically pleasing solution for NOx reduction.

Methodology

Trials at IVL, with a custom setup by Rise, involved a 120 cm long, 5 cm diameter plastic tube. Key components included: Cellulose Composite Papers: Manufactured on a pilot plant machine with up to 45 wt% ZnO-Ts, the paper was filled along the tube's inner walls, serving as the photocatalyst for NOx abatement. LED-UVB Lamp: Positioned centrally, it emitted UV-B light at 365 nm, chosen for its effectiveness in activating the photocatalytic process. Cooling System: Integrated to maintain optimal conditions. Carbonate Paper: Produced using a pilot plant paper machine.

Results and conclusions

A gas mixture of 2L/min 8 ppm NO_2 was introduced into the catalytic tube. Test results showed NO_2 could be destroyed by catalytic decomposition at the ZnO surface using UV-B light. Nitric acid, formed during NO_2 decomposition, was reformed into nonpoisonous calcium nitrate with the introduction of carbonate paper. Carbonate also aided in the catalytic decomposition of NO_2. This led to the idea of integrating catalytic paper and LED light into room lamps for air cleaning and using natural sunlight with filled paper curtains. However, concerns regarding potential intermediates from air pollutant decomposition, hazards of UV-B light exposure, and dust particles containing zinc oxide must be addressed. Initial testing with only carbonate paper is suggested. Additionally, exciting applications for UV/ZnO combinations include potential COVID virus inactivation.

Acknowledgments

Acknowledgement This work was conducted within the Swedish Mistra program Terraclean, focusing on novel adsorbent development.

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RATIONAL TAILORING OF STEREOCOMPLEXED PLA-BASED NANOCOMPOSITES FOR POTENTIAL FILM PACKAGING APPLICATIONS

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Introduction

Polylactide (PLA) is a potential candidate for packaging-film applications if one can overcome its brittleness, low thermal stability and poor barrier properties. Stereocomplexation is a promising strategy to modulate the aforementioned properties by annealing at an optimum temperature window and incorporating nanoparticles such as graphene oxide (GO) and/or carbon nanotubes (CNTs).1,2 Herein, we profoundly investigate the effect of nanoparticles, and their hybrid system on the stereocomplexation to answer the remained challenging questions and unveil the mechanisms behind the changes in stereocomplexation kinetics.

Methodology

Poly(L-lactide)/poly(D-lactide) (PLLA/PDLA) stoichiometric unfilled blends and filled nanocomposite (GO, CNT, and 1:1 hybrid at five loading levels) were prepared by a two-step solution mixing-coagulation technique. The samples were prepared by compression molding at 250 ◦C and 50 bars and quenched into ice-water bath. Annealing for unfilled blends was done at 205 ◦C. We comprehensively analyzed the samples using differential scanning calorimetry and thermal gravimetric analysis.

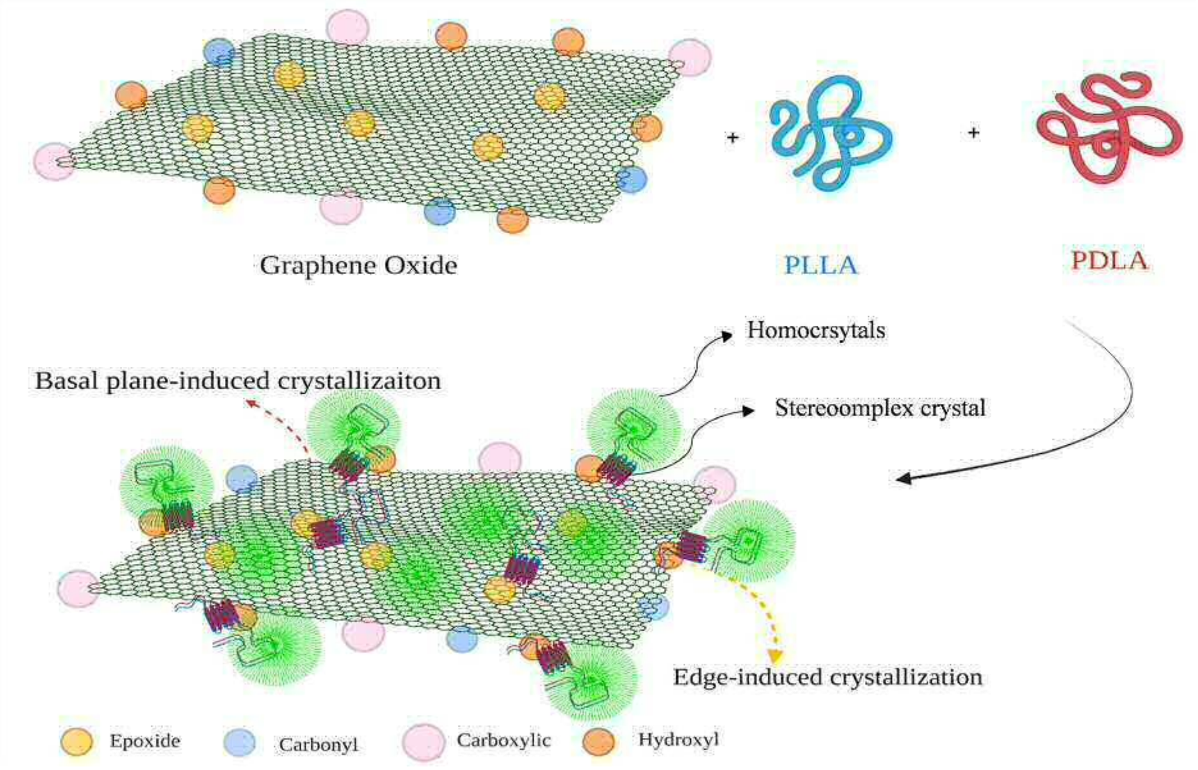

Fig.1 Schematic for the edge- and basal-plane induced stereocomplexation on GO.1

Results and conclusions

We observed that by annealing stereocomplexed PLA (SCPLA), the thermal stability was improved in comparison with PLLA, PDLA, and amorphous SCPLA. We speculate that it was caused by the remaining weakened hydrogen bonds as a result of stereocomplexation. The presence of nanoparticles altered the values of (Rigid amorphous phase fraction) RAFFiller+Crystal. Furthermore, stereocomplexation kinetics and degree were changed due to the dispersion and nucleating capacity of the nanoparticles. Even though the dispersion of CNTs in PLA was worse, the degree of crystallinity was more than that of GO-filled PLA samples. Hybrid samples had almost a similar behavior to that of CNTs, which showed the dominancy of geometry to dispersion quality. We attributed this phenomenon to the distinct filler geometry (2D and tubular), surface oxygen-containing group (Fig.1) density as determining factor and the extent of mutual diffusion and enantiomeric chain configuration on the nanofillers' surface due to the presence of various polar functional groups. We believe that these changes in RAF, the degree of stereocomplexation, and filler dispersion can pave the way for modulating barrier performance.

Acknowledgments

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INNOVATIVE MIXED MATRIX MEMBRANES (MMMS) FOR COST-EFFECTIVE CO2 SEPARATION IN BIOGAS UPGRADING

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Introduction

Biogas – a “green” sustainable gas energy vector that reduces the demand and dependance from fossil fuels – constitutes a potential alternative to significantly reduce the waste and greenhouse gases (GHG) emisions and partially satisfy the world’s insatiable energy demand. As the biogas produced at anaerobic digestion plants is not pure biomethane, CO_2, H_2S and other biogas pollutants produced are all being in need to be removed prior to utilization in order to increase biogas calorific value and reduce corrosion problems, which in turn, enlarge the scope of biogas applications. Within this frame, membrane technology is a competitive methodology due to its decreasing energy consumption, simple and compact engineered modules and small footprint.[1]

The aim of this work is to provide new perspectives to enhance the gas separation membranes development for biogas upgrading by introducing innovative MMMs composed of novel blends of POPs network and polymer matrices, exploiting in synergy the advantages of polymers in mechanical stability, easy processability and low cost, with the strength of dispersed porous networks in terms of gas separation performance.[2]

Methodology

In this study, different POP series have been synthetized via Friedel-Crafts reaction using 1,3,5-triphenylbenzene (TPB) or derivates as starting material and $AlCl_3$ as catalyst. The BET surface areas of the synthetized polymer networks ranged from 900 to 2500 m^2/g. An optimized MMMs fabrication casting protocol has been used, in which PIM-1 has been employed as matrix and the POP networks as fillers in diferent concentrations.

Results and conclusions

Due to the entirely organic nature of POP-based fillers, the interfacial compatibility of the filler – polymer matrix is enhanced and, in addition, the dispersed particles act as scaffolds “freezing” the physical aging and consequently extending the durability of membranes. In terms of gas transport, all the prepared novel MMMs showed enhanced gas permselectivity for CO_2/CH_4 mixtures comparing to the pristine PIM-1, opening new perspectives to develop well-processable, robust, and low-cost high-performance POP-filled MMMs for CO_2/CH_4 mixtures separation of crucial importance in biogas upgrading.

Acknowledgments

This work was supported by Grants TED2021-131170A-100 and CNS2022-135430 funded by MCIN/AEI/10.13039/501100011033 and by European Union NextGenerationEU/PRTR.

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INFRARED SPECTROSCOPY AS A METHODOLOGY TO INVESTIGATE MOLECULAR CONFINEMENT IN POLYMERIC NANOPOROUS MATERIALS

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Introduction

The existence of molecular confinement in nanoporous polymeric samples is a discussion with notable impact that has been opened the past decade. In a previous article [1], the presence of molecular confinement in nanoporous PMMA was studied through a series of analytical techniques, including Differential Scanning Calorimetry (DSC), Raman spectroscopy, and broadband dielectric spectroscopy. This work aims to shed more light on the topic, and lay out an additional way of demonstrating molecular confinement using high-resolution micro ATR spectroscopy.

Methodology

Nanoporous polymeric samples were prepared out of PMMA from different commercial grades and foamed via gas dissolution foaming. Confinement is demonstrated addressing the alterations in both spectral peak areas and peak shifts with changes in pore wall thickness. For this, a new method using Attenuated Total Reflectance (ATR) spectroscopy in microscopic mode is utilized. First, this methodology is compared to previous functional techniques, namely Raman and DSC. Second, utilizing its high resolution, the behavior of bond lengths via peak shifts is evaluated.

Results and conclusions

The spectral analysis through ATR spectroscopy revealed that, as pore walls narrow into below 100 nm, there is an immobilization of polymer chains and group vibrations, being this later caused by a reduction in the molecules' polarizability, result of a shortening in atomic bond lengths. As illustrated in Figure 1, as the wall thickness of the nanoporous material decreases, there is a shift in the peaks corresponding to the symmetric stretching of C-O and C=O, and the antisymmetric stretching of CH_3, all towards higher wavenumbers. This is an indicator of structural changes occurring at molecular level, suggesting a reduction in the bond lengths of these groups. On the other hand, DSC indicates an increase in the glass transition temperature (T_g) as pore wall thickness decreases below 100 nm, suggesting chain enhanced rigidity due to tighter packing with reduced free volume between chains. All these techniques worked together effectively proving confinement in different levels.

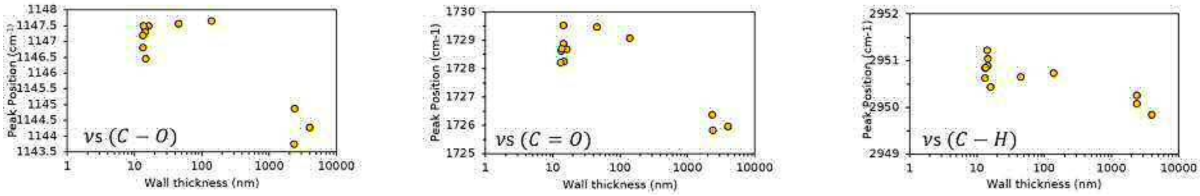

Figure 1. ATR peak shifts for all samples in terms of pore wall thickness, for the symmetric vibration of C-O, the symmetric vibration of C=O, and the antisymmetric vibration of CH_3.

Acknowledgments

Financial assistance from MCIN/AEI/10.13039/501100011033 and the EU NextGenerationEU/PRTR program (PLEC2021-007705), Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04), and Ministerio de Ciencia e Innovación, EU NextGenerationEU/ PRTR program, Regional Government of Castilla y León, and EU-FEDER program “Plan Tractor En Materiales Avanzados Enfocado A Los Sectores Industriales Claves En Castilla Y León: Agroalimentario, Transporte, Energía Y Construcción (MA2TEC)” are gratefully acknowledged.

THE EFFECT OF PEDOT-DBSA NANOPARTICLES ON HYDROGELS FOR VAPOR GENERATION BY SOLAR ACTION

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Introduction

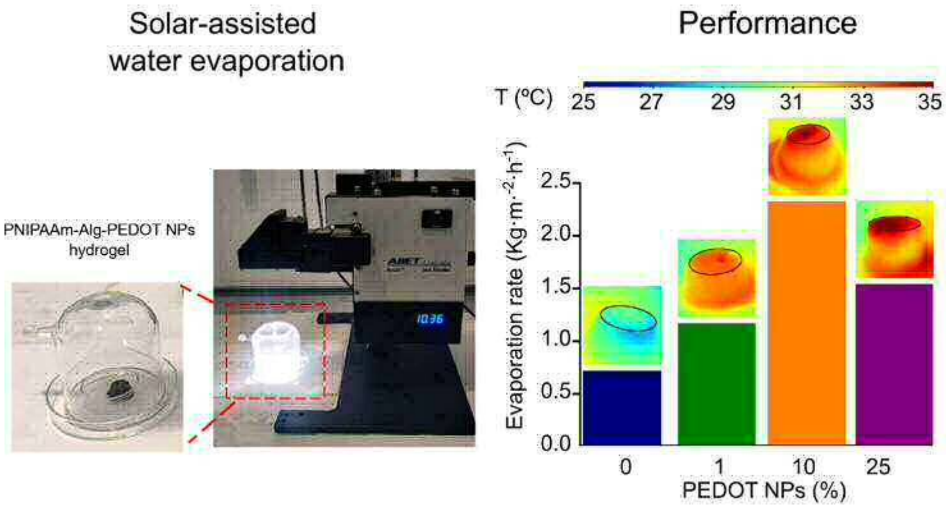
Universal access to clean drinking water is essential for global well-being. However, many challenges persist in guaranteeing access to this resource, especially in the current climate crisis [1]. In response to this problem, the synergistic effect between solar energy and solar absorbent hydrogels (SAH) emerges as a promising perspective to propose a sustainable process to purify brackish water [2]. The present study focuses on the development of a new SAH using the thermosensitive polymer poly(N-isopropyl acrylamide) (PNIPAAm) and alginate (Alg), enriched with conductive nanoparticles of poly(3,4-ethylene dioxythiophene) doped with dodecylbenzene sulfonic acid (PEDOT-DBSA) as an alternative to commercially available PEDOT:PSS suspension [3].

Methodology

In this sense, PEDOT-DBSA nanoparticles were initially synthesized through chemical oxidation. The hydrogels were prepared in two stages: an initial free-radical polymerization for the PNIPAAm monomer and finally an ionic cross-linking stage for the Alg, offering an affordable synthesis in an aqueous solution. The nanoparticles were added in the initial stage at different concentrations. Subsequently, solar-induced evaporation tests were performed on synthetic seawater samples using an artificial sunlight lamp. Likewise, the ratio between free water (FW) and intermediate water (IW) in the hydrogel was determined via Raman spectrometry.

Results and conclusions

The results revealed a notable evaporation rate (2.82 kg·m−2·h−1), corresponding to the lowest value determined for FW/IW inside the gel. The findings of this study support the feasibility and effectiveness of SAHs as a sustainable solution to address the water scarcity crisis, aligning with sustainable development goals. Potential applications of this technology are foreseen, considering at the same time the need for continuous research to improve its performance and scalability.



Solar assisted water evaporation process in a NIPAAm-Alg-PEDOT NPs hydrogel sample and results of the evaporation rate as a function of the PEDOT NPs concentration

Acknowledgments

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INFLUENCIA DE LA RADIACIÓN DE NEUTRONES EN LA MICROESTRUCTURA DE LA CELULOSA EN TEJIDOS DE LINO

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Introducción

El objetivo de este trabajo es analizar las variaciones en la microestructura de la celulosa en muestras de lino moderno irradiadas con neutrones a diversas dosis. Esta investigación forma parte de un proyecto más amplio que busca determinar el efecto de las condiciones medioambientales sobre tejidos de lino, empleando técnicas de análisis no destructivas. Los resultados obtenidos permitirán extrapolar los hallazgos para analizar muestras de lino de alto valor patrimonial. En este estudio se han utilizado las técnicas de RMN en estado sólido y de difracción de rayos X (DRX) para el análisis de las muestras.

Metodología

Las muestras de lino moderno fueron irradiadas en el Reactor de Investigación Lowell Neutron flux de la Universidad de Massachusetts. Las medidas tanto de RMN como de DRX se realizaron en el Instituto de Ciencia y Tecnología de Polímeros del CSIC. Las muestras irradiadas se analizaron mediante C-13 RMN. El grado de cristalinidad se determinó a partir del área de la señal a 89,2 ppm correspondiente al carbono en posición 4, normalizada respecto al del control (no irradiada). En el caso de las medidas de DRX, los difractogramas se obtuvieron situando las muestras en dos direcciones perpendiculares para considerar las variaciones de orientación de las fibras en los tejidos. A partir de los difractogramas, se obtuvieron medidas de cristalinidad y de tamaños aparentes de cristales de la celulosa.

Resultados y Conclusiones

No se han observado modificaciones en la estructura química de la celulosa debido a la radiación de neutrones según los resultados obtenidos mediante RMN y DRX. Sin embargo, en los espectros de C-13 se observa una variación de la fracción cristalina de la muestra con la radiación. Se ha observado un aumento de cristalinidad en torno a una dosis de neutrones de 1.0 1016 n/cm2. Mediante DRX se observan tamaños cristalinos aparentes mucho más pequeños a dosis altas de radiación y variaciones en la cristalinidad. Se presentará una discusión de las variaciones observadas en la microestructura en función de la radiación.

Agradecimientos

Se agradece a Thomas Mc Avoy (University of Maryland, College Park) por la cesión de las muestras irradiadas y a Pedro González Pérez (ICTP-CSIC) por su ayuda con las medidas DRX.

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KINETICS OF EMULSION POLYMERIZATION IN AQUEOUS PHASE USING MICROFLUIDICS

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Introduction

The complete understanding of the fundamentals of emulsion polymerization has been limited by the complexity of the chemical reactions and surface phenomena involved in oil/water systems. A general mechanism of the process is presented in Figure 1, where the primary radicals from the initiator react with the monomer present in the aqueous phase at the solubility limit. Afterwards, the formed oligomers propagate in water and enter into the polymer particles when they become surface active in certain chain-lengths. Then, the polymerization proceeds in the particles until a second radical enter and terminate the reaction. Therefore, the characteristics of the polymer are highly related to the frequency of those radicals entering. The propagation and termination events that take place in aqueous phase are affected by an immense number of variables such as the chemical structure, solubility, ionic force, concentrations, temperature and others. The product of interest remain in the particles, but the aqueous phase plays an important role as source of radicals.

Methodology

On one hand, the study of the kinetics of oligoradicals in the aqueous phase before entry is carried out using a tubular microfluidic reactor. By using short residence times (

Results and conclusions

This work also aims to combine experiments to understand polymerization in the aqueous phase with detailed mathematical modeling of the process. The comparison of molecular weight distributions between the experimental results and the numerical model, suggests three main conclusions: the propagation in aqueous phase is larger than in traditional bulk polymerization, there are significant chain length dependence (CLD) in the propagation and termination steps and finally the type of initiating radical (SO4* or OH*). affects the termination of species due to repulsion forces.

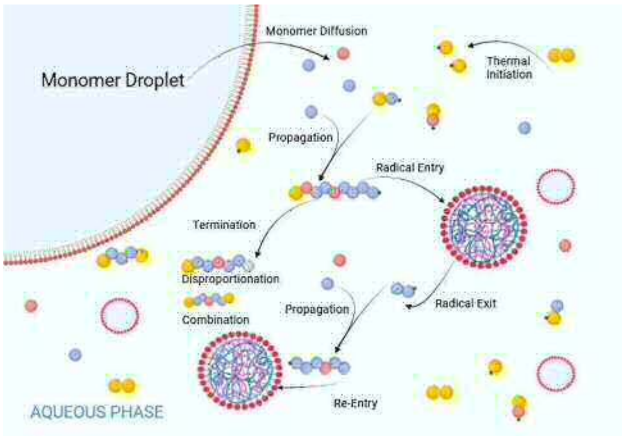

Figure 1. Mechanism of propagation and entry of oligomers in the aqueous phase.

Acknowledgments

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ESTUDIO MOLECULAR Y CONFORMACIONAL DE NUEVOS BIOPOLÍMEROS BACTERIANOS

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Introducción

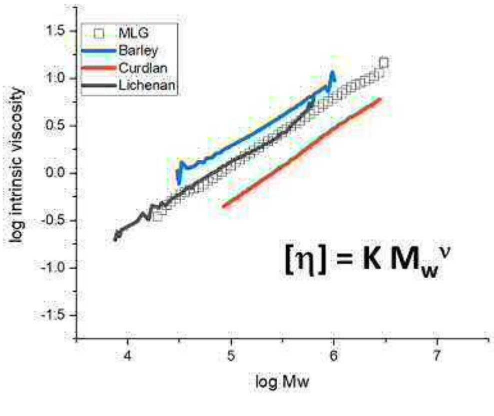
Las bacterias son capaces de producir una amplia gama de biopolímeros con toda una variedad de estructuras químicas y composición dependiendo de la cepa, especie y condiciones de cultivo [1]. Los biopolímeros bacterianos presentan propiedades químicas y reológicas, además de su pureza, que los convierte en materiales de cada vez mayor interés para la industria farmacéutica, alimentaria y química. Poseen, así mismo, ventajas frente a otras fuentes alternativas de obtención de polímeros bio-basados, como plantas o algas, gracias a la estabilidad de su producción bajo condiciones controladas [1]. A pesar de ello, la diversidad de biopolímeros bacterianos está todavía mayoritariamente inexplorada [2]. Desde un punto de vista biotecnológico, los polisacáridos secretados son los de mayor interés, y han demostrado ser aplicables en diferentes sectores industriales como textiles, adhesivos, aditivos alimenticios, detergentes o para tratamiento de vertidos de aceite [3]. Uno ejemplo de polisacárido con potencial para aplicación biotecnológica es el (1-3)(1-4)-β-glucano (*mixed linkage β-glucane*, MLG), identificado recientemente en la bacteria *Sinorhizobium meliloti* tras ser modificada genéticamente [4].

Metodología

Se ha estudiado la naturaleza de este MLG mediante una colección de técnicas de caracterización (FTIR, DSC y GPC/SEC). Las propiedades viscoelásticas de una disolución de polisacárido dependen de la concentración, peso molecular y rigidez de su cadena. Para poder determinar la rigidez de la MLG se ha medido su tamaño hidrodinámico mediante dispersión dinámica de luz (DLS) y se ha usado un sistema de triple detección en el sistema de GPC/SEC para obtener valores de viscosidad intrínseca. Se ha comparado el comportamiento de la MLG con otros polisacáridos que presenten distintas proporciones de enlaces β(1-3) y β(1-4) como curdlan, barley y lichenan; y otros polisacáridos de interés industrial de distinta naturaleza como pullulan, hidroxipropil celulosa y goma arábica.

Resultados y Conclusiones

Los resultados conformacionales apuntan a una gran rigidez de cadena, lo que tiene implicaciones de interés en su uso en aplicaciones biotecnológicas.



Viscosidad intrínseca frente a peso molecular de los polisacáridos MLG (simbolos), Barley (azul), Curdlan (rojo) y Lichenan (gris)

Agradecimientos

PIE202250E035 (CSIC) y TED2021-129640B-I00 (AEI)

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NANOCELLULAR POLYMERS AS A TOOL TO IMPROVE ENERGY EFFICIENCY.

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Introduction

The optimization of energy efficiency is a key objective in sectors such as transport. In order to achieve this, weight reduction and research into lighter materials are being carried out. Cellular polymers are good candidates for this sector, as well as for the construction sector. These are two-phase materials consisting of a solid matrix and a gas phase dispersed in pores. It has been proved that by reducing the cell size to the nanometer scale, the properties of these materials improve due to a double confinement effect occurring in both phases of the material [1]. It has been shown that nanocellular polymers based on high-performance polymers (HPPs) can give rise to materials that, with respect to the starting solid, exhibit reduced densities, improved mechanical properties, high thermal insulation, and even retain transparency. This unique combination of properties makes them suitable candidates for replacing materials in various sectors, thereby reducing weight, and minimizing energy-related issues [1,2].

Methodology

The HPP used was ULTEMTM Resin 1000 - PEI (polyetherimide) provided by SABIC. The nanocellular polyetherimide was fabricated by gas solution foaming. The materials were characterized in terms of solubility, density, structure, and transmittance.

Results and conclusions

By varying the production parameters, a large process window has been found that results in the production of nanocellular PEI with pores in the tens of nanometers range and with different densities, obtaining weight reductions between 15 and 40 %. In addition, these materials exhibit remarkable transparency, reaching in some cases more than 90 % transmittance for the red color (650 nm).

Acknowledgments

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POLY(METHYL)METHACRYLATE-BASED POLYMER OPTICAL FIBERS: CORRELATION BETWEEN PROCESSING-PROPERTY RELATIONSHIP AND LUMINESCENT SOLAR CONCENTRATOR USES

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Introduction

Optical devices based on organic polymeric materials are effective low-cost solutions in the photonic field.1 The growing interest in incorporating functional dopants (organic dyes, quantum dots, metallic clusters) into cylindrical polymer optical fibers (POFs) makes feasible the development of a wide variety of photonic devices (sensors, lasers, solar concentrators). Doped POFs can transmit, by total internal reflection, the absorbed light through their surface to the end of POFs where the photonic cells are and efficiently operate as solar concentrators (LSCs). This work focuses on synthesizing polymeric preforms toward POFs by radical-polymerization and extrusion with poly(methyl) methacrylate (PMMA) as a host material and perylene dye derivatives as active dopants. A comparative analysis of the optical properties, as LSCs, of dye-doped POFs by these two synthesizing methods is performed.

Methodology

The POFs were self-fabricated following a two-step process of preform synthesizing and fiber drawing, using PMMA and four lumogen-dyes (violet, yellow, orange, and red). The preforms were synthesized by extrusion at 165 ºC and by bulk free radical-polymerization (from now on called casting) in a programmable heating oven. A SunLite 11002 solar simulator from Abert Technologies was used to characterize the optical performance of the cylindrical POFs as LSCs.

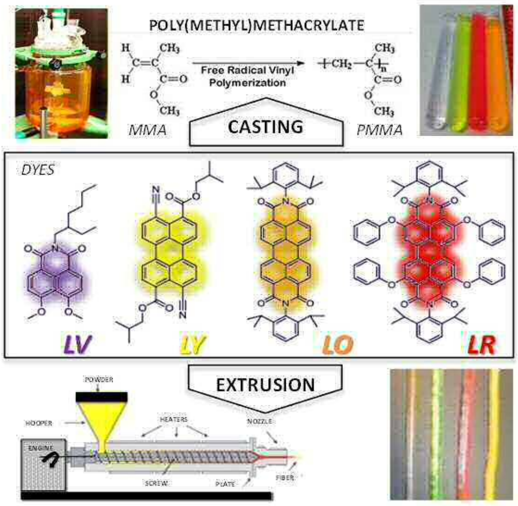

Figure 1. Schematic depiction of the synthetic processes of doped-polymeric optical fibers (POFs).

Results and conclusions

The two types of doped fibers present very similar broad absorption and emission bands within a wide wavelength range, suitable for collecting solar irradiance, with a slight band red-shift and higher intensity for the casting fibers. The output intensities, powers emitted, and optical efficiencies in all fiber samples show that the casting-made fiber with the highest dopant concentration offers the highest values, and the lowest values correspond to the fibers doped with Lumogen violet. The attenuation coefficients also suggest that light scattering is weaker in the fibers made by casting. The slow decays of the output intensity of all the fibers reinforce the high thermal stability of these lumogen-doped fibers. The performance, as LSCs, of the dye-doped fibers fabricated by the casting process is better than by the extrusion process. Therefore, the synthesizing process of the preforms is an important parameter to control the properties of POFs, particularly, their attenuation.

Acknowledgments

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DEVELOPMENT OF FLUORESCENT NANOPARTICLE DOPED-POLYMERIC PREFORMS TOWARD OPTICAL FIBERS FOR SOLAR CONCENTRATORS.

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Introduction

The polymer optical fibers (POFs) present a high interest in the photovoltaic field. Their contribution to the renewable energy, as solar concentrators, makes them a key-block element to be studied. They can be performed in a bulk and coaxial format where their final cylindrical performance facilitates a better light transmission without sun tracking. This work focuses on synthesizing polymeric-preforms with optical capabilities in which both the core and the cladding are made by methacrylate-based copolymers. To optimize the optical performances of the POFs, a subtle hybridization with fluorescent nanoparticles is considered. Manganese-doped zinc sulphide QDs nanocrystals were selected as fluorescent particles.

Methodology

The synthesis of the QDs were performed by solution process at room temperature, in the presence and absence of Mn2+. The polymer matrices were performed by bulk radical polymerization with different comonomeric contribution. The characterisation of the polymeric materials was performed by gel permeation chromatography and differential scanning calorimetry to obtain molecular weight and a glass transition temperature data. The nanoparticle´s characterisation was carried out by TEM, EDS and XRD techniques to determine their distribution, composition and particle size. The optical and fluorescent properties were studied by absorption and fluorescence spectroscopy.

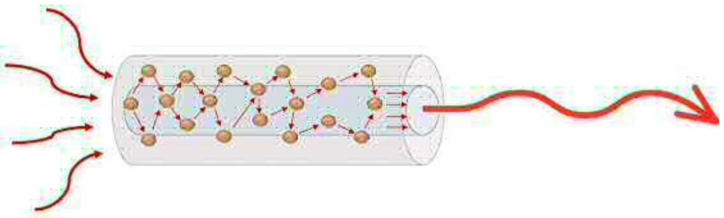

Figure 1. Schematic diagram of the structure of a polymeric optical fiber (POF).

Results and conclusions

The molecular weight values of 100000-120000 g/mol and a glass transition of around 100 °C, were optimized to allow the resulting preforms to be amenable to stretching toward polymer fibers. The QDS size was ~3 nm with maximum excitation and emission wavelengths of 260 nm and 610 nm, respectively. The integration of QDs into the polymeric-matrices exhibited a better performance for the copolymer MMA:HPMA with a composition of 80:20. The resultant preforms based on the methacrylate-derived copolymers are highly resistant to degradation and high temperatures once exposed to solar radiation. They also exhibit a high level of transparency that enables the POFs to have better properties as solar concentrators. Nanoparticles mainly help to enhance the efficiency of optical fibers in the absorption and transmission by total internal reflection, of solar radiation.

Acknowledgments

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NANOCELLULAR POLYSTYRENE AS AN ALTERNATIVE FOR VIP PANEL CORES

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Introduction

Improving the insulation of buildings would significantly reduce the overall energy demand and thus the associated CO2 emissions. Vacuum Insulation Panels (VIPs) are among the materials known as 'super-insulators'. This panel consists of a porous core and an 'envelope' that allows all the air inside the pores to be extracted, drastically reducing the thermal conductivity of the panel. This work explores the possibility of achieving a cheaper, more efficient, stronger and easier to upscale polystyrene-based alternative to the current cores. The purpose of this work is to replace these cores with submicro- or nano-cellular polystyrene manufactured by extrusion foaming. This study will evaluate formulations that can lead to cellular materials with cells in the nanometric scale, low density, and high interconnectivity between pores, three essential requirements for the core of a VIP panel.

Methodology

General purpose polystyrene (Styron 660, Trinseo) was used and SAS triblock copolymer (polystyrene-poly(butyl acrylate)-polystyrene) was added as nucleant. The two materials were blended by extrusion, with copolymer contents ranging from 0.1 to 10 wt.%. The cellular materials have been obtained by two-step gas dissolution foaming in an autoclave using CO2 as the foaming agent. The cell structure of the produced materials was evaluated using Scanning Electron Microscopy (SEM). Density was measured with a balance using the water-displacement method and the open cell content was measured with a gas pycnometer.

Results and conclusions

It was proved that by adding SAS to the polystyrene matrix, pore interconnectivity of almost 100 % can be obtained. Moreover, the cell size is drastically reduced with respect to that obtained with pure polystyrene, reaching diameters of less than 5 µm and even 500 nm with relatively low demanding conditions and very low SAS contents. The densities obtained are in the range of 100 to 400 kg/m3, which is high compared to commercial polystyrene foams but in many cases lower or similar to the cores of the VIP panels currently manufactured.

Acknowledgments

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NEW PHOTOACTIVE REDOX MONOMERS AND POLYMERS FOR ENERGY APPLICATIONS

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Introduction

The growing demand for robust power systems with wireless charging, capacity of communication of the device, and self-healing capabilities, together with the need for improved energy storage, has driven the search for innovative solutions. In this field, our group is developing a new series of organic-based polymeric materials with photochemical and electrochemical activity to enhance battery performance. Our research aims to achieve redox polymers capable of maximizing the power and energy densities, along with other properties such as extending the battery's long-term life. [1]

Methodology

The target molecules are aryl-diene derivatives, whose structures were synthesized by common organic chemistry methodologies; mainly by Friedel-Crafts, Suzuki, and McMurry reactions with or without the assistance of transition metals catalysts. In particular, the crucial step consisted of a homoarene heteroarene coupling to form the dithienylethene moiety. [2] The characterization was made by NMR, UV/Vis measurements, and cyclic voltammetry. [3]

Results and conclusions

A new synthesis route has been found to achieve the new materials possessing dithienylethene groups. The species exhibited photochemical and redox activity when UV radiation and/or current were applied, as was demonstrated by spectral and electrochemical tests.

Acknowledgments

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NEW METHOD FOR POLYMERIC CELLULAR MATERIAL PRODUCTION: ACETONE EFFECTS ON PMMA GEL PRECURSORS

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Introduction

Microcellular polymers are characterized by gas dispersed micro pores within a solid polymer matrix. One of its primary applications is in the insulation industry. Vacuum Insulation Panels (VIPs) are categorized as super insulators. They consist of a gas-tight enclosure surrounding a rigid microcellular polymer core; low densities and interconnected pores (open-cell structure) are mandatory for creating a vacuum inside.

Methodology

This work presents a novel fabrication method for fabricating thick (millimetre-scale) polymeric foams with high open-cell porosity (> 85%) by gas dissolution foaming process [1] using an acetone-PMMA gel [2] as a precursor. Two new methods for incorporating acetone into PMMA are employed: low-content addition and high-content addition. The low-content addition method involves a solvent vapor absorption technique, while the high-content addition method utilizes pulverized PMMA mixed with acetone and agitation in a shaker to achieve a uniform gel. Characterization techniques such as Scanning Electron Microscopy (SEM), rheology of the gel, acetone absorption, and CO2 solubility are utilized to assess the foam and gel precursor properties.

Results and conclusions

The study reveals how varying acetone quantities in the gel precursor results into tailored materials characteristics. It is demonstrated that increasing acetone content leads to lower viscosity gels, resulting in higher solubilities and cell nucleation densities. Using the described new method for fabricating PMMA cellular materials, results in an 80% [3] reduction in fabrication time and energy consumption. This method yields micrometric cell structures and samples with relative densities ranging from 0.2 to 0.45 and open cell percentages ranging from 40-95% with pores connecting the exterior and interior of the samples; making them suitable for VIPs core panels.

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OPTIMIZED ION SELECTIVITY IN NANOFILTRATION MEMBRANES VIA PAH AND PSS LAYER-BY-LAYER SELF-ASSEMBLY

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Introduction

Industrial wastewater management has shifted towards addressing inorganic solvent challenges, crucial in sectors like brine management and water softening. Inorganic scaling, from precipitates like calcium sulfate, hinders treatment systems, making effective pretreatment essential. Nanofiltration (NF) membranes, especially thin film composites, are vital due to their selective removal of multivalent ions while maintaining high permeability for monovalent ions. Positively charged NF membranes offer enhanced performance by reducing fouling and improving ion rejection. This study aims to develop advanced NF membranes using the layer-by-layer (LBL) technique, optimizing their structure and functionality to better manage scaling and improve selectivity, marking a significant advancement in membrane technology for wastewater treatment.

Methodology

The layer-by-layer (LBL) deposition method is a straightforward and widely applicable approach for modifying NF membranes. It provides precise nanoscale control over film thickness, making it ideal for membrane separation applications. In this study, poly(diallyl dimethylammonium chloride) (PDADMAC) and poly(allylamine hydrochloride) (PAH) were used as polycations, while poly(sodium 4-styrene sulfonate) (PSS) served as the polyanion. Various membrane configurations, ranging from 1.5 to 6.5 bilayers, were thoroughly characterized using advanced techniques like ATR-FTIR, contact angle analysis, AFM, FE-SEM, and Raman spectroscopy. These membranes were then tested in a laboratory-scale nanofiltration pilot plant to determine their selectivity and permeability.

Results and conclusions

The ATR-FTIR spectra of the modified membranes revealed additional peaks at 1039 and 922 cm-1, indicative of sulfonate and C-N stretching bonds from the polyelectrolytes, confirming successful coating. Detailed analysis of these findings was compared with the post-experiment permeability measurements. The membrane with 5.5 bilayers showed notably superior performance, with enhanced retention and selectivity. It demonstrated a significant improvement, over 10%, in rejecting divalent ions like Ca2+ and Mg2+, while also doubling the selectivity factor compared to the unmodified membrane.

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FOUR-DIMENSIONAL PRINTED LIQUID CRYSTAL ELASTOMER PHOTOACTUATORS REPROGRAMMED BY MEANS OF LIGHT-REVERSIBLE PERYLENE DIIMIDE RADICALS

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Introduction

Reconfigurable soft actuators exhibit great potential for adaptive robotic functionalities, due to their ability to morph into various 3D shapes under the same stimulus. One of the most popular stimuli in this sense is UV light, as in the case of liquid crystalline crosslinked materials that base their implementation on azobenzene chromophores. However, this wavelength can potentially damage the device and its surroundings, particularly in the presence of living cells.

Methodology

In this presentation, we introduce an innovative ink whose formulation contains a green-absorbing perylene diimide chromophore, leading to light-activated liquid crystalline elastomer (LCE) actuators through direct ink writing. In this system, green light irradiation of the LCE actuators not only triggers photothermal actuation but also generates new absorption bands in the far-red and near-infrared regions, attributed to the formation of radical species.

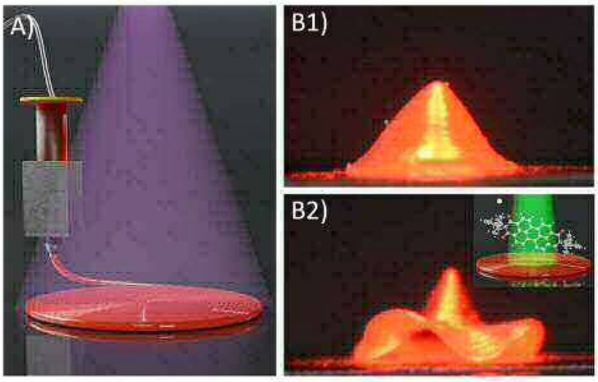

Figure 1: A) Conceptual representation of the 4D printing process of a spiral-like actuator. B) Actuation of the spiral-like actuator under far-red light in its unprogrammed (B1) and its programmed (B2) state.

Results and conclusions

The exposure to the latter wavelength (far-red) causes mechanical actuation and, advantageously, restores the original absorption spectrum. The reconfigurable system facilitates complex deformation modes by simply stimulating the element with uniform far-red light, without requiring any structural modification of the actuator. This material strategy, employing green and far-red light, which is less harmful than ultraviolet light, holds considerable promise for the future development of reconfigurable actuators for biomedical applications.

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OPTIMISATION OF PICKERING PHASE CHANGE EMULSIONS BASED ON PEG400/D-LIMONENE/SIO2 NANOPARTICLES

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Introduction

In pursuit of the development of cutting-edge energy storage technologies, aimed at promoting the energy transition towards a more sustainable energy supply, the implementation of those techniques comprising the utilization of Phase Change Materials (PCM) dispersed in a continuous phase, resulting in the well-known Phase Change Emulsions (PCE), has rapidly emerged [1-2]. These complex systems, characterised by a remarkable thermal energy storage capacity via the solid-liquid phase transition of the PCM, typically include water as one of their main components. Consequently, the application of these PCEs at extreme temperature conditions exhibits inherent limitations [3]. Therefore, this study aims to develop a series of oil-in-oil PCEs for effective cold thermal energy storage, using polyethylene glycol 400 as the dispersed PCM, D-limonene as the continuous phase, and surface-modified fumed silica nanoparticles as the Pickering emulsifying nanoparticles.

Methodology

The prepared PCEs were characterised through differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermal conductivity measurements, as well as through rheological experiments, laser diffraction, and optical microscopy. Bearing in mind that this research focused on the assessment of the SiO2:PEG400 ratio impact on the ultimate mechanical, thermal, and structural properties, such weight ratio was sensibly modified from 0.01 to 0.5.

Results and conclusions

Results indicate that the prepared PCEs demonstrated suitable thermal and mechanical stability. However, their heat transfer properties are compromised, particularly at high silica nanoparticle loads. Despite a thickening effect observed with the addition of the emulsifying agent, the resulting emulsions exhibit promising flow and thermal properties, making them worthy candidates for cold energy storage applications.

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NATURAL POLYMER-BASED HYDROGELS AS INJECTABLE SEMI-SOLID ELECTRODES FOR SUSTAINABLE BATTERIES

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Introduction

Batteries are a fundamental technology to drive the transition towards sustainability, boost green transportation, reduce the carbon footprint, and promote the goal of achieving climate neutrality.. They are employed for a plethora of applications ranging from vehicles, mobile phones, or home appliances up to medical devices such as human recording electrodes and biosensors. In this regard, 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. Nevertheless, the environmental impact of the usage of conventional batteries is a major concern and the development of sustainable batteries has become a challenge for researchers. 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. 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.

Methodology

Supramolecular hydrogels based on natural polymers, alginate and/or chitosan, crosslinked with potassium chloride were employed as matrixes to embed carbon black and Prussian blue giving rise to injectable electrodes. The hydrogel formation was confirmed by inverted tube tests and the chemical interactions were determined by infrared spectroscopy. The injectability properties were assessed by syringe injection tests and rheological characterization. Ionic and electronic conductivity measurements were also performed.

Results and conclusions

Among different hydrogel formulations studied, those made of alginate as polymer matrix presented the best injectability properties, as well as good ionic and electronic conductivities. It was observed that the storage and loss moduli were directly proportional to the polymer concentration. Dynamic strain-stress tests probed the injectability properties of the alginate-based hydrogels. The modulation of the Prussian blue concentration, from 0.17 to 10 mg/mL, allowed us to tune the conductive properties and the final applications moving from condensers to batteries. In addition, the resulting hydrogels exhibited good thermal, mechanical, and electrochemical stability over 1-month to be used as semi-solid electrodes.

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DEVELOPMENT OF ESTER-AMIDE COPOLYMERS FOR APPLICATIONS AS ELECTROLYTES IN SOLID-STATE BATTERIES

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Introduction

In response to the increasing demand for electrical devices and energy storage systems, materials that can improve batteries in terms of high energy density, long life, stability and safety are being actively sought.[1] In this context, solid polymer electrolytes (SPEs) are emerging as a promising solution due to their advantages in mechanical strength, thermal tolerance and electrochemical stability.[2] Our research focuses on the development of SPEs using polyester-amides based on non- contaminating compounds, such as polylactic acid. The goal is to implement these materials in solid-state batteries to achieve more efficient, safer, and less polluting systems.

Methodology

In this study, polyester-amides (PEAs) based on amino acids and L-lactic acid (L-LA) are being prepared by an interfacial polymerization process. For this purpose, a diamine derivative of amino acids and a diacyl chloride derived from L-LA oligomers were used. The monomeric units were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and elemental microanalysis techniques.

Results and conclusions

The synthesis of diamines from α-amino acids involves several steps of protection/deprotection of the functional groups, which makes it a complicated process.[3] In our approach, we succeeded in obtaining a new diamine monomer in a simpler and more direct way using the Fischer esterification method in the presence of p-toluene sulfonic acid monohydrate, a widely used technique for the synthesis of this type of monomers.

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NOVEL -CF3 FREE LITHIUM SALT FOR SEI IMPROVEMENT IN POLYMER ELECTROLYTES

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Introduction

New generation of batteries are envisioned to meet the energy density requirements of today´s industry. While lithium-ion batteries (LIBs) have undergone extensive study over the years, lithium metal batteries (LMBs) are emerging as a promising alternative due to the high theoretical specific capacity (3860 $mAh\cdot g^{-1}$) of the Li^0 anode.[1] Owing to the high reactivity of Li^0 anode, the rational design of the electrolyte becomes a critical step. On this regard, solid polymer electrolytes (SPE) offer advantages over liquid counterparts by mitigating issues such as lithium dendrite growth and flammability concerns.[2] Poly(ethylene oxide) (PEO)/ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), the most employed SPE, presents temperature stability, flexibility and high ionic conductivity above the melting temperature of the polymer; however, it still has some drawbacks such as poor Li electrode compatibility, and low Li-ion conductivities.[3] Hence, the development of new electrolyte materials is needed to overcome these issues. In this work, a novel -CF_3 free lithium salt has been synthesized with the aim of forming a stable and homogeneous SEI to prevent the dendritic growth

Methodology

Self-standing and flexible SPEs based on this new salt and PEO were prepared by solvent casting method. Thermal and electrochemical characterization have been carried out with promising results.

Results and conclusions

Its degradation temperature is well above the operating temperature and it exhibits ionic conductivity of $6.5\cdot10^{-4}$ $S\cdot cm^{-1}$ at 70 ºC which is a value similar to those reported for other lithium salts and PEO blends (LiFSI/PEO, LiDFSI/PEO, etc.). Moreover, it shows stable profiles during cycling at 70 ºC and at a current density of 0.1 $mAh\cdot cm^{-2}$ for more than 400 hours demonstrating a high compatibility of the electrolyte with the lithium metal anode. In addition, $LiFePO_4$-based (LFP) cathodes have been prepared using the new salt and PEO as binder. LFP|| Li^0 cells were cycled at 70 °C and C/10, showing capacities of ≈160 $mAh\cdot g^{-1}$ for more than 100 cycles indicating its high resistance to dendrite formation. This study demonstrates the potential of this novel salt for being used in LMBs

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FORMULATION OF WATER-BASED POLYMERIC ELECTROLYTES FOR CO_2 ELECTROCHEMICAL CAPTURE

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Introduction

In this communication the results derived from the study of the macro/molecular and electrochemical properties of a low-cost polymeric electrolyte with the final objective of CO2 capture will be presented. The electrolyte is composed of polyethylenglycol (PEG) of variable molecular mass, water, a salt support and quinone (Q) as an alternative medium to those currently used for this purpose (1).

Methodology

We will first show the study of different polymer-H2O mixtures with and without CO2 by differential scanning calorimetry (DSC), proton nuclear magnetic resonance (1H-NMR) and their electrochemical stability by Linear Sweep Voltammetry. Subsequently, were studied by cyclic Voltammetry on a three electrode-configuration electrochemical cell. The first electrochemical capture experiments of the electrolyte with and without quinone will be performed by Galvanostatic cycling with potential limitation on a symmetric two electrode cell with a pressure sensor that allows us to see the variation of the gas interacting with the electrolyte.

Results and conclusions

The DSC results of the PEG-H2O mixtures showed a decrease in the melting temperature (Tm) and an increase in the crystallization temperature (Tc) of the polymer in the compositions with higher water content due to an increase in the mobility of the polymer chains, when CO2 is introduced the Tm increases and Tc decreases in all compositions due to a higher rigidity of the polymer chains This fact was also confirmed by 1H-NMR, observing a decrease in the chemical displacement values of the proton corresponding to the hydroxyl functional group of the polymer in the presence of CO2. The electrochemical stability of the PEG and H2O mixtures confirms that it is higher in the compositions with a lower percentage of water, reaching grat potential window. Finally, although these are preliminary results, we can confirm the impact of the electrochemical protocol used in the study, such as: the composition of the electrolyte, the applied current, the voltage window and the residence time on the pressure variation during the oxidation and reduction processes at constant current in the CO2 electrochemical capture cell

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SINGLE-ION CONDUCTING POLYMER NANOPARTICLES FOR SOLID-STATE ELECTROLYTES.

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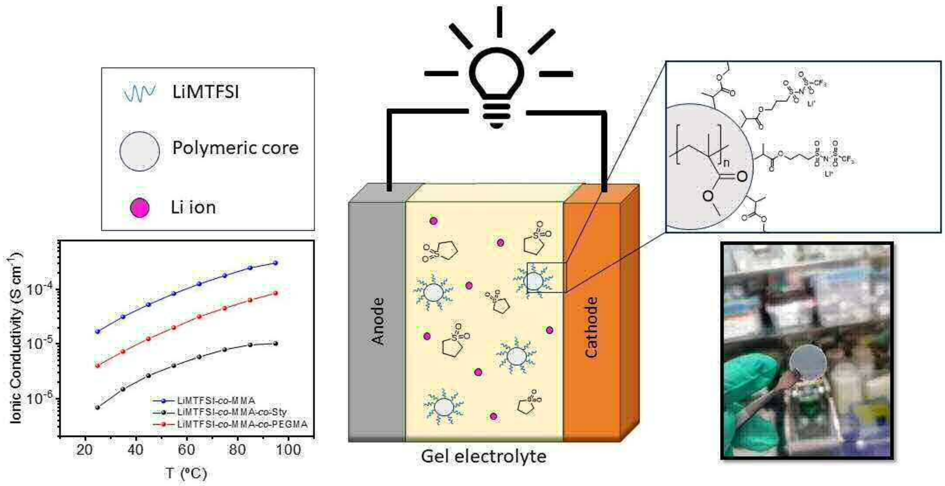
Introduction

Solid-state batteries(SSBs) have gained significant attention due to the increasing energy demands and the limitations of liquid-state batteries (LSBs), such as leakage and flammability. SSBs utilize a solid-state electrolyte, which enhances safety and durability. Among the various types of solid electrolytes, single-ion gel polymer electrolytes (SIGPEs) have garnered attention due to their high lithium transference number (TLi+

Methodology

In this study, we present a novel approach for synthesizing 20 nm single-ion polymer nanoparticles via emulsion polymerization tailored for SSB applications. The nanoparticles are designed to serve in solid polymer electrolytes, providing high ionic conductivity and mechanical stability.



Results and conclusions

Comparative studies evaluated the effect of the different synthesized nanoparticles on these sulfolane-based electrolytes. Preliminary results demonstrate promising properties such as high ionic conductivity and excellent electrochemical stability, making them promising candidates for integration into next-generation SSBs. This work not only introduces efficient and scalable approaches for fabricating advanced materials crucial for the advancement of solid-state battery technology but also provides insights into the performance of these materials by comparing the addition of the different monomers into the copolymer nanoparticle formulation. Moreover, the potential application of these nanoparticles as components of single-ion gel polymer electrolytes is discussed.

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ION TRANSPORT PROPERTIES IN SULFONATED POLYMER MEMBRANES FOR BATTERIES

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Introduction

Ion exchange membranes (IEM) are key components of redox flow batteries (RFB). These systems that act as separators between electrolyte compartments must possess high conductivity and selectivity, while minimizing the crossover of redox species. However, commercial membranes, such as Nafion®, face low selectivity and high costs, compromising both performance and economic feasibility. To overcome these limitations, ongoing research focuses on the development of fluorine-free materials that allow an excellent charge balance and high-capacity retention rates[1]. In this context, sulfonated linear polymeric membranes have been proposed as cation exchange membranes [2], wherein the hydrophilic groups (SO3H) favour the formation of water channels that enhance ion transport through the membrane.

Methodology

Polymer precursor was synthesized from isatin and biphenyl via a superacid catalysed polyhydroxylakylation reaction [3], followed by a modification reaction of the isatin moiety with propanesultone. Polymer membranes were obtained by casting. Permeability and conductivity were assessed through ion diffusion and electrochemical impedance spectroscopy, also galvanostatic cycling limited potential (GCLP) was performed in symmetric flow cells. In-line benchtop NMR studies were performed in order to follow the transport of different ionic species through the membranes.

Results and conclusions

Membrane having alkyl sulfonated groups exhibited high permeability to small cations (e.g. Li+: 1,4·10-7 cm2/s), and reduced crossover to active molecules (e.g. K4Fe(CN)6: 8·10-12 cm2/s). Moreover, they improved ionic conductivity relative to non-sulfonated precursors. Their performance in GCLP for the lithium ferro/ferricyanide redox pair achieved a maximum capacity of 80 mA·h/g at 10 mA/cm2. Their low cost and the promising results observed make these sulfonated materials potential RFB candidates.

Acknowledgments

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NOVEL SINGLE-ION CONDUCTING POLYMER ELECTROLYTES WITH HIGH TOUGHNESS AND HIGH RESISTANCE AGAINST LITHIUM DENDRITES

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Introduction

Ensuring that new generation batteries fulfill the demands of today's industry in terms of energy density is essential. One promising alternative implies the use of lithium metal as anode material owing to its high specific capacity (3860 mAh·g−1). However, employing lithium metal as anode material requires moving to solid-state electrolytes, such as polymer electrolytes (PE), due to their incompatibility with highly flammable liquid electrolytes (LE).1 Solid-state polymer electrolytes (SPE) are considered as an alternative to classic LEs. The use of these electrolytes could eliminate the safety issues presented by LEs due to their lower flammability and superior mechanical strength and adhesive properties that could prevent the formation of dendrites. Most SPEs are based on a lithium salt dissolved in a high molecular weight polymer matrix where both the lithium cation and the anionic counterpart are mobile, forming dual-ion conducting polymer electrolytes. With respect to common dual-ion conductors, single-ion conducting polymer electrolytes (SIC-PEs), which have the anion covalently grafted in a polymer backbone and were only the cation is mobile, are less affected by lithium dendrites growth and thus are particularly interesting SPE.2

Methodology

In this work, novel SIC-PEs are developed, based on an ionomer having poly(ethylene-alt-maleimide) backbone and lithium phenylsulfonyl(trifluoromethanesulfonyl)imide pendant moieties, further blended with poly(ethylene oxide) (PEO) and poly(ethylene glycol) dimethyl ether (PEGDME).

Results and conclusions

These SIC-PEs exhibit ionic conductivity around ~7·10−6 S cm−1 at 70 °C, lithium transference number close to unity and a really high resistance against lithium dendrites growth, by cycling for more than 1200 hours in Li° symmetric cells at a current density of 0.1 mA cm−2 (Fig.1a). Additionally, the electrolytes exhibit excellent mechanical properties as shown in Fig.1b, with fracture toughness over 30 J cm−3. LiFePO4||Li° cells with these SIC-PEs were cycled at 70 °C and C/10, showing initial capacity of almost 160 mAh g−1 and residual capacity of 45% after 100 cycles (Fig.1c). This study demonstrates the potential of SIC-PE derived from poly(ethylene-alt-maleimide) as promising materials for use as electrolytes or binders in lithium metal polymer batteries.

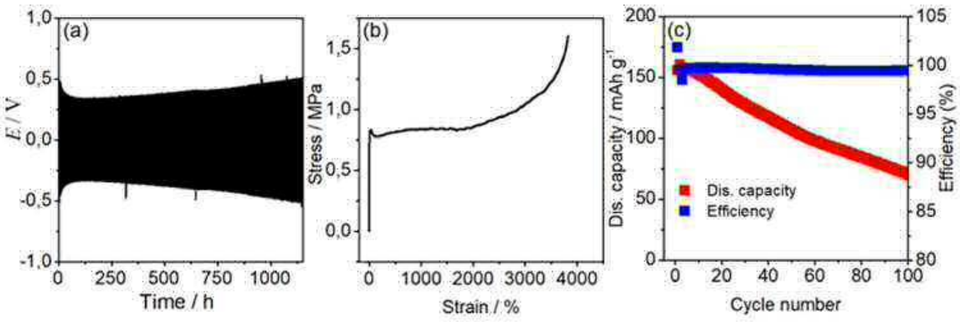

Figure 1: a) Novel SIC-PE-based electrolyte plating and stripping long cycling test in Li°||Li° symmetric cells at 70 °C, b) stress-strain curves for the novel SIC-PE, c) full cell cycling performance of LFP||Li° cell with the novel SIC-PE as electrolyte and catholyte.

Acknowledgments

Polymer Electrolytes for Lithium-Based Batteries: Advances and Prospects. Aid PID2022-143003OB-I00 supported by MICIU/AEI/10.13039/501100011033 and by FSE

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LIGNIN-DERIVED CARBON-BASED ELECTRODES FOR SUSTAINABLE SUPERCAPACITOR PRODUCTION.

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Introduction

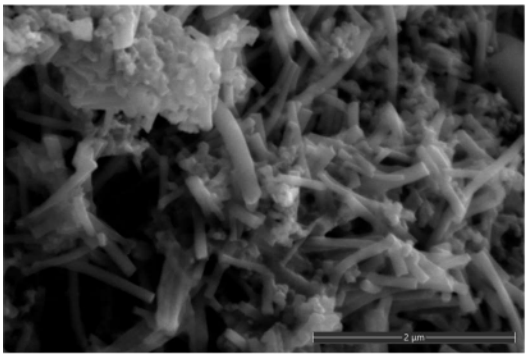
This study explores the potential of utilizing lignin-based carbon nanofibers (LBCNFs) as the main material in the production of electrodes for supercapacitors. Moreover, these electrodes, combined with a previously developed lignin-based thermoelectric material,[1] have the potential to be utilized as ionic thermoelectric supercapacitors (ITESCs) made from clean and sustainable resources which are able to convert temperature gradients into electricity.

Methodology

LBCNFs were produced via electrospinning followed by a thermal stabilization and carbonization process. Thermal stabilization was performed at 280 degrees Celsius for 4 hours, while carbonization was performed at 900 degrees Celsius for 15 minutes. The resulting carbon nanofibers were then mixed with polymers such as carboxymethyl cellulose (CMC) and polyvinylpyrrolidone (PVP) and carbon black to prepare different slurries that are used to produce electrodes on steel plates and nickel foam. The electrochemical measurements were carried out on the prepared electrodes from the lignin-based slurries through cyclic voltammetry and charge-discharge cycles. Additionally, structural characterization of the electrodes was performed through SEM.

Results and conclusions

LBCNFs were successfully incorporated into the slurries, and electrodes were produced from these. The electrodes produced from these lignin-based slurries have shown a marked capacitor behavior, and their performances have been improved through various techniques such as functionalization and activation of the LBCNFs. SEM images of the electrodes revealed the existence of nanofibers homogeneously distributed on the surface of the metal substrates as shown in Figure 1. These results already indicate success in producing electrodes from lignin-based nanofibers, providing the possibility to improve their performance through various techniques. This indicates a successful step towards the goal of combining these electrodes with the aforementioned thermoelectric material in order to produce an ITESC and other energy storage devices made from sustainable resources.



SEM image of a Nickel foam substrate coated with LBCNFs slurry.

Acknowledgments

This work has been developed under the Grant PID2021-124845OA-I00 funded by the MCIN/AEI/10.13039/501100011033 and by the “European Union NextGenerationEU/PRTR”. The authors acknowledged the financial support of the Advanced Materials Program (grant no. MFA/2022/064), supported by the Spanish Ministry of Science and Innovation with funding from the European Union (NextGenerationEU, PRTR-C17.I1) and by the Generalitat Valenciana.

NANOFIBERS OBTAINED FROM LIGNOCELULLOSIC BIOMASS RESIDUE FOR ENERGY APPLICATIONS

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Introduction

As a waste product with few uses to it while at the same time being one of the most abundant biopolymers in nature, lignin is a material which presents many opportunities for research. This study explores the possibility of producing nanofibers from lignin-based precursor solutions through electrospinning. Such nanofibers would be attractive for energy applications due to their high surface area-to-volume ratios and porosity, which can enhance the performance of energy storage devices (1).

Methodology

Lignin nanofibers were prepared through electrospinning of different precursor solutions, focusing on obtaining a variety of water-based and organic solvent-based formulations. The main solid ingredient in the formulations was lignin. Kraft lignin was used in the organic formulations and sulfonate lignin in the water-based formulations. Additionally, different polymers such as polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) were added to aid fiber formation. Characterization of the resulting fibers mats was done through Scanning Electron Microscopy (SEM). Seebeck and electrical conductivity were determined.

Results and conclusions

Several precursor formulations, both water and organic-based, were successfully electrospun into fiber mats. The most successful were water-based lignin-PVA composite nanofibers and organic, dimethylformamide (DMF)-based lignin-PAN composite nanofibers. SEM characterization confirmed that fibers had been successfully produced from the precursor solutions, revealing a tightly knit network of nanofibers in the fiber mats, though no porosity was visualized. Nanofibers have been successfully produced from lignin-based precursor solutions through different formulations, providing an opportunity to create a sustainable material for different applications such as electrodes from a readily available waste product. Additionally, an interesting direction for future research could be to induce porosity in the nanofibers through surface functionalization techniques, thus further increasing their potential for energy applications.

Acknowledgments

Acknowledgements The authors acknowledged the financial support of the Advanced Materials Program (grant no. MFA/2022/064), supported by the Spanish Ministry of Science and Innovation with funding from the European Union (NextGenerationEU, PRTR-C17.I1) and by the Generalitat Valenciana.

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MEMBRANAS DE MATRIZ MIXTA DE POLISULFONA BASADAS EN TRUXENO METILADO PARA PURIFICACIÓN DE H2

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Introducción

El H_2 se está posicionando como alternativa a los combustibles de origen fósil. Sin embargo, el 80% del H_2 se produce a partir del reformado de gas natural, por lo que la separación efectiva de ambos gases es necesaria para conseguir H_2 de alta pureza. Mejoras considerables se han conseguido con membranas de matriz mixta (MMMs) cargadas con polímeros orgánicos porosos (POPs) que ofrecen una mejor compatibilidad con las matrices poliméricas orgánicas. Teniendo en cuenta los excelentes resultados conseguidos por nuestro Grupo con POPs[1,2], en este trabajo nos propusimos utilizar un POP basado en Truxeno metilado (POP-TxMe), que posee una alta superficie específica, y estudiar el efecto de su porosidad en la separación de H_2 de otros gases

Metodología

El truxeno metilado se utilizó como monómero polimerizándose mediante alquilación de Friedel-Craft por síntesis mecanoquímica, un método reciente que no necesita disolventes. Las MMMs se prepararon por casting, añadiendo la cantidad necesaria de POP-TxMe a una solución de polisulfona (PS) en cloroformo con el fin de conseguir membranas con un 20% y 30% de carga (PSPOP-TxMe). La dispersión de la carga se realizó mediante ciclos alternativos de sonicación (10 min) y agitación magnética (20 min). Tras secar las membranas, se caracterizaron y se determinaron las permeabilidades en un equipo de volumen constante diseñado en nuestros laboratorios

Resultados y Conclusiones

El POP-TxMe, obtenido como sólido fino marrón con un rendimiento del 97% presentó elevada área superficial ($S_{BET} = 1076.44\ m^2/g$). El análisis elemental, FTIR y ^{13}C-NMR confirmaron la estructura propuesta en la Figura 1A. Su buena dispersión y compatibilidad en PS se confirmaron por SEM. La presencia de esta carga en las MMMs disminuyó ligeramente la estabilidad térmica a medida que aumentaba su porcentaje en PS, mientras que la interacción polímero-carga no afectaba a la T_g del material.

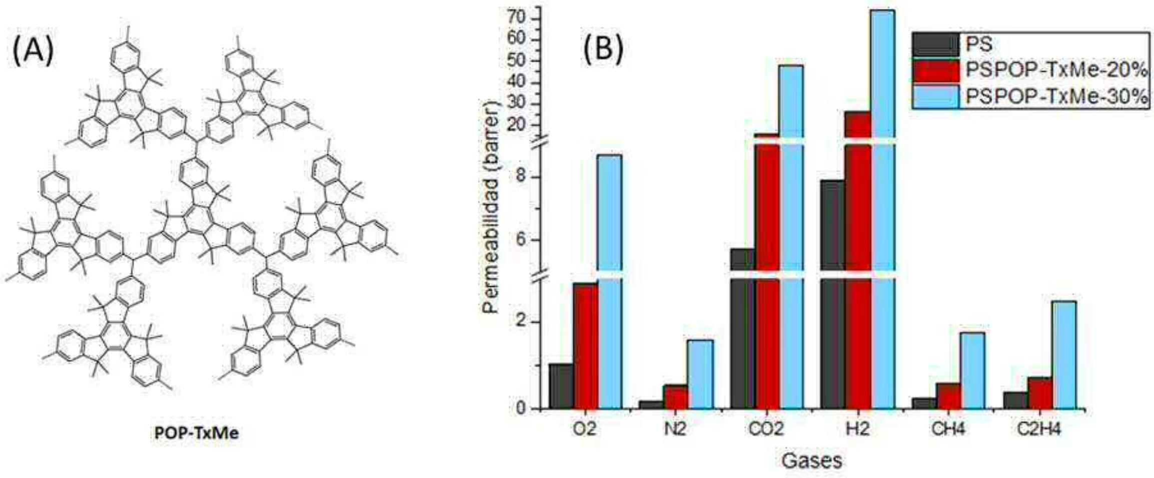

Figura 1. Estructura de la carga (A) y valores de permeabilidad a los gases para las MMMs ensayadas (B)

La permeabilidad aumentó a todos los gases a medida que aumentaba el porcentaje de POP-TxMe añadido (Figura 1B), debido principalmente a un incremento en el coeficiente de solubilidad, atribuido a los poros del POP-TxMe. Además, la selectividad en las separaciones H_2/CH_4 e H_2/C_2H_4 aumentaron un 74% y 40%, respectivamente, lo que les hace materiales muy interesantes para purificación de H_2

Agradecimientos

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REVERSIBLE COLORIMETRIC AND FLUORESCENCE SOLID SENSORS BASED ON ARYL HYDRAZONE DERIVATIVES OF 1,8-NAPHTHALIMIDES FOR CAUSTIC MEDIA AND BIOGENIC AMINE VAPORS

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Introduction

Recently, the development of chemosensors has attracted great attention because of their potential application in different fields, (environmental analytics, medical diagnostics and process control), and their advantages as a tool for sensing analytes, (high sensitivity and selectivity, easy operation, rapid analysis, nondestructive detection, real-time monitoring and cost-effectiveness). A chemosensor is a chemical probe containing photoactive units that teams up with analytes and the interaction is detected by fluorescence changes, or induces a color change which allows the human eye to act as a detector. Naphthalimide derivatives are a type of sensors with thermal, photophysical and electroluminescence properties which can be modulated by including different substituents at the 4 position of the naphthalimide structure. Concerning the target analytes, biogenic amines are of special interest if they can be detected in the vapor phase, since they are related to the food freshness of packaged food. In addition, the development of sensors that work under extreme alkaline conditions is considered necessary, since concentrated strong bases are widely used in many industrial processes that cause pollution and equipment corrosion, and the conventional sensors are generally useful for pH ranges of 1–11. In this work, solid sensors for caustic media and biogenic amine vapors have been developed.

Methodology

Hydrazone derivatives of naphthalimides have been synthesized and anchored to a polymeric membrane obtained by a photopolymerization reaction, which allows the design of polymeric sensors with tailor-made properties as a function of the nature and content of monomers selected. The new naphthalimides and the membranes are evaluated as sensor by determining the change in their absorption and fluorescence properties with pH.

Results and conclusions

The membranes are thermally stable, solid and easily handled to be applied as fluorescence and colorimetric sensors. In basic media, the materials exhibited a strong decrease in their fluorescence intensity. Furthermore, materials are sensitive to trimethylamine vapors through both their absorption and fluorescence bands, and showed a color change from orange to purple. That result is very relevant, since amines are generated through food spoilage and naked-eye detection is a very useful tool for the consumer, as well as for other fields related to food safety and to health and safety at work. Likewise, the polymeric sensors are costless, and as a con-sequence of their solid character and the reversibility of the process, exhibit improved stability and can be reused**.**

Acknowledgments

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EXPLORING STIMULI-RESPONSIVE SINGLE-CHAIN NANOPARTICLES: SYNTHESIS, CHARACTERIZATION, AND SURFACE BEHAVIOR

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Introduction

Interest in stimuli-responsive materials that undergo conformational changes in response to external triggers like light, pH, temperature, etc. has significantly increased in recent years due to their important applications in fields such as nanomedicine, catalysis, and sensing.[1] Our group specialises in the synthesis of Single-Chain Nanoparticles (SCNP) formed by stimuli-responsive monomers. These SCNPs are single polymer chains that fold through intramolecular bonds or interactions, forming globular or sparse nanoparticles.[2]

Methodology

A random copolymer of anthracene (An) and OEGMA (O), PAnO, was synthesised using reversible addition-fragmentation chain-transfer polymerisation (RAFT). Subsequently, SCNPs were prepared by an intramolecular Diels-Alder reaction by using a photoreactor with a 365 nm wavelength. Finally, the formation of the SCNPs was confirmed both in solution and at the air-water interphase via dynamic light scattering (DLS) and atomic force microscopy (AFM), respectively.

Results and conclusions

The synthesised copolymer had the target amount of anthracene (15.9%), confirmed by ^{1}H NMR. The molecular weight for the copolymer was 132.3 kDa with a polydispersity of 1.04 and a hydrodynamic radius of 10.3 nm. Then, the formation of the SCNP was confirmed by UV-Vis and DLS, with the disappearance of the signal around 365 nm and the shrinkage of the SCNP to 6.1 nm, respectively. Finally, the synthetized SCNP were deposited at the air-water interface using a Langmuir trough and studied by AFM. AFM topographical micrographs confirmed the formation of the SCNPs and their transfer to solid substrates.

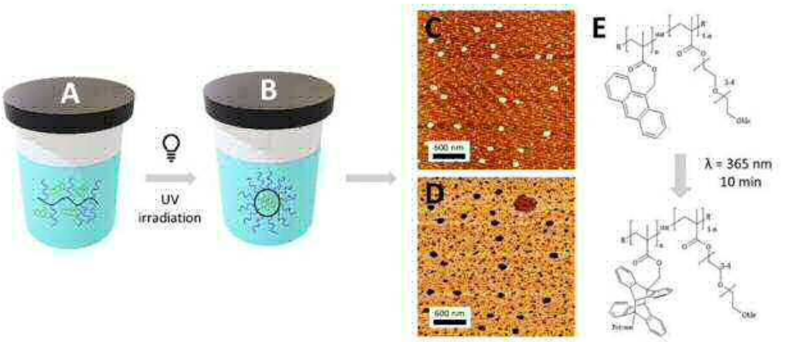

Figure 1. *Schematic representation of the unfolded polymeric chain (A) and SCNP formation under UV irradiation (B). Topography (C) and adhesion (D) AFM images obtained after deposition at the air-water interface. Mechanism of dimer formation (E).*

Acknowledgments

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DESARROLLO DE NUEVOS SISTEMAS DE LIBERACIÓN DE ANTINEOPLÁSICOS BASADOS EN BIOPOLÍMEROS PARA EL TRATAMIENTO DE GLIOBLASTOMA

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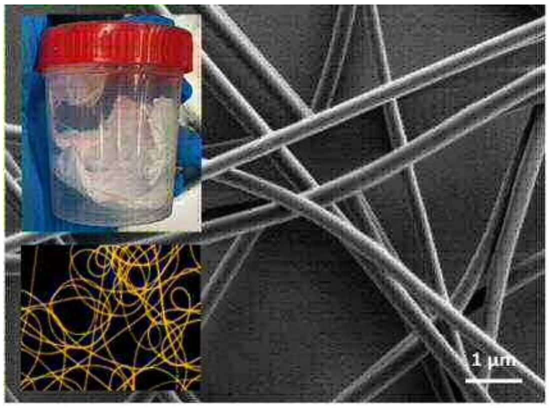
Introducción

El glioblastoma es un tipo de glioma de baja incidencia, pero de alta tasa de mortalidad debido a su malignidad. Los tratamientos actuales se centran en la cirugía seguida por quimioterapia; sin embargo, la administración sistémica de antineoplásicos causa daño en tejidos sanos, por lo que se investiga su administración local y su liberación controlada[1]. Su encapsulación en nanofibras poliméricas puede permitir una liberación controlada y aumentar su biodisponibilidad. En este trabajo se sintetizan nanofibras de poli(metil vinil éter-alt-anhídrido maleico) (PMVEMA), monoetil éster (Es) y ácido (Ac), como sistema de liberación los antineoplásicos carmustina (BCNU) y doxorrubicina (DOX).

Metodología

Para su caracterización morfológica se empleó la microscopía electrónica (FESEM). Por otro lado, se utilizaron técnicas colorimétricas, espectroscopia de infrarrojo, cromatografía líquida (HPLC), espectroscopía UV y microscopía confocal para estudiar la composición de las nanofibras, según las propiedades intrínsecas de los fármacos. Finalmente, se comprobó el efecto antitumoral de los fármacos encapsulados empleando el ensayo colorimétrico de viabilidad celular MTT, en líneas celulares de glioblastoma provenientes de pacientes del Hospital General Universitario de Elche (HGUE-GB).

Resultados y Conclusiones



En el caso de las nanofibras de PMVEMA-Ac/DOX a una concentración de 1:20 (% p/p) respecto al polímero se obtuvieron nanofibras de 311 nm con un 100 % de eficacia de encapsulación (Ver Figura). Por otro lado, las nanofibras de PMVEMA-Es/BCNU a una concentración de 8:25 (% p/p) presentaron un diámetro de 855 nm y una eficacia de encapsulación del 70 %, con un tiempo de liberación máximo de 1 hora, manteniendo la integridad del fármaco en comparación a su estado libre. Finalmente, los fármacos encapsulados disminuyeron la viabilidad de las células de glioblastoma.

La síntesis de nanofibras de PMVEMA mediante electrohilatura permite la encapsulación de doxorrubicina y carmustina, manteniendo sus efectos antitumorales, al disminuir la viabilidad de las líneas celulares HGUE-GB.

Agradecimientos y Referencias/Acknowledgments and References

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