BOOK OF ABSTRACTS

9th International Conference on Bio-Based & Biodegradable Polymers

22-24 JULY 2024
Coimbra

9th International Conference on Bio-based and Biodegradable Polymers

Book of Abstracts

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9th International Conference on Bio-based and Biodegradable Polymers

Welcome to BIOPOL 2024

Dear Participant,

We warmly welcome you to the International Conference on Bio-based and Biodegradable Polymers. This year, the meeting will be held from July 22nd to 24th in the charming and historical city of Coimbra. As the first capital of the Kingdom of Portugal and home to the oldest university in the Portuguese-speaking world (UNESCO World Heritage site since 2013), Coimbra boasts a unique cultural heritage and a vibrant atmosphere as a city of students.

1st and 2nd BIOPOL were organized in Alicante (Spain) in October 2007 and 2009. BIOPOL-2011 was held in Strasbourg (France), BIOPOL-2013 in Rome (Italy), BIOPOL-2015 in Donostia-San Sebastian (Spain), BIOPOL-2017 in Mons (Belgium) and BIOPOL-2019 in Stockholm (Sweden), while the first conference after the COVID-19 pandemics went back to Alicante in November 2022, where the BIOPOL series of conferences was born.

All these previous conferences were successful, with more than 250 researchers from around the world presenting their latest results on this field, indicating the current growing interest for the specific topics addressed.

This year's conference, the 9th in this series, is a special occasion to visit Coimbra. Our aim is to achieve both scientific and social success by bringing together scientists, researchers, and students. We are confident that this environment will foster deep scientific discussions and honor the high-quality contributions that form the basis of the conference program. It is a testament to the scientific vitality of this meeting that many of the presentations are delivered by young scientists. The scientific program covers key areas of Biopolymers, Biodegradable polymers, composites. as well as interdisciplinary topics such as advanced materials, energy and environmental technologies, and food applications.

This meeting will feature one Opening Lecture, two Invited Lectures and seven Keynote Lectures, followed by three parallel sessions with a total of seventy oral communications, aimed at increasing the number of presentations and promoting the diversity of topics and participating institutions. Additionally, two poster sessions will be held.

The success of the previous editions aimed us to organize this 9th edition to be held in Coimbra (Portugal). We look forward to meeting you in Coimbra next July.

Best regards,

The Organizing Committee

FULL PROGRAM

	Monday July 22nd			Tuesday July 23rd			Wednesday July 24th		
9:00 – 9:40	Registration			IL 2			IL 3		
9:40 – 10:10				KL 2			KL 5		
10:10 – 10:40				KL 3			KL 6		
10:40 – 11:20				Coffee Break & Poster Session 1			Coffee Break & Poster Session 2		
11:20 – 11:40				OC9.A	OC9.B	OC9.C	OC17.A	OC17.B	OC18.C
11:40 – 12:00				OC10.A	OC10.B	OC10.C	OC18.A	OC18.B	OC19.C
12:00 – 12:20	Opening Session			OC11.A	OC11.B	OC11.C	OC19.A	OC19.B	OC20.C
12:20 – 12:40	Opening Lecture – IL 1			OC12.A	OC12.B	OC12.C	Poster Session 2		
12:40 – 13:00				OC13.A	OC13.B	OC13.C			
13:00 – 14:30	Lunch			Lunch			Lunch		
14:30 – 14:50	KL 1			KL 4			OC.20.A	OC20.B	OC21.C
14:50 – 15:00							OC.21.A	OC21.B	OC22.C
15:00 – 15:10	OC1.A	OC1.B	OC1.C	OC14.A	OC14.B	OC14.C			
15:10 – 15:20							OC22.A	OC22.B	OC23.C
15:20 – 15:30	OC2.A	OC2.B	OC2.C	OC15.A	OC15.B	OC15.C			
15:30 – 15:40							Closing Lecture - KL 7		
15:40 – 16:00	OC3.A	OC3.B	OC3.C	OC16.A	OC16.B	OC16.C			
16:00 – 16:20	OC4.A	OC4.B	OC4.C			OC17.C	Closure / Biopol 2026 Annoucement		
16:20 – 17:00	Coffee Break			Coffee Break & Poster Session 1					
17:00 – 17:20	OC5.A	OC5.B	OC5.C						
17:20 – 17:40	OC6.A	OC6.B	OC6.C						
17:40 – 18:00	OC7.A	OC7.B	OC7.C						
18:00 – 18:20	OC8.A	OC8.B	OC8.C						
18:20 – 18:30									
18:30 – 19:45	Guided Tour								
19:45 – 20:00	Porto de Honra								
20:00 – 20:30				Conference Dinner / Casa das Caldeiras					
21:00 – 23:00									
23:00 -				Party after dinner					

Monday July 22nd (Morning)

9:00 – 12:00	Registration
12:00 – 12:20	Opening Session
	Chair: Alfonso Jiménez
12:20 – 13:00	Opening Lecture – IL 1: **José M. Kenny**, *Biodegradable polymers, composites and nanocomposites as alternatives to microplastics pollution*
13:00 – 14:30	Lunch

Detailed Scientific Programme, Monday July 22nd (Afternoon)

	Chair: Denise Petri		
14:30 – 15:00	KL 1: **Jalel Labidi**, *Chitin and Chitosan Based Materials*		
	Chair: José M. Kenny	Chair: Luc Averous	Chair: Patrizia Cinelli
15:00 – 15:20	OC1.A: **Fengwei Xie**, *Developing chitosan-based electroconductive inks for cost-effective and versatile 3D printing for EMI shielding and strain-sensing applications*	OC1.B: **Giulia Guidotti**, *Effect of hydrophilicity and stiffness of a PBCE-based copolymer on stem cells' long term culture*	OC1.C: **Catarina Fernandes**, *Synthesis of ecofriendly cationic lignin derivatives for hair cosmetics*
15:20 – 15:40	OC2.A: **Luis Cabedo**, *Studying the biodegradation process to improve bioplastics' end-of-life*	OC2.B: **Antonio J. F. Carvalho**, *Blends of thermoplastic polysaccharides plasticized with deep eutectic solvents*	OC2.C: **Mathie Craquelin**, *Effects of grafted chitosans on the reduction of powdery mildew in wheat*
15:40 – 16:00	OC3.A: **Antonio Greco**, *Crystallization kinetics and mechanical properties of PHB plasticized by commercial and cardanol derivatives*	OC3.B: **Yuya Tachibana**, *Optical properties and recyclability of polycarbosilane containing bio-based bifuran structure*	OC3.C: **Gustave Bertier**, *Abiotic and biotic degradation of PBAT: quantification of generated products by carbon assessment*
16:00 – 16:20	OC4.A: **Stefano Fiori**, *Recent developments on the application of oligomers of lactic acid*	OC4.B: **Cheick Abou Coulibaly**, *Detection and quantification of biodegradable nano and microplastics in biowaste compost*	OC4.C: **Beatriz Almeida**, *Functional properties of hyaluronic acid-like polysaccharide produced by Vibrio sp. Mo245 from glycerol*
16:20 – 17:00	Coffee Break		
	Chair: Nadia Lotti	Chair: Luis Cabedo	Chair: Paulo Abreu
17:00 – 17:20	OC5.A: **Denise F. S. Petri**, *Cetyltrimethylammonium bromide coated kapok fibers for the adsorption of Cr(VI) and bisphenol A*	OC5.B: **Diana C.M. Ribeiro**, *Biobased lubricant from modified vegetable oil: Impact on tribological properties*	OC5.C: **Stephane Serrano**, *High-performance, bio-based, tri-component vitrimer networks based on epoxydized vegetable oils: Control of the network synthesis and morphology*
17:20 – 17:40	OC6.A **Emmanuelle Gastaldi**, *Degradation and environmental assessment of compostable packaging mixed with biowaste in full-scale industrial composting conditions*	OC6.B: **Cristina Mellinas**, *From problem to solution: Bioadsorbents and plasticisers derived from Rugulopteryx Okamurae*	OC6.C: **Allison Vercasson**, *Impact of the individual layers on polymer-coated cardboards properties*
17:40 – 18:00	OC7.A **Beatriz Agostinho**, *Greener recycling of future biobased polymer wastes: PEF and PTF case studies*	OC7.B: **Benedetta Paolino**, *New antifungal encapsulation systems based on HP-β-cyclodextrin, chitosan and essential oils for conservation of organic-media cultural heritage*	OC7.C: **Sandra C.C. Nunes**, *Monte Carlo Simulations for Screening and Optimizing Biopolymer-Based Drug Delivery Systems*
18:00 – 18:20	OC8.A: **Sébastien Livi**, *Ionic Liquids versus Deep Eutectic Solvent: A Tunable Platform for the Design of Biopolymer Blends*	OC8.B: **María José Jiménez**, *Compostable solutions for food packaging aiming at reducing landfill disposal and food waste*	OC8.C: **Zhenjiang Li**, *H-bond donor–Lewis basic anion bifunctional organocatalyst for ring-opening polymerizations*

Detailed Scientific Programme, Tuesday July 23rd (Morning)

	Tuesday July 23rd		
	Chair: Ipsita Roy		
9:00 – 9:40	IL 2: **João F. Mano**, Human-based proteins to engineer a new generation of biomaterials		
9:40 – 10:10	KL 2: **Ana C. Fonseca**, α-Amino acids based poly(ester amides): a myriad of opportunities in the biomedical field		
10:10 – 10:40	KL 3: **Roberto J. Aguado**, Nanocellulose as barrier agent, as binder and as carrier for active compounds in paper-based packaging		
10:40 – 11:20	Coffee Break & Poster Session 1		
	Chair: Jalel Labidi	Chair: Debora Puglia	Chair: António Carvalho
11:20 – 11:40	OC9.A: **José Gámez-Pérez**, *Enhancing the Properties of Biodegradable Polymer Blends Through Compatibilization with Reactive Agents*	OC9.B: **Joana Corrêa Mendes**, *Brown Seaweed Alginate to Develop p53 Encoding pDNA Nanocarriers for Colorectal Therapy*	OC9.C: **Pilar Albaladejo**, *Development of new packaging materials through novel agroindustrial valorization techniques*
11:40 – 12:00	OC10.A: **Carmen S.R. Freire**, *Exploiting polysaccharides for the production of sustainable materials for active food packaging*	OC10.B **Solange Magalhães**, *On the development of novel cellulose derivatives for microplastic flocculation*	OC10.C: **Rafael C. Rebelo**, *Development of Sustainable Cellulose-based Hydrogels for Agriculture*
12:00 – 12:20	OC11.A: **Julio Romero**, *Development of tissue engineering scaffolds based on PLA/PBAT bionanocomposites for bone regeneration using 3D printing coupled with dense CO2 foaming*	OC11.B: **Itziar Otaegi**, *Eggshell powder as potential filler for the manufacture of egg boxes based on PBSA*	OC11.C: **Ignacio Solaberrieta**, *Molecularly imprinted polymers for the selective elimination of aloin from aloe vera skin extracts*
12:20 – 12:40	OC12.A: **Bruno Medronho**, *Probing cellulose-solvent interactions with self-diffusion NMR: Onium hydroxide concentration and co-solvent effects*	OC12.B: **Erfan Oliaei**, *Chemically recyclable cellulosic biocomposites by curing of aliphatic polyester prepolymers*	OC12.C: **Nora Aranburu**, *Improving the toughness of PLA using different industrially scalable strategies*
12:40 – 13:00	OC13.A: **Virginia Venezia**, *Sustainable Active Food Packaging: Incorporation of Humic Substances into Electrospun Films*	OC13.B: **Elona Vasili**, *Processing cellulose by ionic liquid or deep eutectic solvent for potential use in 2D and 3D packaging applications*	OC13.C: **Laia Posada-Quintero**, *Standarization of bacterial nanocellulose production from fique by-products*
13:00 – 14:30	Lunch		

Detailed Scientific Programme, Tuesday July 23rd (Afternoon)

	Chair: João F. Mano		
14:30 – 15:00	KL 4: **Sandra Domenek**, *Critical Insights into the Barrier Performance of Polylactide (PLA) for Sustainable Packaging Applications*		
	Chair: Luis Alves	Chair: Bruno Medronho	Chair: Antonio Greco
15:00 – 15:20	OC14.A: **Joe Kerry**, *Environmentally Friendly Extraction and Characterisation of Pectin from Apple Pomace and Its Validation of Use in Bread Packaging Films*	OC14.B: **Carlos Javier Pelegrín**, *Valorization of horchata by-products as precursors for the isolation of cellulose nanocrystals and antioxidant extracts*	OC14.C: **Cátia S. M. Esteves**, *Polycaprolactone-Based Shell Materials for Microcapsule Applications*
15:20 – 15:30	OC15.A: **Antonella Esposito**, *Critical cooling rate of fast-crystallizing polyesters: The example of poly(alkylene trans-1,4-cyclohexanedicarboxylate)*	OC15.B: **Elena Gabirondo**, *Chemical recycling of polyhydroxybutyrate into high-added value β-Hydroxy acid*	OC15.C: **Simão V. Pandeirada**, *Exploring Innovative Eutectic Systems for Enhanced Recycling of Polyesters Mixed Waste*
15:30 – 15:40			
15:40 – 16:00	OC16.A: **Andreia F. Sousa**, *Sustainable advances in furan-based polymers: From biobased monomers to polymers and recycling*	OC16.B: **Francisco A.G. Soares Silva**, *Development of bio-based paper coatings for food packaging applications*	OC16.C: **Joana F.S. Costa**, *Synthesis of novel polyesters incorporating an ether containing monomer for enhanced biodegradation in soil and water*
16:00 – 16:20			OC17.C: **Yaiza Flores**, *Synthesis of polybutylene succinate using renewable biomass derived monomers*
16:20 – 17:20	Coffee Break & Poster Session 1		

Detailed Scientific Programme, Wednesday July 24th (Morning)

	Chair: María Carmen Garrigós		
9:00 – 9:40	IL 3: **Ipsita Roy**, *Sustainable Polymers for Biomedical Engineering: the way forward for a Net Zero Future*		
9:40 – 10:10	KL 5: **Nadia Lotti**, *Furan-based polymers: An interesting sustainable solution for food packaging*		
10:10 – 10:40	KL 6: **Debora Puglia**, *FURIOUS: Materials, processing and end-of-life opportunities for 2,5-FDCA based polymers*		
10:40 – 11:20	Coffee Break & Poster Session 2		
	Chair: Mário Calvete	Chair: Dina Murtinho	Chair: Sandra Domenek
11:20 – 11:40	OC17.A: **Huixing Cao**, *Non-isocyanate, Bio-Based Covalent Adaptable Networks based on Polyaspartic esters*	OC17.B: **Isabel Lopes**, *Influence of ageing in the ecotoxicity of modified hydroxyethyl cellulose polymers to freshwater biota*	OC18.C: **Gaël Huet**, *Alkaline pretreatment to improve food packagings biodegradation in mesophilic anaerobic digestion*
11:40 – 12:00	OC18.A: **Susana Guzmán-Puyol**, *Upcycling of potato and tomato pomaces for the fabrication of sustainable metal food packaging*	OC18.B: **Charlotte Manoha**, *Effects of sodium sulfite on the rheological behavior of gluten plasticized with glycerol and water*	OC19.C: **Diana Pacheco**, *Harnessing Microalgal Polymers for Cutting-Edge Tissue Engineering Applications*
12:00 – 12:20	OC19.A: **Michelina Soccio**, *Introduction of bark extracts in furan-based polyester for the realization of sustainable active packaging*	OC19.B: **Mariana Ribeiro**, *Hydrogels as promising candidates for the treatment of cutaneous wounds*	OC20.C: **Vinícius de Paula**, *Forging sustainable pathways: advancing chemical recycling techniques to address poly(ethylene 2,5-furandicarboxylate) circularity*
12:20 – 14:30	Poster Session 2 & Lunch		

Detailed Scientific Programme, Wednesday July 24th (Afternoon)

	Chair: Roberto Aguado	Chair: Arménio Serra	Chair: Ana Ribeiro
14:30 – 14:50	OC20.A: **Patrizia Cinelli**, *Agro-food by products valorization in active coatings on plastic and cellulose substrates*	OC20.B: **Pedro Francisco Muñoz-Gimena**, *Thermoplastic starch from avocado seed flour vs extracted avocado starch: a comparative study*	OC21.C: **Anna Magri**, *Active polylactic acid-based films with encapsulated lemongrass essential oil for fresh-cut apples packaging*
14:50 – 15:10	OC21.A: **Paula S. S. Lacerda**, *Advancements in the synthesis of furan-based polyesters via ring opening polymerization*	OC21.B: **Mafalda S. Lima**, *DOPA based poly(ester amide)s as a new generation of biomimetic surgical adhesives*	OC22.C: **Nella Galotto-Galotto**, *A new family of bio-based polyurethanes for cosmetic use*
15:10 – 15:30	OC22.A: **Giuseppina Luciani**, *Multifunctional lignin nanoparticles with reversible swelling through hybrid approach*	OC22.B: **Zhou Fang**, *Accurate Tg prediction by machine learning for accelerating the development of bio-based polyester resins*	OC23.C: **Francisco J. Rodríguez-Mercado**, *Development and Evaluation of Eco-Friendly Plastic Films with Nano-TiO2 for Ethylene Scavenging: Characterization, in vivo Evaluation, and Compostability Analysis*
	Chair: Alfonso Jiménez		
15:30 – 16:00	Closing Lecture - KL 7: **Luc Averous**, *Latest developments in renewable polyurethanes for a greener future*		
16:00 – 16:20	Closure / BIOPOL 2026 Announcement		

LIST OF LECTURES AND COMMUNICATIONS

INVITED LECTURES

IL 1 - José M. Kenny (University of Perugia, Italy)
"Biodegradable polymers, composites and nanocomposites as alternatives to microplastics pollution"

IL 2 - Joao F. Mano (University of Aveiro, Portugal)
"Human-based proteins to engineer a new generation of biomaterials"

IL 3 - Ipsita Roy (University of Sheffield, United Kingdom)
"Sustainable Polymers for Biomedical Engineering: the way forward for a Net Zero Future"

KEYNOTE LECTURES

KN 1 - Jalel Labidi (University of the Basque Country, UPV/EHU)
"Chitin and Chitosan Based Materials"

KN 2 - Ana C. Fonseca (University of Coimbra, Portugal)
"α-Amino acids based poly(ester amides): a myriad of opportunities in the biomedical field"

KN 3 - Roberto J. Aguado (University of Girona, Spain)
"Nanocellulose as barrier agent, as binder and as carrier for active compounds in paper-based packaging"

KN 4 - Sandra Domenek (Université Paris-Saclay, INRAE, AgroParisTech, France)
"Critical Insights into the Barrier Performance of Polylactide (PLA) for Sustainable Packaging Applications"

KN 5 - Nadia Lotti (University of Bologna, Italy)
"Furan-based polymers: An interesting sustainable solution for food packaging"

KN 6 - Debora Puglia (University of Perugia, Terni, Italy)
"FURIOUS: Materials, processing and end-of-life opportunities for 2,5-FDCA based polymers"

KN 7 - Luc Averous (Université de Strasbourg, France)
"Latest developments in renewable polyurethanes for a greener future"

ORAL COMUNICATIONS

OC 1A - Fengwei Xie (Newcastle University, United Kingdom)
"Developing chitosan-based electroconductive inks for cost-effective and versatile 3D printing for EMI shielding and strain-sensing applications"
OC 2A - Luis Cabedo (Universitat Jaume I, Castelló, Spain)
"Studying the biodegradation process to improve bioplastics' end-of-life"
OC 3A - Antonio Greco (University of Salento, Italy)
"Crystallization kinetics and mechanical properties of PHB plasticized by commercial and cardanol derivatives"
OC 4A - Stefano Fiori (Condensia Química S.A, Spain)
"Recent developments on the application of oligomers of lactic acid"
OC 5A - Denise F. S. Petri (University of São Paulo, Brazil)
"Cetyltrimethylammonium bromide coated kapok fibers for the adsorption of Cr(VI) and bisphenol A"
OC 6A - Emmanuelle Gastaldi (Université de Montpellier, France)
"Degradation and environmental assessment of compostable packaging mixed with biowaste in full-scale industrial composting conditions"
OC 7A - Beatriz Agostinho (University of Aveiro, Portugal)
"Greener recycling of future biobased polymer wastes: PEF and PTF case studies"
OC 8A - Sébastien Livi (Université Claude Bernard Lyon 1, INSA Lyon, France)
"Ionic Liquids versus Deep Eutectic Solvent: A Tunable Platform for the Design of Biopolymer Blends"
OC 9A - José Gámez-Pérez (Universitat Jaume I, Castelló, Spain)
"Enhancing the Properties of Biodegradable Polymer Blends Through Compatibilization with Reactive Agents"
OC 10A - Carmen S.R. Freire (Universidade de Aveiro, Portugal)
"Exploiting polysaccharides for the production of sustainable materials for active food packaging"
OC 11A - Julio Romero (University of Santiago de Chile)

“Development of tissue engineering scaffolds based on PLA/PBAT bionanocomposites for bone regeneration using 3D printing coupled with dense CO2 foaming”

OC 12A - Bruno Medronho (Universidade do Algarve, Portugal)

“Probing cellulose-solvent interactions with self-diffusion NMR: Onium hydroxide concentration and co-solvent effects”

OC 13A - Virginia Venezia (University of Naples Federico II, Italy)

“Sustainable Active Food Packaging: Incorporation of Humic Substances into Electrospun Films”

OC 14A - Joe Kerry (Ashtown Food Research Centre, Ireland)

“Environmentally Friendly Extraction and Characterisation of Pectin from Apple Pomace and Its Validation of Use in Bread Packaging Films”

OC 15A - Antonella Esposito (Univ Rouen Normandie, INSA, France)

“Critical cooling rate of fast-crystallizing polyesters: The example of poly(alkylene *trans*-1,4-cyclohexanedicarboxylate)“

OC 16A - Andreia F. Sousa (University of Aveiro, Portugal)

“Sustainable advances in furan-based polymers: From biobased monomers to polymers and recycling”

OC 17A – Huixing Cao (Maastricht University, The Netherlands)

“Non-isocyanate, Bio-Based Covalent Adaptable Networks based on Polyaspartic esters”

OC 18A - Susana Guzmán-Puyol (Universidad de Málaga-IHSM-CSIC, Spain)

“Upcycling of potato and tomato pomaces for the fabrication of sustainable metal food packaging”

OC 19A - Michelina Soccio (University of Bologna, Italy)

“Introduction of bark extracts in furan-based polyester for the realization of sustainable active packaging”

OC 20A - Patrizia Cinelli (University of Pisa, Italy)

“Agro-food by products valorization in active coatings on plastic and cellulose substrates”

OC 21A - Paula S. S. Lacerda (University of Aveiro, Portugal)

“Advancements in the synthesis of furan-based polyesters via ring opening polymerization”

OC 22A - Giuseppina Luciani (University of Naples Federico II, Italy)

“Multifunctional lignin nanoparticles with reversible swelling through hybrid approach”

OC 1B - Giulia Guidotti (University of Bologna, Italy)

“Effect of hydrophilicity and stiffness of a PBCE-based copolymer on stem cells’ long term culture”

OC 2B - Antonio J. F. Carvalho (University of São Paulo, Brazil)

“Blends of thermoplastic polysaccharides plasticized with deep eutectic solvents”

OC 3B - Yuya Tachibana (Gunma University, Japan)

"Optical properties and recyclability of polycarbosilane containing bio-based bifuran structure"

OC 4B - Cheick Abou Coulibaly (Université de Montpellier, France)

"Detection and quantification of biodegradable nano and microplastics in biowaste compost"

OC 5B - Diana C.M. Ribeiro (University of Coimbra, Portugal)

"Biobased lubricant from modified vegetable oil: Impact on tribological Properties"

OC 6B - Cristina Mellinas (University of Alicante, Spain)

"From problem to solution: Bioadsorbents and plasticisers derived from Rugulopteryx Okamurae"

OC 7B - Benedetta Paolino (University of Campania Luigi Vanvitelli, Italy)

"New antifungal encapsulation systems based on HP-β-cyclodextrin, chitosan and essential oils for conservation of organic-media cultural heritage"

OC 8B - María José Jiménez (Packaging, Transport & Logistics Research Center, ITENE, Spain)

"Compostable solutions for food packaging aiming at reducing landfill disposal and food waste"

OC 9B - Joana Corrêa Mendes (Polytechnic Institute of Leiria, Portugal)

"Brown Seaweed Alginate to Develop p53 Encoding pDNA Nanocarriers for Colorectal Therapy"

OC 10B - Solange Magalhães (University of Coimbra, Portugal)

"On the development of novel cellulose derivatives for microplastic flocculation"

OC 11B - Itziar Otaegi (University of the Basque Country, UPV/EHU)

"Eggshell powder as potential filler for the manufacture of egg boxes based on PBSA"

OC 12B - Erfan Oliaei (KTH Royal Institute of Technology, Sweden)

"Chemically recyclable cellulosic biocomposites by curing of aliphatic polyester prepolymers"

OC 13B - Elona Vasili (University of Pisa, Italy)

"Processing cellulose by ionic liquid or deep eutectic solvent for potential use in 2D and 3D packaging applications"

OC 14B - Carlos Javier Pelegrín (University of Alicante, Spain)

"Valorization of horchata by-products as precursors for the isolation of cellulose nanocrystals and antioxidant extracts"

OC 15B - Elena Gabirondo (University of the Basque Country UPV/EHU)

"Chemical recycling of polyhydroxybutyrate into high-added value β-Hydroxy acid"

OC 16B - Francisco A.G. Soares Silva (Universidade Católica Portuguesa, Portugal)

"Development of bio-based paper coatings for food packaging applications"

OC 17B - Isabel Lopes (University of Aveiro, Portugal)

"Influence of ageing in the ecotoxicity of modified hydroxyethyl cellulose polymers to freshwater biota"

OC 18B - Charlotte Manoha (Université Jean Monnet, France)

"Effects of sodium sulfite on the rheological behavior of gluten plasticized with glycerol and water"

OC 19B - Mariana Ribeiro (University of Coimbra, Portugal)

"Hydrogels as promising candidates for the treatment of cutaneous wounds"

OC 20B - Pedro Francisco Muñoz-Gimena (Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, Spain)

"Thermoplastic starch from avocado seed flour vs extracted avocado starch: a comparative study"

OC 21B - Mafalda S. Lima (University of Coimbra, Portugal)

"DOPA based poly(ester amide)s as a new generation of biomimetic surgical adhesives"

OC 22B - Zhou Fang (Maastricht University, The Netherlands)

"Accurate T_g prediction by machine learning for accelerating the development of bio-based polyester resins"

OC 1C - Catarina Fernandes (University of Coimbra, Portugal)

"Synthesis of ecofriendly cationic lignin derivatives for hair cosmetics"

OC 2C - Mathie Craquelin (Université Artois, France)

"Effects of grafted chitosans on the reduction of powdery mildew in wheat"

OC 3C - Gustave Bertier (Université de Montpellier, France)

"Abiotic and biotic degradation of PBAT: quantification of generated products by carbon assessment"

OC 4C - Beatriz Almeida (NOVA University Lisboa, Portugal)

"Functional properties of hyaluronic acid-like polysaccharide produced by Vibrio sp. Mo245 from glycerol"

OC 5C - Stephane Serrano (Université de Toulon, France)

"High-performance, bio-based, tri-component vitrimer networks based on epoxydized vegetable oils: Control of the network synthesis and morphology"

OC 6C - Allison Vercasson (University of Montpellier, France)

"Impact of the individual layers on polymer-coated cardboards properties"

OC 7C - Sandra C.C. Nunes (University of Coimbra, Portugal)

"Monte Carlo Simulations for Screening and Optimizing Biopolymer-Based Drug Delivery Systems"

OC 8C - Zhenjiang Li (Nanjing Tech University, China)

"H-bond donor–Lewis basic anion bifunctional organocatalyst for ring-opening polymerizations"

OC 9C - Pilar Albaladejo (Packaging, Transport & Logistics Research Center, ITENE, Spain)
"Development of new packaging materials through novel agroindustrial valorization techniques"
OC 10C - Rafael C. Rebelo (University of Coimbra, Portugal)
"Development of Sustainable Cellulose-based Hydrogels for Agriculture"
OC 11C - Ignacio Solaberrieta (University of Alicante, Spain)
"Molecularly imprinted polymers for the selective elimination of aloin from aloe vera skin extracts"
OC 12C - Nora Aranburu (University of the Basque Country, UPV/EHU, Spain)
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OC 13C - Laia Posada-Quintero (Universidad Pontificia Bolivariana, Colombia)
"Standarization of bacterial nanocellulose production from fique by-products"
OC 14C - Cátia S. M. Esteves (University of Coimbra, Portugal)
"Polycaprolactone-Based Shell Materials for Microcapsule Applications"
OC 15C - Simão V. Pandeirada (University of Aveiro, Portugal)
"Exploring Innovative Eutectic Systems for Enhanced Recycling of Polyesters Mixed Waste"
OC 16C - Joana F.S. Costa (University of Coimbra, Portugal)
"Synthesis of novel polyesters incorporating an ether containing monomer for enhanced biodegradation in soil and water"
OC 17C - Yaiza Flores (Universitat Politècnica de València, Spain)
"Synthesis of polybutylene succinate using renewable biomass derived monomers"
OC 18C - Gaël Huet (Université de Montpellier, France)
"Alkaline pretreatment to improve food packagings biodegradation in mesophilic anaerobic digestion"
OC 19C - Diana Pacheco (University of Coimbra, Portugal)
"Harnessing Microalgal Polymers for Cutting-Edge Tissue Engineering Applications"
OC 20C - Vinícius de Paula (University of Aveiro, Portugal)
"Forging sustainable pathways: advancing chemical recycling techniques to address poly(ethylene 2,5-furandicarboxylate) circularity"
OC 21C - Anna Magri (University of Campania Luigi Vanvitelli, Italy)
"Active polylactic acid-based films with encapsulated lemongrass essential oil for fresh-cut apples packaging"
OC 22C - Nella Galotto-Galotto (Intercos S.p.A., Italy)
"A new family of bio-based polyurethanes for cosmetic use"
OC 23C - Francisco J. Rodríguez-Mercado (University of Santiago de Chile)
"Development and Evaluation of Eco-Friendly Plastic Films with Nano-TiO_2 for Ethylene Scavenging: Characterization, *in vivo* Evaluation, and Compostability Analysis"

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INVITED LECTURES

IL 1

Biodegradable polymers, composites and nanocomposites as alternatives to microplastics pollution

José M. Kenny
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Polymer composites are already relevant in many industrial applications that have changed our lives in the last 70 years: aeronautical, naval, car, furniture, domestic appliances, sport goods, electronic and biomedical devices are only some of the industrial sectors where polymer composites have provided clear advantages with respect to traditional materials. However, the compelling concern regarding the environmental impact of polymers and polymer composites, and the growing presence of microplastics, requires the development of environmental friendly solutions, including circular economy concepts and the use of renewable and biodegradable materials. Taking these concerns in consideration, there is a growing interest in the development of composite and nanocomposite with bio-polymeric matrices and biobased reinforcements. In particular, our research group has been a pioneer on the development of natural fiber composites and, in recent years, we have developed a consistent research program on biobased and biodegradable polymer nanocomposites.

Following this approach, cellulose and lignin have attracted special attention due to its renewable nature, wide variety of source materials, low cost and density, high surface functionality and reactivity. The combination of bioresorbable and sustainable polymers with bio-based nanostructures opened new perspectives in the self-assembly of nanomaterials for different applications with tuneable mechanical, thermal and degradative properties reducing the burden of microplastics in the environment.

Advanced modification chemistry has generated a high number of functional cellulose and lignin-based polymeric compounds integrated with both the intrinsic features of bio nanoparticles and additional properties of polymers. We started to focus our research on reinforcing polymer composites through nanosized cellulose and lignin and how they could affect, when dispersed in different biopolymers (i.e. gluten, PLA, PVA, chitosan) the optical, thermal, mechanical, dimensional stability, desintegrability, antioxidant activities and antibacterial performance of bio-nanocomposites. The potential synergic effect between lignin and cellulosic nanostructures has been also investigated, demonstrating how this innovative strategy could enlarge the use of green based nanoparticles to the food packaging sector.

In this lecture a review of the activities of our research group in the functionalization of cellulose and lignin nanoparticles and their incorporation in different polymeric matrices will be presented. The processing behaviour of the nanocomposites and their physicochemical properties are reported and reviewed in a critical analysis with other international research groups.

The results obtained in this research program confirm the feasibility of the processing and development of cellulose and lignin based bionanocomposites for different environmentally friendly industrial applications with particular attention to food packaging.

IL 2

Human-based proteins to engineer a new generation of biomaterials

João F. Mano
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A wide variety of materials have been explored in Tissue Engineering (TE) solutions, as a structural support for adherent cells and as a vehicle to provide relevant biochemical and biophysical signals to control cell behavior. Different types of natural-based macromolecular materials have been proposed to prepare scaffolds for TE, including porous structures, hydrogels or microparticles. We have been suggesting the use of human-derived proteins that, upon chemical modification, could be used to generate adequate microenvironments to interact adequately with cells. We have selected two sources of such materials: (i) platelet lysates, containing mostly globular proteins including relevant growth factors and other soluble proteins with highly regenerative potential; and (ii) proteins from amniotic membrane, composed of fibrilar proteins such as collagens and other components of the extra-cellular matrix. Due to their hydrophilic nature and richness in chemically active groups, these proteins can be chemically modified to generate materials with new or improved properties, while maintaining the biochemical features of human tissues. Some examples on the use of such systems are presented, namely: (i) in the development of 3D in vitro models, where bioengineered disease tissues are employed to test drugs; (ii) in therapies, in particular in regenerative medicine, where these proteins can be processed in the form of 3D-(bio)printed scaffolds, hydrogels or microparticles.

IL 3

Sustainable Polymers for Biomedical Engineering: the way forward for a Net Zero Future

Ipsita Roy[a,b]
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[b]Insigneo Institute of *In Silico* Medicine, University of Sheffield, UK

Biomedical applications involve the use of a huge quantity of plastics for packaging, implants, tissue engineering and drug delivery. However, there is hardly any attention paid to their sustainability and environmentally friendly properties. This group of plastics leads to a huge environmental impact.

In this work we have focused on the production and use of bacteria-derived sustainable biomaterials for use in biomedical applications. Two main types of biomaterials have been focused on, including Polyhydroxyalkanoates (PHAs)[1] and bacterial cellulose (BC)[2]. PHAs are polyesters produced by a range of bacteria including *Ralstonia eutropha*, *Psuedomonas putida* and *Bacillus subtilis*. These polymers are biodegradable in the soil and in the sea. In addition, they are also resorbable in the human body and are highly biocompatible. Hence the PHAs can be used for the development of green packaging materials and coatings. In addition, they can be used for direct biomedical applications such as the development of scaffolds for hard and soft tissue engineering and drug delivery. BC can also be produced by a range of bacteria including *Gluconobacter xylinus and Sarcinia ventriculi.* BC is also a green polymer, is sustainable and degradable in the soil. It is also highly biocompatible and can be used in biomedical applications.

Polyhydroxyalkanaotes are polyesters with monomer chain length ranging between C_4-C_{16}. They are divided in to two main types, short chain length PHAs (scl-PHAs) with monomer chain length between C_4-C_5 and medium chain length PHAs (mcl-PHAs) with monomer chain length between C_6-C_{16}.The sclPHAs are normally hard and brittle whereas the mcl-PHAs are soft and elastomeric in nature. Hence, the scl-PHA, Poly(3-hydroxybutyrate) has been used for bone tissue engineering [3], drug delivery [4], medical devices such as coronary artery stents, and the mcl-PHAs for cardiac [5], nerve [6], pancreas, kidney and skin regeneration. For bone tissue engineering neat P(3HB) and composites of P(3HB) with Bioglass, hydroxyapatite and carbon nanotubes have been used. The mcl-PHAs have been used for the development of cardiac patches[6], nerve guidance conduits[5], wound healing patch, bioartificial pancreas and bioartificial kidney. Processing techniques used include additive manufacturing, electrospinning and melt electrospinning.

Bacterial cellulose has also been produced under static culture conditions using *G. xylinus*. This is a highly nano-fibrillated structure and hence is a great substrate for cell attachment and growth. BC has been surface modified to create antibacterial bacterial cellulose. BC has also been used as a filler for P(3HB) based composites since BC is one of the stiffest known materials.

In conclusion, we have successfully used bacteria-derived sustainable biobased materials for a variety of biomedical applications and have initiated their use in environmentally friendly applications. Both PHAs and bacterial cellulose have a lot of potential in the future as sustainable materials of choice, a step forward towards a Net Zero future.

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KEYNOTE LECTURES

KN 1

Chitin and Chitosan Based Materials

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Chitin is the earth's second most abundant carbohydrate polymer (after cellulose). Despite being one of the most widespread natural polysaccharide, chitin was for a long time considered as an intractable polymer due of its lack of solubility in common solvents, which limits its processing and practical use.

Due to the mentioned limitations of chitin, it is usually converted to chitosan by deacetylation. Chitosan is well-known biopolymer with widespread application in various fields' material science, food, health, and agriculture

However, recent studies have mainly focused on chitin nanoparticles and their applications in different fields.

In nature, chitin occurs as micro/nanofibrils that form a composite together with proteins, pigments and calcium carbonate and has a structural role in the exoskeleton of crustaceans and insects. The unique properties of chitin nanoparticles – such as their renewable and biodegradable character, extremely small size, low density, chemical stability, biological activity, and non-cytotoxicity – make them excellent candidates for use in extensive range of medical applications, nanocomposite fields, water treatment, cosmetics, electronics devices, etc.

The diversity of properties of chitin nanoparticles (size, shape, crystallinity, aspect ratio and morphology) depend on the chitin source; and the isolation process of the nanoparticles. Different approaches are employed to isolate the most common chitin nanoparticles types: chitin nanocrystals and chitin nanofibers.

The present work will give an overview of the research developed in our research group related to chitin and chitosan.

KN 2

α-Amino acids based poly(ester amides): a myriad of opportunities in the biomedical field

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α-Amino acid-based poly(ester amide)s (AAA-PEAs) have attracted renewed interest due to their potential applications in the biomedical and pharmaceutical fields. This growing interest stems from the unique combination of the excellent biodegradability of polyesters and the robust mechanical properties characteristic of polyamides within these materials. AAA-PEAs offer versatility in structure, allowing for precise tuning of their physicochemical properties such as hydrophilicity, stiffness, and degradability. In addition, the presence of α-amino acids facilitates interaction with cells, resulting in improved cell adhesion and proliferation.

In recent years, the PolySyc Group at the University of Coimbra has developed AAA-PEAs with diverse structures and properties. These materials have been utilized in the creation of various biomedical devices, ranging from electrospun mats to 3D scaffolds, as well as microparticles and bioadhesives.

Therefore, this presentation aims to provide an overview of the significant results achieved, emphasizing the extensive potential of the AAA-PEAs family for biomedical applications.

KN 3

Nanocellulose as barrier agent, as binder and as carrier for active compounds in paper-based packaging

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Chitin is the earth's second most abundant carbohydrate polymer (after cellulose). Despite being one of the most widespread natural polysaccharide, chitin was for a long time considered as an intractable polymer due of its lack of solubility in common solvents, which limits its processing and practical use.

Due to the mentioned limitations of chitin, it is usually converted to chitosan by deacetylation. Chitosan is well-known biopolymer with widespread application in various fields' material science, food, health, and agriculture

However, recent studies have mainly focused on chitin nanoparticles and their applications in different fields.

In nature, chitin occurs as micro/nanofibrils that form a composite together with proteins, pigments and calcium carbonate and has a structural role in the exoskeleton of crustaceans and insects. The unique properties of chitin nanoparticles – such as their renewable and biodegradable character, extremely small size, low density, chemical stability, biological activity, and non-cytotoxicity – make them excellent candidates for use in extensive range of medical applications, nanocomposite fields, water treatment, cosmetics, electronics devices, etc.

The diversity of properties of chitin nanoparticles (size, shape, crystallinity, aspect ratio and morphology) depend on the chitin source; and the isolation process of the nanoparticles. Different approaches are employed to isolate the most common chitin nanoparticles types: chitin nanocrystals and chitin nanofibers.

The present work will give an overview of the research developed in our research group related to chitin and chitosan.

KN 4

Critical Insights into the Barrier Performance of Polylactide (PLA) for Sustainable Packaging Applications

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INTRODUCTION

Utilizing biodegradable and biobased materials presents an opportunity to reduce the environmental footprint of packaging systems while promoting local circularity of agronomic resources. In addition to that, these materials could be also integrated in new reuse or recycling systems. Whatever end-of-life treatment aimed, these materials must, during their service life, comply with the high safety and performance standards of food packaging. Gas and vapor permeability of polymers are one of the most critical factors for successful application. This optimization primarily hinges on understanding the relationship between transport properties and microstructure and dynamics of the amorphous phase in polymers. Polylactide (PLA) is today the most produced biodegradable and biobased polymer, used for a large part in packaging. It is also a widely researched model polymer to understand structure/function relationships, because is morphological properties can be tuned by its stereochemistry.

RESULTS AND DISCUSSION

To understand the relationship between microstructure and barrier properties of PLA enhance gas barrier properties of PLA, various microstructures were engineered. These approaches included confining the amorphous phase between crystalline lamellae, a method which leads to monomaterial containers. We showed that the coupling of the amorphous phase with the crystalline phase plays a central role in governing barrier properties. Nanocelluloses, which are an important innovation in the paper industry, can be used to increase properties using only small amounts and different architectures, such as nanocomposites or multilayers. Materials including small amounts and nanometric layer thickness were produced, keeping the possibility of different end-of-life treatments. The quantitative relationships of barrier properties and material morphology were modelled. Mechanistic analysis showed that water vapor transport in multilayers and nanocomposites is subject to non-Fickian diffusion. Shielding of nanocelluloses by surface grafting, even with low grafting density in composites or multilayers is the key to increase overall properties by decreasing the non-Fickian part of diffusion. The practical conclusion is that multilayers, even using only nanometric nanocellulose coatings, were far more efficient to increase oxygen barrier properties at low relative humidity, while nanocomposites offered a more stable performance over a large relative humidity range. The remaining challenge lies in uniting both properties to obtain efficient shielding of nanometric cellulose layers.

CONCLUSIONS

The morphology of polymers and architecture of materials has a significant impact on gas permeability. The quantitative knowledge of these structure/function relationships helps to tune the materials architecture with regards to the required service properties and a given end-of-life treatment. Extensive knowledge has been gained and a high number of materials were developed. To bring these advancements now successfully to market there is a need for collaboration across the supply chain for successful integration of their different constraints.

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KN 5

Furan-based polymers: an interesting sustainable solution for food packaging

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INTRODUCTION

Although common citizens think plastics is the main responsible of environmental pollution, in case of plastics food packaging the problem is particularly complex and a whole series of considerations must be made. Plastics packages protect adequately food, extending its shelf life and thus reducing food waste, which is the main plagues of the modern era [1]. Food loss and food waste indeed amounts to about one-third (1.3 billion tons) of all food produced worldwide [2], generating a food waste environmental impact higher than the one due to plastics waste [2]. The innovation of food packaging materials play a substantial role within the composite approach needed to solve this complex issue. In this scenario, 2,5-furandicarboxylic acid (FDCA) can be considered an interesting bio-based chemical building block to realize sustainable mono-material packaging, with excellent mechanical and gas barrier properties. Of particular interest, the eco-design of novel furan-based polyesters for the realization of flexible films, which are more sustainable than rigid one, being very effective in protecting food with the minimum amount of material used and waste generated [4]. This contribution aims to present an overview of the most important results obtained by the research group I coordinate on furan-based polymers designed for food packaging applications.

EXPERIMENTAL

All homopolymes and copolymers were obtained by 2-step melt polycondensation, an eco-friendly solvent-free process, starting from the dimethyl ester of FDCA and different glycols, and/or different diacids. All the materials were subjected to a preliminary molecular (1H-NMR and GPC) characterization, then on their compression-moulded free-standing films, a thermal characterization (DSC and TGA) was carried out. As to the functional properties, mechanical and barrier performances to dry and humid O2 and CO2 food grade gases were also checked. In some cases, the effect of food simulant fluids was evaluated, together with lab scale compostability.

RESULTS AND DISCUSSION

As to the main results obtained, it is worth mention the good mechanical properties and low GTR values, which means low permeability to gases of all furan-based materials. In particular, in most cases, the outstanding gas barrier properties are kept, in some cases, even improved, in humid conditions. Such features are of particular importance for the design of materials that will be used for food packaging purposes.

CONCLUSIONS

The structure-property relations extrapolated from these studies proved to be a powerful and reliable predictive tool for the ecodesign of new furan-based polyesters to be used for a novel sustainable food packaging.

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KN 6

Furious: materials, processing and end of life opportunities for 2,5-FDCA based polymers

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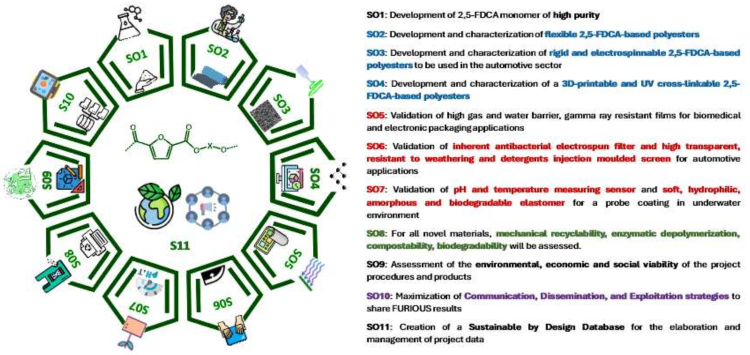
Up to now, the intriguing physical/mechanical, oxygen and vapour barrier properties of furan-based polyesters make them the most credible alternative to conventional plastics. However, the best studied furan-based polyester, PEF, is basically stiff, which strongly limits its applications in sectors where particularly flexible materials are required. Additionally, limited information is available on the processability of this new class of polymers with respect to conventional polymer processing techniques. The FURIOUS project (https://www.furious-project.eu/) aims to exploit all the established polymer synthetic strategies to obtain a new class of versatile 2,5-FDCA-based biopolymers (PXF), in terms of ad hoc designed chemical structure, processability and recyclability (Figure 1). Furthermore, through a circular approach in terms of End of Life (EoL) options, it contributes to progress in terms of circular economy with zero waste perspectives. This approach will lead to a) an advancement in the synthesis of new polymers from 2,5-FDCA with distinct and versatile structures, by generating at the same time valorised products to be applied in demanding sectors, such as b) biomedical and electronic packaging, where resistance to sterilization and high barrier properties are required, coupled to tuneable processability to cover both rigid and flexible films, as well as c) automotive sector, where resistance to UV weathering and intrinsic antibacterial properties are the key objectives, obtainable by selecting electrospinning and injection moulding as reference applicable processes and d) the extreme underwater environment (where the photoreactivity and the biodegradability in seawater of the new polymers will advance in parallel with mouldability of these polymers by 3D printing technologies).



SO1: Development of 2,5-FDCA monomer of **high purity**

SO2: Development and characterization of **flexible 2,5-FDCA-based polyesters**

SO3: Development and characterization of **rigid and electrospinnable 2,5-FDCA-based polyesters** to be used in the automotive sector

SO4: Development and characterization of a **3D-printable and UV cross-linkable 2,5-FDCA-based polyesters**

SO5: Validation of high gas and water barrier, gamma ray resistant films for biomedical and electronic packaging applications

SO6: Validation of **inherent antibacterial electrospun filter and high transparent, resistant to weathering and detergents injection moulded screen** for automotive applications

SO7: Validation of **pH and temperature measuring sensor** and **soft, hydrophilic, amorphous and biodegradable elastomer** for a probe coating in underwater environment

SO8: For all novel materials, **mechanical recyclability, enzymatic depolymerization, compostability, biodegradability** will be assessed.

SO9: Assessment of the **environmental, economic and social viability** of the project procedures and products

SO10: Maximization of **Communication, Dissemination, and Exploitation strategies** to share FURIOUS results

SO11: Creation of a **Sustainable by Design Database** for the elaboration and management of project data

Figure 1. FURIOUS objectives

Acknowledgements: This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement "GA101112541" project FURIOUS (Call : HORIZON-JU-CBE-2022)

KN 7

Latest developments in renewable polyurethanes for a greener future.

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Nowadays, the use of renewable carbon feedstock from different sustainable resources is highly taken into consideration because it offers the intrinsic value of a reduced carbon footprint with an improved life cycle analysis (LCA). Compared to conventional fossil-based materials, innovative macromolecular architectures with improved or additional properties can be then obtained. In this presentation, we report the last developments of our active research with several collaborations with academics and companies (Figure 1) on the synthesis, characterization and processing of innovative and renewable polyurethanes (PUR[1], PIR, TPU and NIPU[2]). These systems present controlled macromolecular architectures with different designs and morphologies (membranes, foams[3]), for a large range of applications. These materials are synthesized from different biobased building blocks, which can be directly extracted from biomass or obtained from white biotech (fermentation,): (i) linear aliphatic structures from different glycerides and derivate (dimer fatty acids,), sugar-based molecules, bacterial polyesters, (ii) cycloaliphatic from different sustainable building blocks[4] and (ii) aromatic from lignins[5,6] tannins[7], furans... A large range of renewable materials with improved properties and durable applications are developed/synthesized, for a greener and durable future. The end of life of these materials is also now largely considered, by e.g. bio-recycling[8,9], from cradle to cradle or through different vitrimer architectures[10].

Figure 1: Insulation panels based on aromatic and biobased foams, produced at industrial Level, from our research activities.

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ORAL COMMUNICATIONS

OC 1A

Developing chitosan-based electroconductive inks for cost-effective and versatile 3D printing for EMI shielding and strain-sensing applications

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INTRODUCTION

The growing fascination with biopolymer 3D printing stems from its ability to precisely craft customized, complex structures, leveraging the inherent advantages of biopolymers such as renewability, chemical functionality, and biosafety. However, the availability of affordable and adaptable 3D-printable biopolymer-based inks is severely limited. Our recent study [1] presents a lightweight, cost-efficient, electroconductive ink designed for versatile direct-ink-writing (DIW) 3D printing, distinguished by its straightforward preparation and commendable printability and material properties.

RESULTS AND DISCUSSION

The ink utilizes chitosan (Cs) as a binder, carbon fibres (CF) as a low-cost electroactive filler, and a small quantity of silk fibroin (SF) as a structural stabiliser. Both the CsCF and CsCF/SF inks exhibited shear-thinning behaviour, with a structural recovery of about 92–94% within 34–36 s. These inks demonstrated outstanding post-printing structure retention without the need for additional crosslinking or curing treatments during or after printing. The structural density of the 3D-printed grids was measured at 0.33 ± 0.008 g/cm3 and 0.29 ± 0.007 g/cm3 for CsCF and CsCF/SF, respectively. The electroconductivity of CsCF and CsCF/SF was determined to be 2.84 ± 0.043 and 2.64 ± 0.065, respectively. Incorporating SF into the CsCF composite at a moderate level (6.25%) did not significantly alter the electrical and rheological properties but notably enhanced printing accuracy and stability, while slightly increasing tensile strength and density. The 3D printed CsCF and CsCF/SF composites exhibited EMI shielding effectiveness ranged from 28 to 34 dB and 30 to 31 dB, respectively, indicating very good to excellent shielding performance by blocking over 99.0% of incident electromagnetic waves in all composites. Furthermore, we demonstrated the freeform 3D printing of linear and spiral strain sensors using CsCF/SF composite ink. These sensors exhibited commendable sensitivity to finger bending and compression, as indicated by $\Delta R/R0$ (see Figure 1).

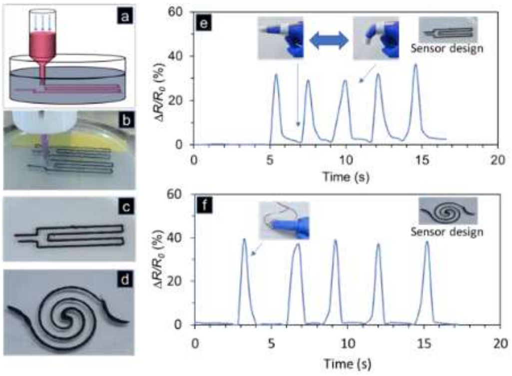

Figure 1. Freeform 3D printing of linear and spiral strain-sensors (c, d) using CsCF/SF ink via liquid-in-liquid extrusion process; and strain sensing tests by finger bending (e) and pressing (f) using these respective sensors.

CONCLUSIONS

Given their low density, high conductivity, and ease of manufacture, the biopolymer-based composites showcased here hold promise for development as conductive foams or tailored 3D structures on both small and large scales. These materials could find applications in the electronics and aerospace industries.

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OC 2A

Studying the biodegradation process to improve bioplastics' end-of-life

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The phenomenon of biodegradation is a natural process whereby a material is transformed into simpler molecules by the action of living organisms. In the case of polymeric materials, this process involves the transformation of the carbon within the polymer into carbon dioxide (under aerobic conditions) and methane (under anaerobic conditions), a process known as carbon mineralization.

This biodegradation process occurs only in certain plastic materials that, due to their chemical nature, are sensitive to the enzymatic activity of various microorganisms. Consequently, most plastic materials lack this characteristic, resulting in much slower carbon transformation, which can take decades or even hundreds of years in the nature. This slow degradation rate is a major problem for plastic materials, as it causes their waste to persist in the environment, becoming a massive source of pollution. In contrast, biodegradable polymers, which can break down quickly serving as a food source for microorganisms, offer a significant technological opportunity to control the end-of-life of plastic products and thus avoid the contamination associated with the accumulation of plastic waste.

However, the use of biodegradable polymers for plastic applications still presents significant challenges. These challenges are related not only to the performance of biodegradable polymers, which requires further development of new commercial materials and grades to meet market specifications, but also to the complexity of the biodegradation process itself. This process occurs unevenly and is not yet fully understood or controlled, making the management of biodegradable polymer waste problematic and the prediction of the time required for the full biodegradation in natural environments, challenging.

The presentation will highlight various studies on the biodegradation process applied to bioplastics, mainly from the polyhydroxyalkanoates family, to demonstrate the technological relevance of controlling this process for both waste treatment conditions, and plastic applications where subsequent recovery is not anticipated (such as plastics intended for direct environmental exposure).

The presentation will discuss the variables that influence the biodegradation process and how these factors affect the end-of-life of plastics. It will also present results from biodegradation studies of plastic materials in various environments, analysing the importance of both material type and environmental conditions, with the ultimate goal of improving the prediction of plastic biodegradation. Finally, the presentation will explore some technological opportunities offered by a better understanding and control of the biodegradative process.

OC 3A

Crystallization kinetics and mechanical properties of PHB plasticized by commercial and cardanol derivatives

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INTRODUCTION

The present study investigates the thermal and mechanical characteristics of poly (3-hydroxybutyrate) (PHB) plasticized with commercial polyethylene glycol (PEG) and natural cardanol derivatives. The impact of plasticisers on isothermal and non-isothermal crystallisation kinetics and their ability to increase polymer toughness were investigated using differential scanning calorimetry (DSC) and mechanical analysis.

EXPERIMENTAL

Pure poly(3-hydroxybutyrate) (PHB) Y3000p, from Enmat, was mixed with different plasticizers (Commercial polyethylene Glycol (PEG), cardanol (C), cardanol acetate (CA) and epoxidated cardanol acetate (ECA)) at 17% by weight of plasticizer using a Haake Polylab OS twin screw extruder from Thermo Scientific, Germany. DSC analysis was performed using a Mettler Toledo 822.

RESULTS AND DISCUSSION

The Avrami plots [1] for PHB isothermal crystallization, as reported in Figure 1, show that the slope increases with increasing crystallization temperature, indicating the existence of different crystallization regimes. The same behaviour was observed for plasticized PHB. Therefore, the Ozawa model, very often used for analysis of dynamic crystallization [1], did not provide a good fit of the experimental data. In contrast, the Mo plot [2], reported in Figure 2, shows a satisfactory agreement with experimental data. From the Mo plot parameters, it was possible to build the continuous cooling transformation (CCT) curves for PHB and plasticized PHB, as reported in Figure 3. In any case, addition of plasticizer does not allow to obtain an amorphous structure. Due to the high degree of crystallinity, plasticized PHB shows a brittle behaviour, as reported in Table 1.

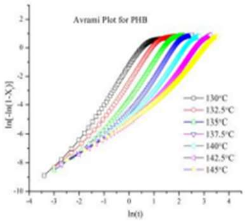

Figure 1: Avrami plot for PHB

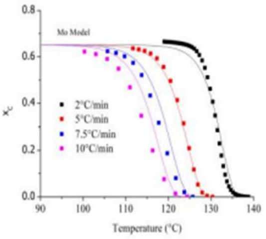

Figure 2: curve fitting by the Mo model

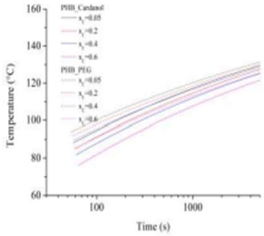

Figure 3: CCT curves

Composition	Tensile Strength (MPa)	Strain at Break (%)	Young's Modulus (GPa)
PHB	35.7±1.6	2±0.3	2.4±0.2
PHB-C	28±1.4	1.9±0.2	1.5±0.3
PHB-CA	36.6±0.8	2.7±0.4	1.5±0.2
PHB-ECA	34.4±1.2	2.5±0.2	1.6±0.4
PHB-PEG	38±1.1	2.1±0.4	2.1±0.3

Table 1: tensile properties of plasticized PHB

CONCLUSIONS

Plasticization of PHB reduces the temperatures for PHB crystallization, but does not allow to reduce the amount of crystalline phase formed during cooling. As a consequence, despite the efficient plasticization of PHB, as evidenced by the modulus reduction, the resulting material is still characterized by a brittle behavior.

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OC 4A

Recent developments on the application of oligomers of lactic acid

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Introduction

During the last years, important developments in the field of polymers based on lactic acid (LA) have been reported [1,2]. The controlled polymerization of L-lactic (L-LA) has been previously perfomed by our research group [3,4]. This presentation summarizes the most significant results obtained in the synthesis of additives based on oligomers of lactic acid (OLA) to be further introduced in biopolymers and biocomposites formulations. The aim of our proposal is the expansion in the use of additives based on LA by introducing a new series of oligomers adequate to be used as thermal, compatibility and mechanical modifiers for poly(lactic acid), PLA, and its blends. This work is based on the modification of the OLA chemical structure to obtain innovative bio-based and biodegradable additives. These products meet the criteria of biodegradability and ecological label [5].

Discussion

Today, for almost every conventional plastic material and the corresponding application, a bioplastic alternative exists; they comprise of a whole family of materials with different properties and applications. Currently, bioplastics represent about one percent of the about 350 Mtonnes of plastic produced annually [6], but as demand is rising and with more sophisticated biopolymers, applications, and products emerging, the market is continuously growing. Bioplastics are utilized in an important number of applications *e.g.*: packaging, catering products, consumer electronics, automotive, agriculture and toys etc. For this reason, Condensia offers a wide range of additives specially designed for using in combination with bioplastics, mainly PLA (polylactic acid), but also PHA (polyhydroxy alcanoate) and starch blends, which can perform various purposes depending on the type and dosage used, thus acting as: plasticizers, impact modifiers, nucleating agents, filler compatibilizers and ompostability/biodegradability promoter. As a plus, they show low volatility, low migration, good thermal stability, and high biodegradability.

Lactic acid oligomers

Obtained from bio-renewable raw materials and fully biodegradable and compostable (UN 20200:2006). When used in mixture with PLA and its blend, they allow to obtain stretch films with excellent mechanical properties without loss of transparency. Furthermore, they can be used such as impact strength modifiers, chain extender, nucleating agents, compatibilizer for fillers and other reactive polymers. GLYPLAST® OLAs are internationally patented and EU food approved.

Product name	*Density g/cm3 (25 °C)*	*Viscosity (mPa.s)*	*Applications*
Glyplast OLA 2	1.10	90 (40ºC)	Completely biodegradable PLA impact modifier
Glyplast OLA 8 *Glyplast OLA 550*	1.11	22.5 (100ºC)	Completely biodegradable PLA, PHA, starch-based material plasticizers. Cling films, calendered object, rope, cable, tissues
	1.12	40 (100ºC)	Completely biodegradable nucleating agent for PLA

Glyplast OLA 5023	1.14	90 (40ºC)	Completely biodegradable chain extender for PLA
Glyplast OLA 5028 *Glyplast OLA 526*	1.13	50 (40ºC)	Completely biodegradable compatibilizer for grafting of nanocellulose, montmorillonite, nano filler etc., it works also as chain extender
	1.21	7600 (25ºC)	Completely biodegradable biobased material, specially developed for photocurable resins and paints.

Conclusions

A new series of bio-based and biosource additives based on copolymers of L-lactic acid were prepared and tested with potential interest for the biopolymer industry.

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OC 5A

Cetyltrimethylammonium bromide coated kapok fibers for the adsorption of Cr(VI) and bisphenol A

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INTRODUCTION

In this work, lignocellulosic kapok fibers (KFs) were modified cetyltrimethylammonium bromide (CTAB) to obtain positively charged surfaces. Although CTAB-coated KFs have been reported to facilitated the polymerization of acrylonitrile on the fibers [1], a deep understanding about the adsorption of CTAB on KFs is still missing. Herein the adsorption of CTAB on KFs was systematically investigated. CTAB modified KFs were characterized by elemental analysis (CHN), X-ray photoelectron spectroscopy (XPS), FTIR, SEM, and X-ray diffraction (XRD). The CTAB-coated KFs were used as adsorbents for Cr(VI) and bisphenol A (BPA) in batch and column adsorption studies. The hypothesis is that CTAB positively charged head interacts with the chromate ions, whereas the hydrophobic BPA might be removed by the CTAB hydrophobic tail [2]. XPS measurements were performed to better understand the adsorption mechanism.

RESULTS AND DISCUSSION

The experimental data of the adsorption isotherm of CTAB on KFs at 25 ^{o}C fitted well to the Langmuir model, yielding the adsorption amount of 0.75 mmol/g; this value corroborated with the CHN analysis (0.80 mmol/g). XPS high resolution indicated that the orientation of the quaternary ammonium groups to the air. XDR patters of KFs changed significantly after CTAB adsorption. SEM images (Figure 1a) showed that the morphonology was not affected by the CTAB adsorption. Figures 1b and 1c display the adsorption isotherms of Cr(VI) and BPA on the CTAB-coated KFs, respectively, along with the nonlinear fitting to different models. XPS high resolution spectra revealed that upon adsorbing, chromated displaced bromate, whereas BPA adsorption was driven by ion-dipole interactions.

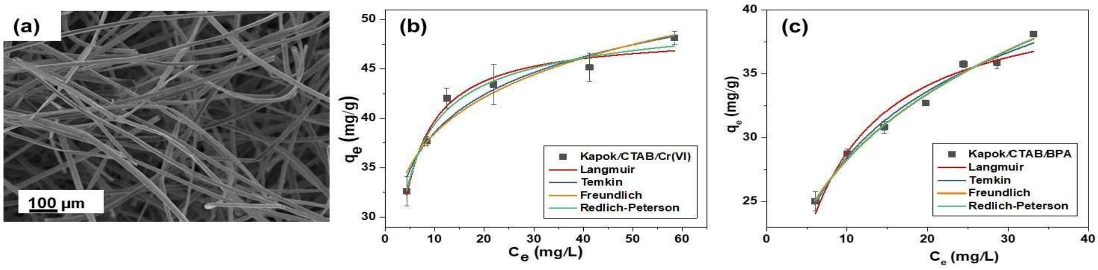

Figure 1. (a) Typical SEM image of CTAB-coated KFs. Adsorption isotherms of (b) Cr(VI) and (c) BPA on the CTAB-coated KFs, and the fittings to different models.

CONCLUSIONS

CTAB molecules are arranged on the KFs as highly ordered monolayers. The CTAB-coated KFs were efficient adsorbents towards Cr(VI) and BPA contaminants.

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OC 6A

Degradation and environmental assessment of compostable packaging mixed with biowaste in full-scale industrial composting conditions

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INTRODUCTION

Compostable materials represent an innovative solution to reduce the environmental impact of plastic materials, by providing an alternative route for end-of-life treatment. With the mandatory separation of bio-waste at source, some of these materials could be treated in industrial composting plants in combination with food waste, and thereby contribute to the circular bioeconomy by creating valuable compost, which serves as a beneficial organic soil amendment for agriculture. However, while lab-scale measurement methods exist to certify the biodegradability of a material under industrial composting conditions, they cannot perfectly replicate the real processing conditions. The presence of biodegradable food packaging therefore represents a challenge for organic waste management processes, and it is crucial to assess their biodegradation performance under real conditions[1].

EXPERIMENTAL

A large-scale experiment was carried out on 40 tons of biowaste directly collected from households at an industrial composting station using open-air windrow technology. After manual cleaning, two batches of 20 tons containing the same initial biowaste mixture were studied, one as "Control" and the other as "Materials" in which 1.28 wt% (323 kg) of certified compostable plastics have been introduced. The composting process of the two batches was monitored for 4 months, during which time representative samples were taken to analyze the degradation mechanism of each major family of compostable materials (e.g., starch blends, PLA, polyhydroxyalkanoates (PHAs)). The data generated by this experiment were used for assessing the environmental impacts of composting process versus incineration of the plastics.

RESULTS AND DISCUSSION

Results indicated that no effect of the incorporation of these compostable materials on the composting process was observed[2]. An analysis of the safety and quality of the final compost, carried out by an independent accredited laboratory, certifies that the "Materials" compost complies with the requirements of standard NF U44-051 relating to compost and organic soil improvers, as well as with organic farming criteria. No ecotoxicity has been demonstrated on plants, earthworms or daphnia. Agronomic fertilizing and amending quality were high, the "Materials" compost even enhancing barley growth. The compostable materials showed rapid biodegradation after 4 months with around 2 wt% of very small residual fragments consisting mainly of PHA, which disintegrated more slowly due to geometric factors. The evolution of the morphology of the materials revealed specific degradation mechanisms depending on the polymers introduced. The environmental assessment demonstrated an advantage for composting over incineration for seven of the eight indicators considered.

CONCLUSIONS

This large-scale composting study evidenced the successful integration of compostable materials with biowaste upholding product safety and quality. The compostable materials lost 98% of their mass in less than 4 months, which is the usual composting time. The environmental assessment indicated that composting biodegradable plastics with biowaste had less impact than incineration. In short, compostable materials can be part of sustainable waste management strategies.

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OC 7A

Greener recycling of future biobased polymer wastes: PEF and PTF case studies

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INTRODUCTION

Global polymer production has increased exponentially since its start in the 1950s, reaching a total of 400 Mt in 2022[1]. However, the vast majority of these polymers are non-biodegradable under environmental conditions nor adequately recyclable, which leads to their accumulation in landfills or leak into terrestrial or aquatic settings. An additional concern is the fact that the majority of most of the currently produced polymers are fossil-based, so more sustainable alternatives are needed. In this vein, during the last decade, several biobased alternatives have emerged [2]. Among those are bio-based furanic polyesters such as poly(ethylene 2,5-furandicarboxylate) (PEF)[3] and poly(trimethylene 2,5furandicarboxylate) (PTF), which have comparable mechanical properties to poly(ethylene terephthalate) (PET) and even enhanced barrier properties for packaging applications[4]. However, these bio-based alternatives keep raising the same environmental persistence challenges during their End-ofLife (EoL), and since current recycling processes are still poorly efficient, the development of alternative recycling approaches is of the utmost importance.

EXPERIMENTAL

In this work, we report the design of a continuous, mild, and close-loop recycling approach applied to furanic polyesters by making use of the superior capacity of Deep Eutectic Solvents (DESs) to catalyse both alcoholysis and polyesterification reactions[5].

RESULTS AND DISCUSSION

Both PEF and PTF were recycled using a urea-based DES reaching a maximum yield of 91% and 92% for PEF and PTF, respectively.

CONCLUSIONS

The proposed recycling approach confirms the potential of DESs to catalyse de-/re-polymerization in a continuous way, as an efficient and greener option to chemically recycle persistent polyester wastes, promoting a more circular approach for its EoL.

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OC 8A

Ionic Liquids versus Deep Eutectic Solvent: A Tunable Platform for the Design of Biopolymer Blends

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INTRODUCTION

The European countries foster the Industry to reconsider production methods in order to decrease the use of fossil resources and to minimize the environmental impact of the products throughout their whole life cycle. In line with political and ethical demands of our times, scholars and industries are pushed to the advancement of bioplastics in several domains, including packaging and mulching films, in order to foster innovative approaches towards achieving sustainability in agriculture. Various authors have reported the use of PHB in the PBSA matrix leading to a significant increase in toughness and elongation at break as well as a considerable improvement of the oxygen barrier properties (reaching a rate of 14.8 cm3.mm/m^2.24h).[1,2] Nevertheless, the compatibility between PBSA and PHB is not sufficient due to the poor interactions at a molecular level.[2] Recently, our research group have highlighted that Ionic Liquids (ILs) can be used as interfacial agents of polymer blends leading to high-performance materials[3].

RESULTS AND DISCUSSION

In this work, two IL-based phosphonium (P-Ph) and imidazolium (Im-Cl) and a deep eutectic solvent (DES) were used to compatibilize polymer blends based on PBSA/PHB (80/20)[4]. Then, 2 wt. % of these interfacial agents were introduced into PBSA/PHB blends inducing a partial miscibility of the PHB phase indicating by DSC and the Fox equation. Then, we have demonstrated that the addition of only 2 wt. % of these interfacial agents simultaneously led to a considerable improvement in the mechanical performances of the blends (2.2 GPa, 300%). In terms of thermal stability, the use of P-Ph or DES stabilized the PBSA/PHB blend and retarded its thermal degradation (+ 100 °C), Finally, the oxygen and water permeability were also investigated confirming that the synergistic effect of P-Ph or DES with the PHB induced a significant reduction in permeability (93 % for oxygen and 82 % for water vapor) which can be also explained by an increase of the tortuosity and an increase of the hydrophobic behavior limiting the sorption of water or gas at the PBSA/PHB blends.

CONCLUSIONS

ILs and deep eutectic solvent offer a new alternative to conventional compatibilizers allowing the preparation of high-performance polymer blends with the use of small amounts of theses additives and for the first time led to biodegradable polymer blends with enhanced properties opening new perspectives in the field of packaging or mulcher films.

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OC 9A

Enhancing the Properties of Biodegradable Polymer Blends Through Compatibilization with Reactive Agents

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INTRODUCTION

Polyhydroxyalkanoates (PHBV) and poly(butylene succinate adipate) (PBSA) blends present a promising sustainable alternative to conventional plastics, particularly for packaging applications due to their biodegradability1.. This study explores the effects of various reactive agents on the compatibilization, properties, and biodegradation of PHBV/PBSA blends, focusing on enhancing their application potential without compromising environmental benefits.

EXPERIMENTAL

PHBV and PBSA were blended with reactive agents—HMDI, Luperox®, and Joncryl®—and analyzed using scanning electron microscopy (SEM), thermal analysis (TGA and DSC), mechanical testing (tensile and tear tests), and biodegradation assessments under composting conditions[2].

RESULTS AND DISCUSSION

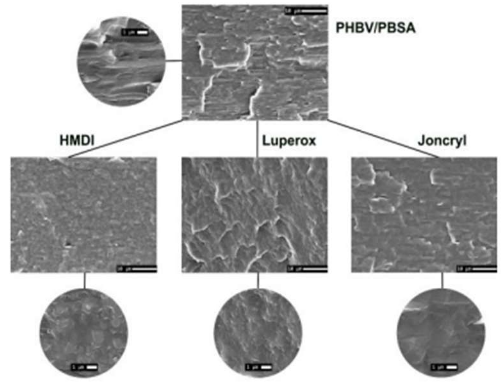

Figure 1. SEM micrographs revealing the PBSA droplets size within the PHBV matrix

SEM analyses revealed distinct improvements in the interfacial adhesion and dispersion of PBSA within PHBV matrices upon the addition of reactive agents, especially with HMDI and Luperox®, which exhibited a "drop-in-matrix" morphology indicative of enhanced phase compatibility. Thermal analysis showed a slight shift in degradation temperatures, suggesting improved thermal stability of the blends. Mechanical testing highlighted that the inclusion of HMDI and Luperox® significantly increased the elongation at break, indicative of improved toughness. The biodegradation studies confirmed that all materials maintained high biodegradation rates, aligning with international standards for biodegradability.

CONCLUSIONS

The addition of specific reactive agents significantly improved the mechanical properties and compatibility of PHBV/PBSA blends while maintaining their biodegradability. These findings enhance the understanding of modifying biopolymer blends for better performance and environmental impact, supporting their use in sustainable packaging solutions.

ACKNOWLEDGMENTS

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OC 10A

Exploiting polysaccharides for the production of sustainable materials for active food packaging

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INTRODUCTION

The combination of biopolymers and active packaging technologies is among the emerging trends for the implementation of a more sustainable food packaging industry. Polysaccharides, such cellulose, starch and xylans, among others, have gained relevance in this field due to their properties (biodegradability, easy of functionalization, film-forming ability and good mechanical properties). The present communication describes advanced polysaccharide-based materials, fabricated following ecofriendly approaches. Focus will be given to thermoplastic starch-bacterial nanocellulose films enriched with gallic acid,[1] and wood inspired films composed of xylans, nanocellulose and lignossulfonates.[2]

RESULTS AND DISCUSSION

In the first study, bioactive transparent films of thermoplastic starch (TPS) reinforced with bacterial nanocellulose (BNC) (1%, 5% and 10% w/w, relative to starch) and enriched with gallic acid (1 and 1.5% w/w, relative to starch) were prepared by solvent casting.[1] The addition of BNC improved both the mechanical properties (Young´s Modulus: 1.2 -2.0 GPa vs. 1.0 GPa in TPS; tensile strength: 23 - 39 MPa vs. 20 MPa in TPS) and the water resistance of the films. The addition of GA imparted them with UV-blocking properties and antioxidant activity (DPPH scavenging activity above 80%). The film with 10% w/w of BNC and 1% w/w of GA revealed to have good oxygen barrier property with a coefficient of permeability of 0.91 ± 0.12 $cm^3 \mu m\ m^{-2}\ d^{-1}\ kPa^{-1}$ and antibacterial activity against S. aureus (reduction of about 4.5 log10 colony forming units (CFU) mL-1 after 48 h).

In the second work, functional wood inspired biopolymeric nanocomposite films were prepared by solvent casting of suspensions containing commercial beechwood xylans, cellulose nanofibers (CNF) and lignosulfonates in a proportion of 2:5:3 wt.%, respectively.[2] The incorporation of CNF into the xylan/lignosulfonates matrix provided good mechanical properties to the films (Young's modulus between 1.08 and 3.79 GPa and tensile strength between 12.75 and 14.02 MPa). The presence of lignosulfonates imparted the films with antioxidant capacity (DPPH radical scavenging activity from 71.6 to 82.4%) and UV barrier properties (transmittance ≤ 19.1% (200 – 400 nm)). Moreover, the films obtained are able to successfully delay the browning of packaged fruit stored over 7 days at 4 ºC.

CONCLUSIONS

The developed polysaccharide-based films presented good mechanical performance, UV-blocking properties, and antioxidant and antibacterial activities, that are fundamental for application in active food packaging.

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OC 11A

Development of tissue engineering scaffolds based on PLA/PBAT bionanocomposites for bone regeneration using 3D printing coupled with dense CO_2 foaming

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INTRODUCTION

Tissue engineering scaffolds are extracellular matrices used to promote bone regeneration, among other applications [1]. The demand for bone replacement materials has increased due to diseases and injuries that affect bone density and remodelling. Traditional bone grafts and metallic implants have limitations and risks, emphasizing the need for custom scaffold structures. Solvent-free fabrication techniques, synthetic biopolymers, and nanoparticles play a crucial role in enhancing scaffold properties [2]. This work focuses on the research and characterization of the chemical, physical, and structural phenomena related to the fabrication of materials with potential application as scaffolds for bone tissue engineering from bionanocomposites using 3D printing and a dense CO_2 foaming treatment in order to tune the primary and secondary porosity of the scaffold. The novelty of this work lies in the scarcely studied poly(lactic acid)/poly(butylene adipate-co-terephthalate)/hydroxylated nano montmorillonite (PLA/PBAT/DK2) material composite, which could offer several advantages due to its modifiable structural properties, making it an effective extracellular matrix for scaffolds used in bone regeneration.

EXPERIMENTAL

This work has focused on the characterization of a PLA/PBAT/DK2 composite in the form of pellets, 3D printing filaments and foamed scaffolds through FT-IR spectroscopy, DSC, TGA, mechanical strength, tensile and impact resistance, and SEM.

RESULTS AND DISCUSSION

Nanocomposites were developed with a PLA/PBAT/DK2 blend for creating filaments, 3D printed scaffolds, and foamed scaffold. In the mechanical tests, the scaffolds with added DK2 showed increased impact resistance, demonstrating enhanced mechanical properties. The values obtained for Young's modulus and maximum stress indicate biomechanics similar to that of spongy bone, enhancing its potential use as a replacement for this type of tissue, which has not been widely studied. Despite using mild foaming conditions, low pressure, and temperature, SEM images showed the existence of microporosity in the scaffolds after the foaming process, with an average pore size of up to 27.95 µm in the material without DK2 and 18.99 µm in the material with DK2.

CONCLUSIONS

The incorporation of DK2 into the PLA/PBAT blend resulted in the effective improvement of the scaffolds' mechanical properties. This was attributed to the combined primary and secondary porosities, which were attributed to the 3D printing channels design and the CO_2 foaming. These findings suggest that this material could be used for the fabrication of scaffolds for effective bone regeneration.

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OC 12A

Probing cellulose-solvent interactions with self-diffusion NMR: onium hydroxide concentration and co-solvent effects

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ABSTRACT

Cellulose has a peculiar hierarchical organization and complex network of interactions which makes its processing into novel advanced materials (e.g., fibres, films, or foams) a non-straightforward task. As cellulose cannot be melted without chemical derivatization, it often requires initial solubilization. The list of suitable solvents is rather restricted and the key mechanisms governing such process are still debatable. Among other factors, a good solvent for cellulose involves high diffusivity, aggressiveness in decrystallization, and capability of disassociating the cellulose chains. Over the years, several classes of efficient cellulose solvents from wildly different chemical families have been developed. A successful example relies on using strong hydroxides composed of bulky organic ions, such as tetrabutylammonium hydroxide (TBAH). TBAH belongs to a family of aqueous solvents based on alkylammonium hydroxide (also referred to as onium hydroxides) which display notable capacity of solubilizing large cellulose concentrations in reasonably mild conditions. In this work, the molecular self-diffusion coefficients were accessed in solutions of microcrystalline cellulose, dissolved in 30 wt% and 55 wt% TBAH (aq), and in mixtures of 40 wt% TBAH (aq) with an organic co-solvent, dimethylsulfoxide (DMSO), through pulsed field gradient stimulated echo NMR measurements [1]. A two-state model was successfully applied to estimate α (*i.e.*, average number of ions that "bind" to each anhydroglucose unit) and Pb (*i.e.*, fraction of "bound" molecules of DMSO, TBAH or H2O to cellulose) parameters. The α values suggest that TBA$^+$ ions can bind to cellulose within 0.5 TBA$^+$ to 2.3 TBA$^+$/AGU. On the other hand, the Pb parameter increases when raising cellulose concentration for TBA$^+$, DMSO and water in all solvent systems. Data suggests that TBAH interacts with the ionized OH groups from cellulose forming a sheath of bulky TBA+ counterions which consequently leads to steric hindrance between cellulose chains.

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OC 13A

Sustainable Active Food Packaging: Incorporation of Humic Substances into Electrospun Films

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INTRODUCTION

This study develops composite films of electrospun poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer with humic substances (HS) as natural additives [1,2]. HS are known for their phenolic and carboxylic groups, which promote plant growth and have antiviral and anti-inflammatory properties. Despite their potential, HS are not widely used due to leakage and degradation in aqueous environments and are typically considered waste and used mainly for soil amendment. This research uses HS as natural fillers in a polymeric matrix to develop reproducible systems with remarkable biocidal activity, even with less refined industrial bio-waste. Several emulsions composed of PHBV in trifluoroethanol and different amount of HS in aqueous solution, have been prepared to produce bioactive, biodegradable, and sustainable nanocomposite nanofibers (PHBV/HS) through the electrospinning technology. These electrospun mats were converted into 'biopapers' (PHBV/HS films) and characterised for their morphological, thermal, optical, moisture/light barrier, mechanical, antioxidant, antibacterial and antifungal properties to assess their potential for active biopackaging.

RESULTS AND DISCUSSION

The resulting materials exhibit remarkable antioxidant, antimicrobial, and antifungal properties, making them very suitable for food packaging applications. The films demonstrated promising water vapor and limonene permeability, as well as favourable optical and mechanical properties, indicating their potential for preserving food freshness and aroma. The PHBV/HS film effectively preserved cherries during a 14-day storage period at room temperature, maintaining freshness and quality due to its antioxidant, antimicrobial, and barrier properties. These findings underscore the potential of PHBV/HS films to extend the shelf life of perishable fruit and vegetables.

CONCLUSIONS

This study highlights a significant achievement in the field of electrospinning technology by producing fibers composed of PHBV biopolymer and HS used as functional natural additives. For the first time, HS extracted from a commercially available agrifood compost supplied by the Sardinian company Verde Vita (s.r.l.), was explored as natural functional fillers for polymeric matrix, obtaining reproducible systems with outstanding biocide action even using a less refined industrial bio-waste. This novel approach integrates electrospinning with a waste-to-wealth strategy. Electrospinning effectively regenerates and upgrades HS, overcoming key limitations in their use. The combination of low-cost, highly bioavailable HS with a biodegradable support offers a promising strategy to increase stability, reduce costs and improve circularity of materials.

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OC 14A

Environmentally Friendly Extraction and Characterisation of Pectin from Apple Pomace and Its Validation of Use in Bread Packaging Films

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INTRODUCTION

Sustainability, the reduction of waste, and creating environmentally friendly manufacturing processes have just been some of the challenges facing the food industry in recent times. The concept of a circular economy (CE) initiative is something that appeals to consumers and is aimed at creating future sustainability. Apple Pomace (A.P) is an abundant waste stream from the apple juicing industry. India alone produces over 1 million tons of apple pomace waste per year, of which only 1 % is utilized [1] Globally, A.P waste produced is estimated to be as high as 4 million tons annually [2]. The extraction of pectin commercially uses harsh mineral acids (HCl), creates harmful wastewater, requires high energy inputs, and has a direct negative effect on the quality of pectin being extracted. The objective of this research is to optimize the extraction of pectin from A.P using environmentally friendly processes through organic acids that matches or surpasses current industrial methods. This paper aligns with a circular economy initiative of the reintroduction of apple pomace into the food industry as a valuable waste stream. High quality extracted pectin is then incorporated into food packaging systems for use in the bread sector to promote the future use of effective and sustainable packaging systems.

EXPERIMENTAL

Four separate extraction solutions will be prepared using HCl, Citric Acid (CA), Lactic Acid (LA), and Acetic Acid (AA). Apple pomace will undergo acidic treatment individually with each acid. Four parameters are assessed in this work; Extraction time, Precipitation time, pH, and Temperature. Following extraction, pectin is redissolved in a formulated solution before film casting. Subsequent films are then analysed and characterised for their use in the protection of bread products.

RESULTS AND DISCUSSION

Green, organic extractions achieved similar, or greater pectin yields when compared to harsh mineral acids, such as HCl. Environmentally friendly extraction techniques were achieved through shortened precipitation times, reduced energy consumption, and the use of organic acids. The pectin extracts examined by FTIR spectrum all achieved a demethylation (DM) value of > 50 %. The significance of this is the extracted pectin will form a gel within an acid-based system (pH 2.0 - 3.5). All DM values confirmed through titration methods that use phenolphthalein as an indicator. C.A. consistently preformed best when compared to other acids, due to the enhanced solubility of pectin within citric acid solutions. Citric Acid can extract > 20 % pectin yield at 70 ºC, for 1 hour, at pH 2.5 following a precipitation period of 20 minutes. The use of organic acids in this research has numerous advantages when compared to commercial standards; Biodegradable, less corrosive, lower toxicity, reduced environmental impact (renewable resources), regulatory compliance (GRAS), easier waste treatment. High methoxyl pectin (HMP) can form compact mechanical structure in the production of biodegradable films. With the addition of glycerol, the application of hydrophobic coatings, and controlled atmosphere conditioning, this packaging system boasts significant potential for food packaging applications ***(Figure 1).***

CONCLUSION

This work successfully demonstrates the potential of pectin to be used in the food packaging sector in an environmentally friendly manner. The abundance of apple pomace waste annually is a lost opportunity at taking advantage of a valuable resource that can contribute to circular economies. For a process to be truly environmentally friendly, all aspects must be scrutinized. Therefore, pectin's extraction process has been thoroughly analysed and improved to meet these standards. The incorporation of waste streams, environmentally friendly extractions and formation of biodegradable films is in-keeping with current industrial trends and consumer expectations, and contributes to the overall ambition of creating a sustainable future.

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Figure 1: Comparison of ethanol casting vs controlled atmosphere oven condition

OC 15A

Critical cooling rate of fast-crystallizing polyesters: the example of poly(alkylene *trans*-1,4-cyclohexanedicarboxylate)

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Polymers play an increasing role in manufacturing processes, and their production keeps on growing, especially in the packaging industry [1]. However, the decline of fossil resources, and the raise of collective awareness about the impact that waste has on the environment, impose to look for possible alternatives to petroleum-based polymers with reduced environmental risks. For this reason, bio-sourced and/or biodegradable polyesters have attracted much attention from both academic researchers and industrials.

Industrial processing techniques such as injection molding or additive manufacturing (laser bed fusion, 3D-printing…) often involve extremely high cooling rates, with major consequences on polymer microstructure and molecular mobility. Controlling the cooling rate and understanding its consequences on polymer properties remain a major challenge. Conventional calorimetric measurements provide scanning rates generally limited to a few tens of degrees per minute. Fast Scanning Calorimetry (FSC) allows the extension of the experimental window of several orders of magnitude (in terms of scanning rate), giving access to cooling rates up to 40000 K s^{-1}, which is ideal to reproduce industrial processing conditions [2].

A series of biodegradable and potentially bio-based thermoplastic polyesters was synthesized from trans-1,4-cyclohexanedicarboxylic acid and diols of different lengths. These materials have interesting barrier and mechanical properties for food packaging applications [3-7], but also a very different aptitude to crystallize depending on the number of methylene groups in their repeating unit (odd-even effect). The cooling rate required for full quenching is thus very different for each one of these materials, with different consequences for the ones being able to crystallize compared to the ones that cannot.

This work illustrates how to estimate the critical cooling rate for fast-crystallizing polyesters, and the possible consequences of a fast-quenching process on an amorphous polyester [8], taking the example of a series of poly (alkylene trans-1,4-cyclohexanedicarboxylate) (PCHs) with a number of methylene groups varying from 3 to 6.

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OC 16A

Sustainable advances in furan-based polymers: from biobased monomers to polymers and recycling

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INTRODUCTION

Polymeric materials are ubiquitous in our daily lives due to a set of exceptional properties (e.g., lightweight, durability, and versatility) [1]. However, they are still predominantly synthesised from fossil resources, they are overused, and, moreover, they commonly have a non-circular fate after use, hence, raising severe pollution and climate changes issues [1]. In this context, Sousa group started a burgeoning surge for more sustainable approaches to polymers, targeting their circularity. In particular our group focused on the investigation of biobased key building-block chemicals such as, for example, the 2,5-furandicarboxylic acid (FDCA), for polyesters and polyesteramides, their greener synthesis, as well as their ensuing recycling.

RESULTS AND DISCUSSION

In this work the synthesis and characterisation of poly(ethylene 2,5-furandicarboxylate) (PEF) [1]), poly(trimethylene 2,5-furandicarboxylate) (PTF), and several other (bio)degradable aliphatic-furanic copolymers were achieved by a simple bulk polyesterification approach, or instead using atomeconomy Ring Opening Polymerization approach [2]. Structure-property studies through thermal and X-ray diffraction analysis showed the ability to modulate properties depending on the molar composition of stiff furanic moieties. Further, the potential of urea : zinc acetate deep eutectic solvent (DES) to assist the continuous, eco-friendly and closed-loop approach for their recycling polyesters into virgin-quality recycled polymers in high yield was also demonstrated (Figure 1) [3].

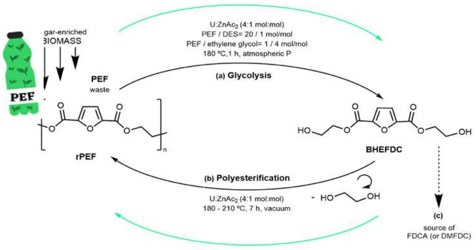

Figure 1 Advanced recycling of PEF through continuous greener DES-assisted de-/repolymerisation approach.

CONCLUSION

Our research demonstrates key advances in the lifecycle of poly(2,5-furandicarboxylate) (PFD), from initial polymerisation to recycling, fostering the development of polymers with enhanced properties and the circular economy.

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OC 17A

Non-isocyanate, Bio-Based Covalent Adaptable Networks based on Polyaspartic esters

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ABSTRACT

Polyaspartic esters (PAE) are a type of two-component (2K) thermosetting coating resins with a fast curing speed, low viscosity, and good chemical and weather resistance, which use a low amount or even no volatile organic compounds (VOC) [1]. PAE finds applications as coatings for e.g. building decoration, metal anti-corrosion, UV light protection, etc. However, the classical synthesis route of PAE uses toxic isocyanate chemicals, which are hazardous to health, and REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) is restricted [2]. Considering the thermoset nature of the resulting coatings, they are difficult to repair upon the damage, limiting their lifetime and thus durability. One strategy to overcome these challenges is the implementation of reversible covalent bonds in the PAE network [3]. Herein, vinylogous urethane covalent adaptive networks (VUCANs) were designed and investigated via a solvent-free, green synthesis route without the need for toxic isocyanates using biobased raw materials.

The VUCAN-based coatings show good chemical resistance and mechanical properties in combination with good cross-linking efficiency. The VUCANs have good creep resistance and the selfhealing potential of the coatings was demonstrated. Next to the good functional properties of the VUCAN-based coatings, they decrease environmental impact compared to the commercial products. As such they act as an advanced candidate to replace the traditional PAE coatings.

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OC 18A

Upcycling of potato and tomato pomaces for the fabrication of sustainable metal food packaging

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Keywords: Food packaging; Circular bioeconomy; Sustainability; Food by-products.

Food packaging protects food during its transport, handling, and storing, extending its shelf life and maintaining its nutritional value and sensory qualities. A wide variety of materials is available in the current food packaging market. Among them, metal packaging appears as the best solution for the protection of food for long periods and harsh logistics. Most used metals for can fabrication are aluminum, coated steels, and stainless steels. Depending on the chemical nature of the metal and the canned food, an inner polymer coating is needed to prevent metal corrosion and the migration of toxic substances from the metal to the food. Until now, bisphenol A (BPA) lacquers have been massively used as can coating mainly due to their excellent anti-corrosion behavior, mechanical robustness, thermal stability, chemical inertness, easy processability, and low price. However, recently its use has been banned in Europe, making necessary the quest for alternatives.

In this work, we present the upcycling of tomato pomace (the resultant by-product of industrial tomato fruit processing) and industrial potato peels as a source of fatty acids by using a basic media. After, and based in our previous studies [1-3], the fabrication of bio-based lacquers by green and large-scalable methodologies without the use of catalysts will be showed. This method consists in the spraying of the metal substrates with the fatty acids' solutions in green solvents followed by a melt polycondensation in an oven. Moreover, the main properties of these lacquers in terms of morphology, mechanical properties, water and oil contact angles, and anticorrosion performance will be presented and compared with commercial BPA-based resins. Finally, the overall sustainability of the process will be analyzed by life cycle assessment (LCA).

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OC 19A

Introduction of bark extracts in furan-based polyester for the realization of sustainable active packaging

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INTRODUCTION

The development of sustainable materials with improved functional properties is fundamental for the effective implementation of green chemistry and circular economy principles. The work focuses on the preparation of fully biomass-derived blends from furan-based polyester and natural extracts to yield an innovative active packaging.

EXPERIMENTAL

Poly(hexamethylene furanoate) (PHF) was synthesized by a two-step solvent-free polycondensation. Triterpenoids and suberin were isolated from silver birch (Betula pendula) bark through subsequent solvent extractions and methanolysis processes. Bark extracts/PHF blends were prepared by compression moulding the solvent-cast mixtures of the two components.

RESULTS AND DISCUSSION

The blends were characterized from the molecular, structural, thermal and mechanical point of view. Other functional properties such as gas barrier and antioxidant/antimicrobial activity were also tested. The results evidence a modulation of the surface hydrophobicity, a significant increase in flexibility and toughness, excellent gas barrier performance. The addition of natural extracts allows for the implementation of antioxidant and antibacterial features otherwise absent in the pristine polymer [1].

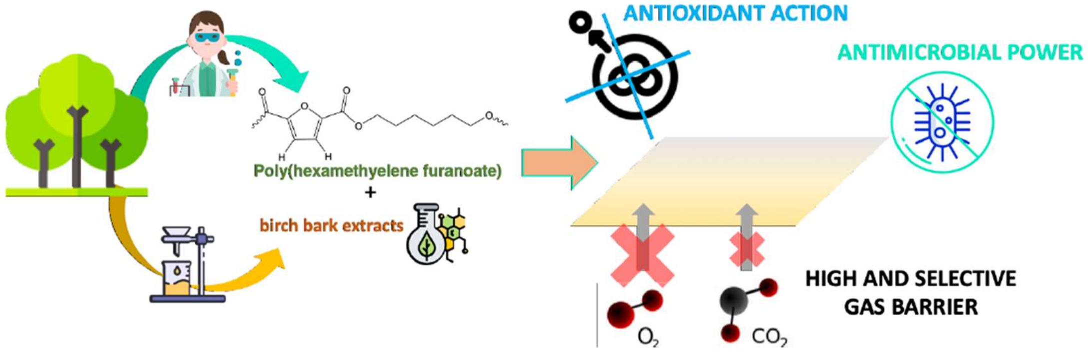

Figure 1. General representation of the study.

CONCLUSIONS

The incorporation of the bark extracts permitted to modulate the physico-mechanical characteristics of the polymer matrix depending on the nature and content of the filler and to introduce additional features to obtain fully biomass derived active packaging.

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OC 20A

Agro-food by products valorization in active coatings on plastic and cellulose substrates

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INTRODUCTION

Chitin, chitin nanofibrils (Chn) and chitosan are proposed as coating on plastic and cellulose substrates to improve barrier to oxygen and introduce anti-microbial activity on the substrates. Chitin/chitosan can be derived from traditional crustaceous sources but most recently are proposed even from alternative sources such as insect's exoskeleton. Farming of insects is an emerging, growing activity with positive exploitation in proteins production for animal feed and also investigated for potential degradation of plastics in soil as investigated in the CBE project RECOVER GA. 887648 "Development of innovative biotic symbiosis for plastic biodegradation and synthesis to solve their end of life challenges in the agriculture and food industries". Chitosan and chitin coatings on plastic films are further exploited in new project for the production of active, soil biodegradable mulch and food packaging films.

EXPERIMENTAL

Chitin, Chn and chitosan either from crustaceous and insect's sources were applied as wet coating after dispersion in aqueous/acetic acid solvent, on lab. and pilot scale, on cellulose substrates, on industrially compostable food contact plastic films, PBS/PHBV based, or on mulch films PBAT/starch based.

RESULTS AND DISCUSSION

Morphology, thermal, mechanical, barrier properties were compatible with planned applications in packaging and mulching. Films were validated respectively on perishable food (chicken breasts) and in open field.

Figure 1. Food packaging and mulch plastic films coated with chitosan and chitin nanofibrils

CONCLUSIONS

Chitin/Chitosan either from crustaceous and insect's sources were efficient as active packaging on easy perishable food, chicken breasts and as mulches tested in open field for weed and pests control.

ACKNOWLEDGEMENTS

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OC 21A

Advancements in the synthesis of furan-based polyesters via ring opening polymerization

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INTRODUCTION

Synthetic polymers constitute a vast family of unique and versatile materials having outstanding properties, where polyesters (PEs) are one of the most widely produced class due to their broad range of applications, spanning from packaging materials to medical devices. In recent years, in a quest for more sustainable polymers, PEs synthesis turned to a drop-in strategy replacing fossil-based buildingblocks by renewable counterparts [1,2]. In this vein, furan-based polyesters are some of the most spotlighted polymers, although their synthesis still rely on energy-intensive bulk polymerization approaches, besides the need to remove by-products to shift the equilibrium and attain high molecular weight (MW) polymers. To overcome these issues, ring opening polymerization (ROP) of macrocyclic esters has been proposed as an attractive and promising alternative strategy to yield high MW polyesters with atom efficiency, according to Green Chemistry principles [3].

RESULTS AND DISCUSSION

Herein, in the one hand, the synthesis of two furan-based macrocycles, namely macrocyclic ethylene 2,5-furandicarboxylate (CEF) and macrocyclic hexamethylene 2,5-furandicarboxylate (CHF) via cyclodepolymerization of the corresponding low MW linear polyester species under high dilution conditions will be discussed. On the other hand, the ROP of these two macrocycles, employing different reaction conditions aiming to produce high MW polyesters will also be assessed. Structural characterization of ensuing biobased polyesters, using various analytical techniques will be addressed.

CONCLUSION

The present work focuses on employing greener routes for the synthesis of poly(alkylene 2,5furandicarboxylate)s with high molecular weight using mild reaction conditions and biobased furan monomers. This aligns with the broader goal of reducing dependence on fossil resources and minimizing the environmental footprint of polymer production.

Acknowledgments

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OC 22A

Sustainable Active Food Packaging: Incorporation of Humic Substances into Electrospun Films

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INTRODUCTION

This study develops composite films of electrospun poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer with humic substances (HS) as natural additives [1,2]. HS are known for their phenolic and carboxylic groups, which promote plant growth and have antiviral and anti-inflammatory properties. Despite their potential, HS are not widely used due to leakage and degradation in aqueous environments and are typically considered waste and used mainly for soil amendment. This research uses HS as natural fillers in a polymeric matrix to develop reproducible systems with remarkable biocidal activity, even with less refined industrial bio-waste. Several emulsions composed of PHBV in trifluoroethanol and different amount of HS in aqueous solution, have been prepared to produce bioactive, biodegradable, and sustainable nanocomposite nanofibers (PHBV/HS) through the electrospinning technology. These electrospun mats were converted into 'biopapers' (PHBV/HS films) and characterised for their morphological, thermal, optical, moisture/light barrier, mechanical, antioxidant, antibacterial and antifungal properties to assess their potential for active biopackaging.

RESULTS AND DISCUSSION

The resulting materials exhibit remarkable antioxidant, antimicrobial, and antifungal properties, making them very suitable for food packaging applications. The films demonstrated promising water vapor and limonene permeability, as well as favourable optical and mechanical properties, indicating their potential for preserving food freshness and aroma. The PHBV/HS film effectively preserved cherries during a 14-day storage period at room temperature, maintaining freshness and quality due to its antioxidant, antimicrobial, and barrier properties. These findings underscore the potential of PHBV/HS films to extend the shelf life of perishable fruit and vegetables.

CONCLUSIONS

This study highlights a significant achievement in the field of electrospinning technology by producing fibers composed of PHBV biopolymer and HS used as functional natural additives. For the first time, HS extracted from a commercially available agrifood compost supplied by the Sardinian company Verde Vita (s.r.l.), was explored as natural functional fillers for polymeric matrix, obtaining reproducible systems with outstanding biocide action even using a less refined industrial bio-waste. This novel approach integrates electrospinning with a waste-to-wealth strategy. Electrospinning effectively regenerates and upgrades HS, overcoming key limitations in their use. The combination of low-cost, highly bioavailable HS with a biodegradable support offers a promising strategy to increase stability, reduce costs and improve circularity of materials.

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OC 1B

Effect of hydrophilicity and stiffness of PCBE-based copolymers on stem cells' long-term culture

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INTRODUCTION

The proper tuning of mechanical properties of biomaterials is for sure one of the main objectives of tissue engineering, as cells are able to transform physical stimuli coming from the external environment into biochemical signals [1]. These last, in turn, can induce cells to assume a peculiar shape and/or function [2]. Therefore, the *in vitro* study of the effect of these stimuli on stem cells as well as the mechanotransduction pathway involved in the process is of primary importance.

EXPERIMENTAL

To this aim, a random copolymer of poly(butylene *trans*-1,4-cyclohexanedicarboxylate) (PBCE) containing ether oxygen atoms was synthesized by melt polycondensation and processed in compression moulded film. Molecular characterization as well as thermal, wettability, and stress–strain measurements were carried out. After preliminary long-term adhesion and proliferation analysis of bone-marrow multipotent mesenchymal/stromal cells (hBM-MSCs), the expression of proteins involved in the mechanotransduction process was also studied.

RESULTS AND DISCUSSION

According to the results obtained, the solid-state properties can be nicely tailored simply acting on chemical structure. Thus, the copolymer is characterized by a higher hydrophilicity and a lower elastic modulus than PBCE, thanks to the presence of ether oxygen atoms. Cell proliferation and viability were good on both the films with respect to the control. Interestingly, by culturing hBM-MSCs on films, the activation of distinctive mechanotransduction pathways was demonstrated, resulting in the acquisition of an elongated cell shape on the copolymeric film and the maintenance of the canonical morphology on PBCE (Figure 1), as a consequence of the different stiffness of the substrates.

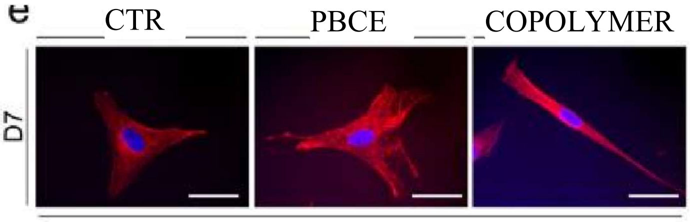

Figure 1. Example of hBM-MSCs cultured on films compared to control (CTR) after 7 days of culture.

CONCLUSIONS

The materials under investigation were both suitable for the long-term culture of hBM-MSCs. However, through a proper chemical modification and, in particular, the tailoring of mechanical stiffness, it was possible to trigger the reorganization of the cytoskeleton architecture and the acquisition of a new morphology in hBM-MSCs.

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OC 2B

Blends of thermoplastic polysaccharides plasticized with deep eutectic solvents

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INTRODUCTION

Natural eutectic solvents NADES [1] are a class of eutectic solves (DES) of great interest today due to its interesting characteristics such as low volatility, water-compatibility, non-flammability, nontoxicity, biodegradability, biocompatibility and its origin from natural resources [1]. These solvents are considered one kind of ionic liquid with several advantages over ILs being their use as solvent and plasticizers for biopolymers increasing recently. A wider classification for DES that did not show melting point, but instead, glass transition temperature is the class of the low temperature transition mixtures (LTTMS) [2].

Here we describe thermoplastic chitosan plasticized with tow kind of choline chloride-based DES and its blends with glycerol-plasticized thermoplastic starch. The addition of chitosan to TPS can improve not only its mechanical properties, but also given to it biocide and fungicide characteristics.

EXPERIMENTAL

Choline chloride and glycerol or polyol were mixed in proportions chloride/glycerol (1:2) and choline chloride/aliphatic polyol (1:1) at 100°C giving rise to a clear viscous liquid. The polyol is a ten carbon and four hydroxyl groups molecule ($C_{10}H_{24}O_4$) and was described in [3]. The mixtures were cooled to room temperature, mixed with chitosan in a mortar, and stored overnight in order to diffuse into chitosan. Starch was mixed with glycerol in the proportions of starch/glycerol of 80:20 and 75:25 and stored overnight prior processing. Blends were processed in a 16 mm extruder at a temperature profile from feed to die of 100°C, 105°C and 110°C. Materials were characterized by DSC. DMA and MEV and mechanical tensile tests. Chitosan content in TPS blends was varied from 3.5 to 10 wt%.

RESULTS AND DISCUSSION

LTTM based on choline chloride and glycerol or polyol proved to plasticize chitosan allowing the preparation not only thermoplastic chitosan, but also clear blends with TPS. Figure 1 shows pictures of a film with 1 mm thickness, optical microscopy of a thin film and scanning electron microscopy of fragile fracture surfaces of the PTS film and its blends containing 5% of chitosan. Thermal characterization and mechanical properties confirm the plasticization of DES to chitosan.

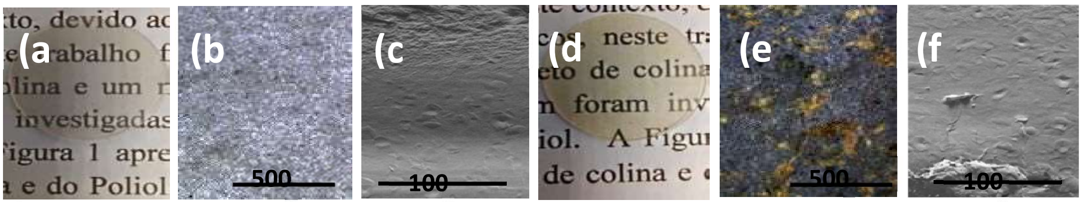

Figure 1. (a), (b) and (c) TPS and (d), (e) and (f) TPS/chitosan 95:5 for the films, optical mic. and SEC, respectively

CONCLUSIONS

Thermoplastic chitosan and its blends with TPS were prepared by extrusion of chitosan/DES and chitosan/DES with starch/glycerol. The process used proved to be efficient for the production of thermoplastic chitosan compositions, allowing its wide use in several areas of interest, such as in films by extrusion and other products by injection molding and other technique applied for thermoplastic materials. The authors acknowledge Suzano SA, CAPES and CNPq.

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OC 3B

Optical properties and recyclability of polycarbosilane containing bio-based bifuran structure

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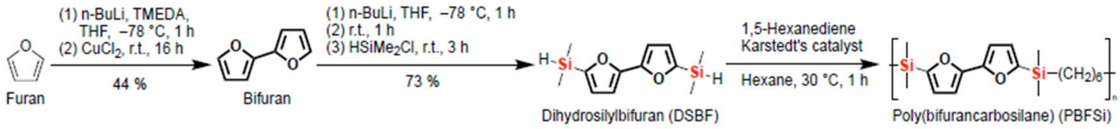
INTRODUCTION

Two of the most fundamental principles for the development of next-generation polymers are production from renewable biomass and well-designed recyclability. Bifuran derivatives represent promising building blocks for functional polymers on account of their high rigidity, strong inter-chain interactions, and extended π-conjugation.[1] In this study, a polycarbosilane (PBFSi) containing a bifuranbased repeat unit was prepared via the hydrosilylation of dihydrosilylbifuran and 1,5-hexadiene (Scheme 1). [2]

Scheme 1. Synthesis of poly(bifurancarbosilane) (PBFSi).



RESULTS AND DISCUSSION

The crystallinity and thermal properties of the bifuran-based polycarbosilane were superior to those of an analogous compound containing a single-furan-based repeat unit and comparable to those of the benzene-based analogue, due to the rigidity and inter-chain interactions of the poly(bifurancarbosilane) unit. The bifuran structure causes a red-shift and strong UV absorption in the polycarbosilane compared to those bearing the single-furan-based and benzene-based analogues. Additionally, the bifuran structure is strongly fluorescent, while the polycarbosilanes containing the benzene and single-furan rings did not exhibit fluorescence. These desirable photoproperties result from the extension of the σ-π conjugation. Furthermore, the chemical recyclability is a unique and attractive property of the bifuran-based polycarbosilane; the generated bifuran can regenerate the monomer, and the trifluoroacetate silane can be up-cycled to polysiloxane (Figure 1).

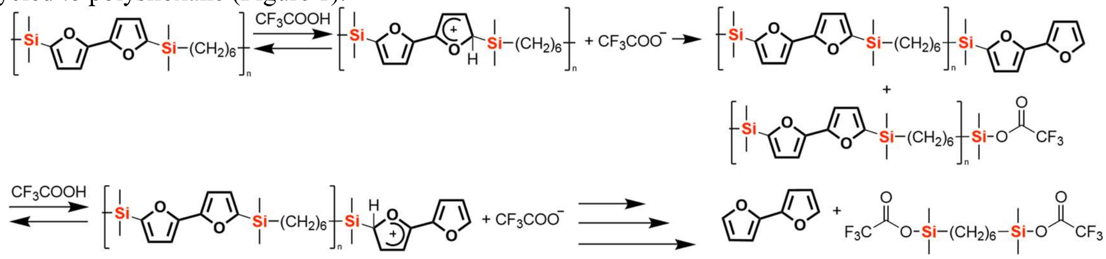


Figure 1. Plausible mechanism of the proto-desilylation of PBFSi with TFA

CONCLUSIONS

The bifuran-based polycarbosilane exhibits superior optical properties and unique chemical recyclability.

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OC 4B

Detection and quantification of biodegradable nano and microplastics in biowaste compost

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INTRODUCTION

The end-of-life of compostable packaging can be treated by industrial composting in combination with biowaste to be converted into compost. As this compost is then used as an agricultural soil improver, it is essential to analyze the transient and persistent degradation products, such as micro- and nano plastics, generated by biodegradable and conventional plastics. There is currently no standardized method for detecting and quantifying nano and microplastics in such a complex organic matrix [1]. This study will develop an effective, non-destructive protocol to identify and quantify biodegradable and conventional micro- and nano plastics present in compost using FTIR and Raman micro spectroscopy, and thermal analysis (Pyrolysis-GC-MS) [2].

EXPERIMENTAL

Micro- and nano plastics were extracted from the compost matrix by density difference and oxidative digestion (Fig. 1). Based on their chemical fingerprint, microplastics were identified and quantified (mass estimated by calculation from surface area, volume, and density) by µFTIR, and nano plastics by µRaman spectroscopy. Pyr-GC-MS was used to quantify the polymer content of microplastics.

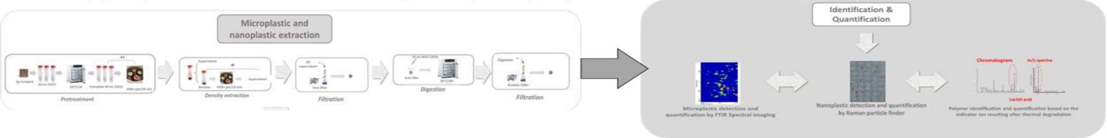

Figure 1: preparation and analysis process

RESULTS AND DISCUSSION

The methodology for extracting microplastics from compost has been optimised and validated, with a recovery rate of over 92%. This was achieved while preserving the physical and chemical integrity of microplastics. Analysis of the biodegradable microplastics in a compost sample yielded a correlation coefficient of at least 70% against the internal library of reference spectra representing known materials (Table 1). The analysis time was relatively short for FTIR (4 hours per sample), as previously reported by Song et al. [3] and much longer for Raman.

Table I: Analysis FTIR results for compost sample

Material	Corr (%)	Area_mean (μm^2)	Thickness (µm)	Volume (μm^3)	Density ($g.\mu m^{-3}$)	Mass_mean (µg)	SD
PBAT/Starch	90	9,87 x 10^6	48	0,47 x 10^9	1,30 x 10^{-12}	616	2
PLA	70	0,70 x 10^6	381	0,27 x 10^9	1,30 x 10^{-12}	346	132
PHBV	70	0,03 x 10^6	720	0,02 x 10^9	1,30 x 10^{-12}	30	15

CONCLUSIONS

A simple and effective method for extracting biodegradable and micro- and nano plastics from compost was developed and validated. Several analytical techniques using infrared and Raman microspectroscopy and thermal analysis were also proposed for identification and quantification.

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OC 5B

Biobased lubricant from modified vegetable oil: Impact on tribological properties

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Abstract

Growing environmental concerns are driving demand for vegetable oil-based lubricants, valued for their lubricity and biodegradability. Chemical modifications enhance stability and lubricating properties, addressing limitations such as the presence of unsaturated fatty acids and improving the capacity to serve as a base oil for the dispersion of nanoadditives. This study synthesize a biolubricant (ESBO-M1) from Epoxidized Soybean Oil (ESBO) under mild reaction conditions and in the absence of catalysts or solvents. The capacity of the oil to disperse graphene over long periods was observed and physicochemical properties of the oils were analyzed, exploring friction reduction in a pin-on-ring system. A pin was pressed against a rotating ring, with line contact geometry, applying a constant load of 30N (Maximum Hertz pressure of 220 MPa). Friction tests were performed at sliding speeds ranging from 0.04 to 1.49 m/s. The results reveal the capacity to maintain a stable graphene suspension and enhanced performance, particularly in boundary lubrication, showcasing the potential for environmental sustainability and improved tribological properties.

INTRODUCTION

Due to the concern about environmental sustainability, the demand for lubricants derived from vegetable and renewable oils are increasing. These base oils have excellent lubricity, viscosity index (VI) and biodegradability. However, vegetable oils have poor thermal and oxidative properties due to the presence of unsaturated fatty acids and lack of capacity to maintain a stable dispersion of nanoadditives such as graphene [1]. Through chemical modification, such as epoxidation it is possible to replace the unsaturations with an oxirane ring that improves the stability of the oil and its properties as lubricant [2]. In the field of tribology, most lubricants form a thin film between surfaces to separate them, reducing friction and wear. This film forming capacity was early studied by Stribeck curve, relating the coefficient of friction (COF) to oil viscosity, applied load and speed, considering three lubrication regimes (boundary, mixed and hydrodynamic) [3]. This curve allows for understanding the performance of formulated lubricants. The chemical composition of most biolubricants consists of fatty acid (FA) esters which form a thin film at the point of contact between two objects. The performance of boundary lubrication is influenced by both the attraction of the lubricant molecules to the surface and any potential reactions with the surface [4]. The present study aims to synthesizing a biolubricant from epoxidized soybean oil (ESBO) by their reaction with a compound (ESBO-M1) at mild reaction temperatures without the use of catalysts or solvents, and to analyse this biolubrificant capacity to maintain a stable dispersion of different graphene percentages (0.01 to 0.08%). Additionally, the ability of the biolubricant to reduce friction, measured by the coefficient of friction, in a tribological system employing the pinon-ring configuration was also evaluated.

EXPERIMENTAL

Briefly, ESBO, and the reactant compound were added to a 250 mL reactor equipped with a mechanical stirrer, and then placed in a silicon bath at 80 °C (Fig.1a). The molar ratio ESBO: reactant compound used in all the reactions was 1:10. The reaction was allowed to proceed for 10 h. At the end of the reaction, the oil is purified with temperature and vacuum. For graphene suspensions, the different graphene percentages were added and dispersed using ultrasound. To understand the capacity of our lubricant to form a film in different lubrication regimes, a pin on ring tribometer model was used, a pin was pressed against a rotating ring, with line contact geometry, applying a constant load of 30N (Maximum Hertz pressure of 220 MPa) (Fig.1b). Friction tests were performed at sliding speeds ranging from 0.04 to 1.49 m/s.

RESULTS AND DISCUSSION

Considering the Stribeck curve (Figure 1), it is possible to conclude that modification ESBO-M1 it is the best and this biolubricant, is excellent in reducing coefficient of friction (COF) in all lubrication regimes, especially at boundary lubrication.

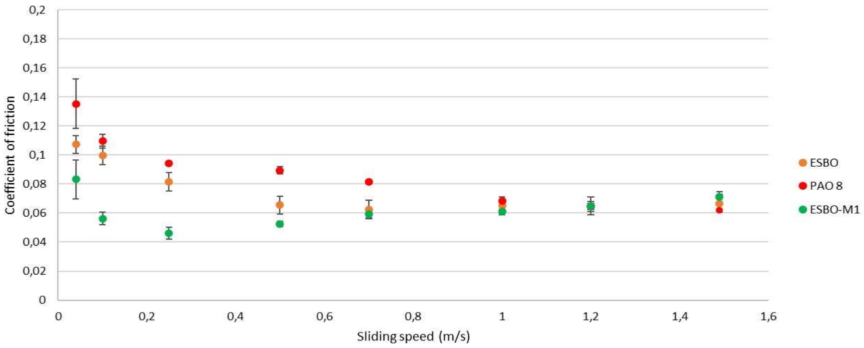

Figure 1 Stribeck curve for commercial base oil (PAO 8), ESBO and synthetized biolubricant (ESBO-M1).

CONCLUSIONS

It is possible under mild conditions reaction to obtain a biolubricant with improved chemical and tribological properties by the chemical modification of vegetable oils. Mainly the lubricant ESBO-M1, show remarkable effectiveness in reducing (COF) in all lubrication regimes, particularly in boundary lubrication and allow the stable dispersion of graphene in different percentages. That biolubricant with excellent properties can be used as base oil in different applications.

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OC 6B

From problem to solution: bioadsorbents and plasticizers derived from *Rugulopteryx okamurae*

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INTRODUCTION

Rugulopteryx okamurae (RO) is a species of brown seaweed belonging to the *Dictyotaceae* family, that recently invaded Mediterranean coasts, including the Spanish and Portuguese shorelines. RO is rich in polysaccharides, dietary fiber (soluble and insoluble), carotenoids, vitamins, minerals, fatty acids, and polyphenols [1]. For this reason, RO has an enormous potential as a source of novel functional materials with specific applications. The aim of this work is the integral valorisation of RO by microwave assisted extraction (MAE), after a pre-treatment with natural deep eutectic solvent (NADES), to obtain fractions rich in fatty acids that can be used as plasticizers in food packaging materials. In addition, the solid residue obtained after the MAE process has been evaluated as bio-adsorbent to remove heavy metals from residual waters.

EXPERIMENTAL

RO powder was mixed with NADES, and microwave heating was performed in a closed vessel for 15 min at 100 °C. Then, the powder obtained was used for the oil extraction. MAE was performed for 30 min at 56 ºC, using 2:1 solvent-solid ratio. The fatty acid composition was determined by gas chromatography-mass spectrometry (GC/MS). Sodium alginate (SA) films were prepared by casting using a 20 wt% glycerol (control) or RO oil at different concentrations (10 wt%, 20 wt%, 30 wt%). Optical, thermal, mechanical and barrier properties were evaluated. Adsorption tests were performed using 300 mg of solid residue and 50 ppm of cadmium, nickel, lead, and cobalt stock solutions. Contact between films and solutions was maintained for 3 h under magnetic agitation. The metal concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP/OES).

RESULTS AND DISCUSSION

The incorporation of RO oils to SA films did not affect significantly the thermal and barrier properties ($p>0.05$), even though some slight changes were observed with the addition of RO oil extract at different concentrations when compared to the control film, with OTR.e value of 0.7 ± 0.1 cm^3 mm m^2 day. However, the mechanical properties of films are significantly improved by the incorporation of the RO oil ($p<0.05$). The tensile strength and the elastic modulus increased in SA films with RO oil, but no significant differences ($p>0.05$) were observed between the different concentrations of RO oil. Finally, the adsorption tests showed that the RO solid residue can remove more than 80% of the analysed metals, with an adsorption capacity of 75 ± 1, 36 ± 2, 44 ± 1 and 98 ± 1% for cadmium, cobalt, nickel and lead, respectively, when a multi-standard solution was used.

CONCLUSIONS

The results confirmed the potential use of RO oil as a suitable plasticizer for alginate-based films and the solid residue obtained after MAE process as an adequate bio-adsorbent for heavy metals in waters.

ACKNOWLEDGMENTS

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OC 7B

New antifungal encapsulation systems based on HP-β-cyclodextrin, chitosan and essential oils for conservation of organic-media cultural heritage

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INTRODUCTION

Biological colonization represents one of the main causes of degradation in organic-media artworks. Biocidal and preservative products currently available on the market for conserving and restoring cultural heritage are based on Quaternary Ammonium Salts (QACs). However, there are increasing concerns regarding their safety and eco-toxicity profiles, as well as the risk of developing bio-resistance due to their intensive use [1]. Recently, research has focused on studying plant-based bio-active substances, such as essential oils, which have already demonstrated good antifungal properties [2]. In this context, the present study evaluates the use of two essential oils (lavender and rosemary) encapsulated in a polymer matrix as antifungal treatment for artworks. The main goal of this work is to obtain a ready-to-use formulation allowing homogeneous application of the bio-active substance in an aqueous medium, without using surfactants or solvents that may interfere with the artistic substrates.

EXPERIMENTAL

The chemical profile of lavender and rosemary essential oils (EOs) were obtained by GC-MS and FTIR. EOs were encapsulated in HP-β-cyclodextrin and chitosan by Spray drying. Thermogravimetric and differential scanning calorimetry analysis (TGA, DSC) of encapsulated samples was performed, whereas morphological analysis was carried out by scanning electron microscopy (SEM). The timedependent release of volatile compounds from encapsulated EOs was evaluated by HS-SPME-GC-MS. Antifungal activity of encapsulated samples was studied towards fungi previously isolated from an historic newspaper archive (1921) and identified by molecular techniques (DNA extraction and fungi identification). Antifungal activity was tested in poisoned culture media (PDA) and on paper support, and monitored for 12 days at concentrations of 50, 100, and 150 mg/mL.

RESULTS AND DISCUSSION

Encapsulated materials showed good performance in terms of Encapsulation Efficiency and Yield, with values of 95% and 54% for encapsulated lavender (LEEO), and 86% and 76% for encapsulated rosemary (REEO), respectively. The studied materials also showed improved thermal stability and spherical morphology. Antifungal *in vitro* tests demonstrated up to 90% of growth inhibition for mycelial plugs, while a complete absence of growth was observed for the pre-germination phase. The paper models treated with LEEO and REEO and subjected to artificial aging showed a colorimetric variation $\Delta E<3$ and a surface pH of 6.5.

CONCLUSIONS

This research has demonstrated the potential of using antifungal encapsulated essential oils for the conservation of artistic objects in cultural heritage. These materials can perform a dual action by preserving the artworks from biological damage as well as acting as a deacidifying treatment for the support.

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OC 8B

Compostable solutions for food packaging aiming at reducing landfill disposal and food waste

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INTRODUCTION

Plastics consumption has grown significantly in recent years, reaching 390.7 MT in 2021, 44% of which was used for packaging [1]. This turns into a large increase in the accumulation of plastic waste and, therefore, packaging waste in landfills. To curb this trend, different strategies have been investigated, as the development of compostable solutions, in line also with the European strategy for plastics [2].

Biomaterials need to be optimized for food packaging applications in order to have a similar behaviour than conventional materials, hence different studies such as the incorporation of active substances, biocomposites or nanosized particles have been done lately [3]. The extension of the use of compostable materials could reduce the accumulation of waste in the environment and the emission of greenhouse gases, thus ensuring a sustainable use of natural resources [4].

The study carried out by ITENE has focused on the development of compostable formulations to optimise the process of converting in final packaging and their mechanical properties, considering the application of coatings to improve barrier properties. Thus, the objective has been to reduce waste of flexible and rigid food packaging by developing organically recyclable materials suitable for diverse applications, such as fresh salad or ready-to-eat products.

EXPERIMENTAL

Different compostable formulations based on PBSA (poly (butylene succinate-co-adipate)) were developed by compounding technologies, combining it with other biopolymers and inorganic/organic additives. These compounds were employed to obtain flexible films by using blown film extrusion processing combined with coating technology applied by rotogravure printing, while rigid trays were processed by injection molding. Films were used to form bags in which fresh-cut salad was packed and trays were employed to preserve ready-to-eat rice. Shelf life was analyzed by determining different parameters such as atmospheric evolution, microbiological load, or sensory analysis.

RESULTS AND DISCUSSION

In the case of flexible packaging, two coated films were developed, reaching an improvement of barrier to oxygen and water vapor of 92 and 87%, respectively, comparing with the base PBSA. After shelf-life evaluation, it was concluded that both materials were suitable for fresh-cut salad packaging from a microbiological, weight loss and MAP maintenance point of view, up to 5 days after the expiry date.

For rigid packaging two formulations were evaluated, obtaining positive results since the microbiological load was similar to the control reference and the visual appearance of the compostable packaging was excellent at the end of the test. This proved that the materials developed can keep the pre-prepared rice selected in good conditions for human consumption up to 35 days packaged.

CONCLUSIONS

Home compostable materials were successfully developed and validated for packaging applications, demonstrating that can extend shelf life of the food product. As a result of this research, packaging solutions to reduce packaging and food waste, will hopefully be on the market in the near future.

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OC 9B

Brown Seaweed Alginate to Develop p53 Encoding pDNA Nanocarriers for Colorectal Therapy

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INTRODUCTION

Being the third most incident and the second deadliest (1) colorectal cancer (CRC) battle calls for innovative approaches. In the realm of gene therapy non-viral vector are gaining attention as delivery vehicles and p53 has stood as one of the most studied tumor suppressor(2). Biopolymers like alginate are especially attractive due to their low cost, simplicity, and biocompatibility(3).

Overall, this work aimed to develop a biopolymer-based nanocarriers from alginate extracted from brown algae, emphasizing the environmental sustainability and efficiency of this new method. This nanocarrier was then loaded with p53 encoding pDNA (p53) and its biological effect was tested in the CaCo-2 cell line.

EXPERIMENTAL

The sodium alginate was extracted from a brown alga (Saccorhiza polyschides) collected in Peniche (Portugal), the extraction was made by acid treatment followed by an alkaline step, and the biopolymer was characterized by FTIR, H-NMR, SEMEDX, STA and also total polyphenols, and protein content was measured. The extracted alginate was used to formulate p53-encoding pDNA polymer-based nanoparticles. These nanoparticles were characterized by FTIR, SEM/ EDX, and STA. The swelling and release kinetics were also evaluated. Lastly, the nanocarrier was tested in CRC cancer cell line (CaCo-2) and healthy cells (fibroblasts).

RESULTS AND DISCUSSION

The alginate extraction yield reached 20% for optimal conditions, FTIR, STA and EDX analysis confirmed the success of extraction and the polymer purity. The alginate-based nanoparticles showed a mean size of 163.3 ± 12.9 nm, and a PDI of 0.193 ± 0.024, the release of pDNA was pH dependent (Figure 1. A). The nanocarrier loaded with pDNA exhibited 30% cytotoxicity in CRC cancer cells after 72 hours (Figure 1. B).

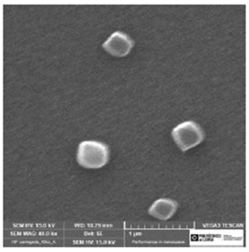

Figure 1- SEM image of Alginate nanoparticles (40 kx)

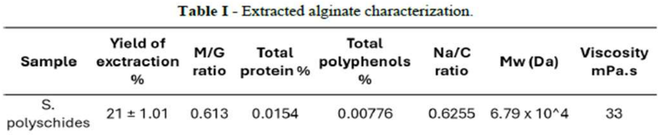

Table I - Extracted alginate characterization.

Sample	Yield of exctraction %	M/G ratio	Total protein %	Total polyphenols %	Na/C ratio	Mw (Da)	Viscosity mPa.s
S. polyschides	21 ± 1.01	0.613	0.0154	0.00776	0.6255	6.79 x 10^4	33

CONCLUSIONS

Comparative analysis showed that this new approach of the traditional extraction method enhances the efficiency and sustainability of sodium alginate extraction.

Due to the simplicity of the nanoparticle formulation and the positive outcomes (such as the size, PDI, encapsulation efficiency, among others), the present nanocarrier shows promising applications in the biomedical field, particularly for CRC therapy. Additionally, there is potential to adapt these nanocarriers to other cancer therapies.

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OC 10B

On the development of novel cellulose derivatives for microplastic flocculation

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INTRODUCTION

Many studies delve into the potential of cellulose as a substitute for common synthetic polymers prevalent in the industrial landscape[1]. Cellulose, being a polymeric material, exhibits several favourable attributes. However, it also poses challenges, such as poor solubility in common solvents and lacks of thermoplasticity. Addressing these limitations requires strategic chemical modifications to enhance cellulose reactivity and permit further derivatizations. In our research, we employed controlled modification strategies, specifically cationic and hydrophobic modifications, to achieve derivatives with different degrees of substitution, molecular weight, and hydrophobicity, aiming at their use as flocculation agents for microplastic removal from wastewaters. The cationization process involved a two-step method: initially, an oxidation with sodium periodate, followed by a reaction with a cationic agent (Girard T reagent). Additionally, hydrophobic modification of cellulose was pursued, grafting fatty acids on cationic cellulose, following to the principles of green chemistry, utilizing renewable feedstocks (i.e., plant oils) as source of fatty acids. The flocculation performance and the ecotoxicity of cationic- hydrophobically-modified cellulose derivatives, with variable substitution degrees (i.e., DS +0.3, +1, +1.8, and DS -1H), were evaluated. Two different model microplastics were used (PE and PET), to access the flocculation performance, and the ecotoxicity was evaluated in four representative species from different freshwater trophic levels.

RESULTS AND DISCUSSION

The obtained derivatives were evaluated regarding their flocculation performance in effluents contaminated with microplastics by laser diffraction spectroscopy (LDS), optical and scanning electron microscopy. The biofloculants developed in this study were found to successfully aggregate and remove model microplastics from aqueous media. The ecotoxicity assays revealed low or absence of toxicity to aquatic organisms in the concentrations used to flocculate the microplastics.

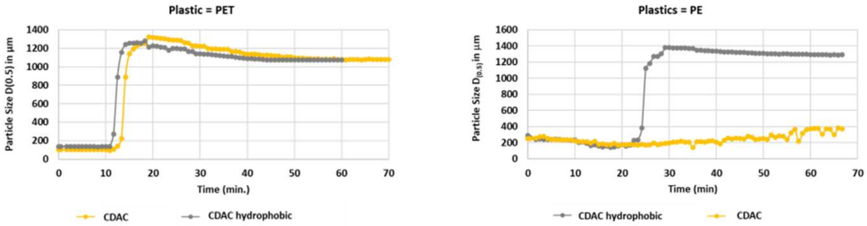

Figure 1. Polyethylene terephthalate (PET) and Polyethylene (PE) flocculation tests using the cationic and hydrophobic cationic cellulose derivative. Evolution of particle size as function of time, using LDS, with a flocculant concentration of 0.001wt%, at room temperature.

CONCLUSIONS

Overall, this work demonstrates that "greener" approaches based on biobased flocculants can be promising solutions for removing microplastics from aqueous media thus contributing to minimize their potential negative effects on aquatic environments.

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OC 11B

Eggshell powder as potential filler for the manufacture of egg boxes based on PBSA

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INTRODUCTION

On the one hand, eggshells are made up of calcium carbonate, which is a commonly used filler in the plastic industry [1]. On the other hand, single-use packaging is one of the major causes of plastic waste in the environment, which is why biodegradable polymers are being explored as an alternative. Poly(butyl succinate-co-adipate) (PBSA) is a type of biodegradable aliphatic polyester that is biobased, biodegradable and biocompatible and characterized by its ductility and toughness, but it lacks stiffness and strength. This study aims to examine how adding eggshell powder (ESP) of different particle sizes and contents affect the mechanical, thermal, and morphological properties of composites based on PBSA. The ultimate goal is to determine if these composites can be used to manufacture thermoformable biodegradable egg boxes.

EXPERIMENTAL

PBSA/ESP composites were prepared with 10%, 20%, and 30% ESP content. The composite with 20% ESP content was selected due to its favorable balance of properties to study the effect of the particle size. The ESP particles were sorted into three different size ranges: 50-125 µm, 125-250 µm, and 250320 µm. The composite materials were prepared using melt mixing, and the required specimens were injection molded. The thermal, mechanical, and morphological properties of these materials were studied to assess their performance.

RESULTS AND DISCUSSION

Figure 1a shows that the stiffness of the material increased significantly with the increase in ESP content. However, both ductility (1b) and impact strength (1c) decreased. On the other hand, in PBSA/ESP 80/20 composites, Figure 1d illustrates that unsorted ESP powder provided the highest stiffness while maintaining high ductility values (1e).

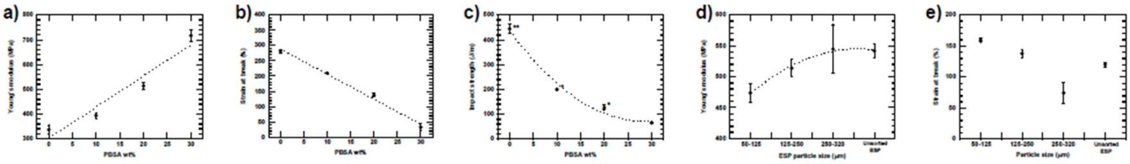

Figure 1. a) Young's modulus, b) strain at break and c) impact strength of the PBSA/ESP composites against the ESP content, and d) Young's modulus and e) strain at break of PBSA/ESP 80/20 composites against the ESP particle size. In Figure 1c), impact strength, (**) indicates no break and (*) indicates partial break.

CONCLUSIONS

When eggshell powder (ESP) is added to PBSA, it makes the material stiffer but less ductile and less impact-resistant. The PBSA/ESP 80/20 composite maintains good ductility (about 140%) and toughness (about 130 J/m), while increasing the modulus of the PBSA by 53%. The mechanical performance of the material is not improved by sorting the ESP particles by size, and in fact, using unsorted ESP powder results in better stiffness. Therefore, it is not necessary to sort the particles when treating the eggshell powder.

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OC 12B

Chemically recyclable cellulosic biocomposites by curing of aliphatic polyester prepolymers

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INTRODUCTION

Cellulosic biocomposites considered here are polymer matrix composites where the fiber reinforcement is provided by plant fibers, in particular wood-based pulp fibers. Such composites offer improved mechanical properties compared with neat polymers. Composites from biodegradable aliphatic polyesters are usually prepared by melt-processing [1]. This limits the mechanical properties since fiber volume fraction is typically below about 30-40 vol%. In addition, fibers become mechanically damaged and shortened so that the reinforcement effect is compromised. Liquid molding of aliphatic polyester monomers followed by in-situ polymerization would address this problem, but ring-opening polymerization is very sensitive to impurities such as moisture, which is always present in plant fibers under ambient conditions. For this reason, crosslinking reactions of polyester prepolymers are of interest. Although aliphatic polyesters have been crosslinked for biomedical applications, there is very little work on such efforts towards semi-structural composites.

The objective is to investigate caprolactone and lactide-based prepolymers and attempt liquid impregnation followed by in-situ polymerization in cellulosic reinforcements [2]. Since these composites have thermoset matrix, chemical recovery of molecules from the thermosets will be investigated as well as recovery of the reinforcement. Green chemistry and circular economy aspects are analyzed.

EXPERIMENTAL

Experimental details of the main concept for PCL-based thermosets are provided in ref [2]. Recently this has been extended to prepolymers based on lactic acid. Briefly, polyester prepolymers are prepared forming star prepolymers consisting of polyester oligomers. Some end-groups are carboxyls and some are hydroxyls, so that step-growth polymerization can take place by esterification. Gel content after curing is measured for different prepolymer candidates. Pulp fiber and nanofiber reinforcements are impregnated and cured. Mechanical properties are measured and chemical recycling of small molecules and the reinforcement is investigated.

RESULTS AND DISCUSSION

The main approach is illustrated in Figure 1, where caprolactone is the starting monomer. About 50% of the arms of the prepolymers are carboxyls and 50% are hydroxyls.

The reinforcement was oriented random-in-plane and was wood pulp fibers for one group of materials and cellulose nanofibrils of rather coarse dimensions for the other group of materials. Still, the biocomposites reinforced by nanofibers showed much higher ductility (up to 16% strain to failure) and higher tensile strength (60 MPa at 50 wt% nanofibers) at comparable weight fraction than those based on pulp fibers. Still, it was possible to make wood fiber composites with 77 wt% with a tensile strength of 82 MPa and a modulus of 6.6 GPa. This is much higher than typical data for PCL composites in the literature.

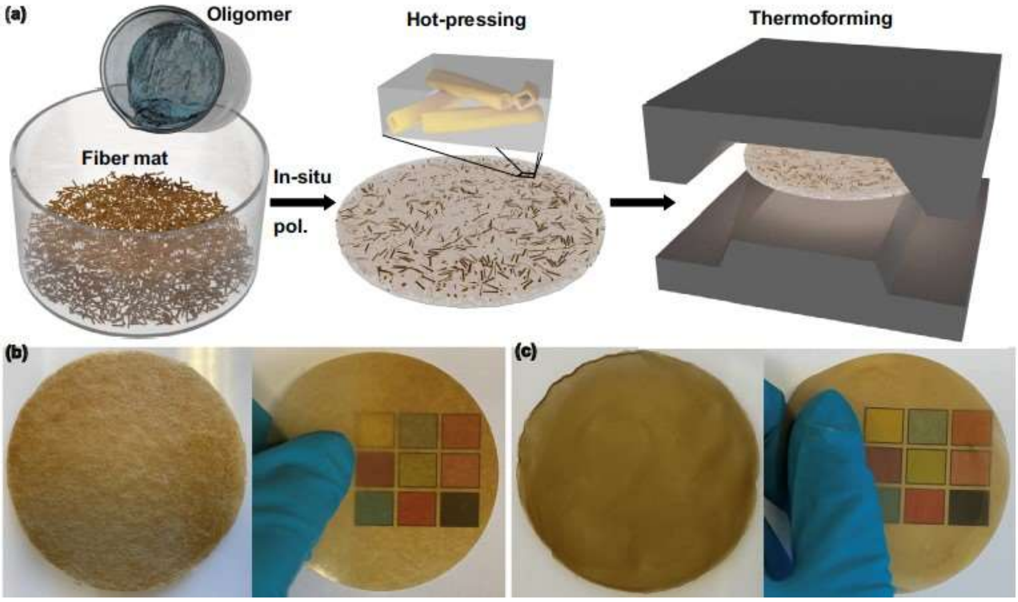

Figure 1. Concept for preparation of degradable biocomposites from PCL thermosets [2].

The biocomposites were subjected to accelerated hydrolytic degradation using weak alkali. Interestingly, the nanofiber reinforced composites degraded much faster than those based on wood fibers. For lactic acid prepolymers, it was possible to recover the monomers from the cured composite. This is unusual for thermosets, but lactic acid offers unique possibilities in this respect.

CONCLUSIONS

Liquid molding of biocomposites is a scalable approach to composites processing. Using aliphatic polyesters for the prepolymers opens new avenues towards fully biobased and degradable biocomposites with mechanical performance suitable for semi-structural components. Since hydrolytic degradation is the main mechanism, it is likely that these materials are unsuitable for most outdoor applications. The mechanisms for cross-linking reactions are of critical importance and should be further explored in this line of investigation.

ACKNOWLEDGEMENTS

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OC 13B

Processing cellulose by ionic liquid or deep eutectic solvent for potential use in 2D and 3D packaging applications

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INTRODUCTION Cellulose materials possess several advantageous properties, including high crystallinity, high mechanical strength, and high availability [1]. However, industrial processing of cellulose in solution requires harsh solvents and cellulose dissolution with greener and safer solvents still remains an active area of research. Ionic liquids (IL) and deep eutectic solvents (DES) have attracted considerable attention as alternative solvents for dissolving cellulose. In this study an Ionic liquid [1butyl-3-methylimidazolium acetate (BmimAc)] and a deep eutectic solvent (DES) [$ZnCl_2/H_2O$/formic acid (HF)] were used to obtain cellulose solutions for 3D printing and solvent casting. When water is added to the produced objects, cellulose can coagulate and undergo a rearrangement of its structure, which can thereafter proceed to dry.

EXPERIMENTAL Wood-derived cellulose 12% w/w was dissolved in BmimAc or in $ZnCl_2/H_2O/HF$ (1:1:4 mol ratio). All solutions were prepared by mixing under controlled conditions (T=90°C for ILs and RT for DES) and their viscosity was measured with a rheometer (Haake MARS II, Germany). For 3D printing process the following parameters were used: Needle = 25G, P = 50-200 kPa, Flow rate = 5mm/s, T (printing syringe) = 25-50°C, T (printing bed) = 10-15°C. The printed structures were placed in distilled water for coagulating cellulose and removing solvent. For the solvent casting, a roller with a thickness of 150 μm was employed obtaining a sheet that was then coagulated in a bath of water/glycerin (90/10 w/w).

RESULTS AND DISCUSSION The printability value (Pr) and the diffusion rate value (Dr) determined for 3D printing utilizing BmimAc were Pr = 1 ± 0.001 and Dr = 0.124. While, using $ZnCl_2/H_2O/HF$, the obtained values were: Pr = 0.818 ± 0.009 and Dr = 0.454. The film produced by casting using BmimAc exhibited good mechanical properties, low water and oxygen permeability; otherwise, the film produced using DES become brittle with time. The dissolving solvent and its interaction with the cellulose determine the printability value and performance of the film over time (Figure 1).

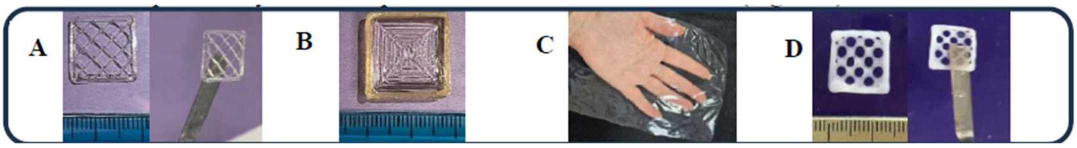

Figure 1. Cellulose items: **A)** Grid structure, 1.5 x 1.5 cm with infill 15 %, **B)** Box structure, 2 x 2 cm with height 5 cm and **C)** casting film after drying using BmimAc, **D)** Grid structure, 1.5 x 1.5 cm, with infill 15 % using $ZnCl_2/H_2O/HF$.

CONCLUSIONS 3D printed cellulose patterns possessed a flexible and long-lasting structure, making them potentially suitable for use in biomedical packaging systems due to the complexity and smaller scale production process; differently, films produced by casting can be most suitable for larger scale packaging applications, due to its straightforward and cost-effective procedure compared to 3D printing.

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OC 14B

Valorization of *horchata* by-products as precursors for the isolation of cellulose nanocrystals and antioxidant extracts

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INTRODUCTION

Agro-waste produced during the processing of *horchata de chufa* (*Cyperus esculentus L)* represents an environmental and economic problem. In particular, it is known that the plant left in the fields after harvest (DP) is rich in polyphenols and can be a source of compounds with high added value [1]. On this basis, the valorization of DP is considered as a way to obtain antioxidant extracts and cellulose nanocrystals (CNCs). In this work, eco-friendly and antioxidant films based on poly(lactic acid) (PLA) and loaded with CNCs and DP extract (DPE) were prepared in order to evaluate their effect on some of the limited properties of the matrix [2].

EXPERIMENTAL

Green extraction techniques, such as microwave (MAE) and ultrasound assisted extraction (UAE), were used to obtain extracts rich in polyphenols and cellulose from DP. CNCs were obtained by acid hydrolysis of the pre-treated material. Then, PLA-based formulations containing different amounts of CNCs (0, 1 and 2 wt%) and DPE (0, 2.5 and 5 wt%) were processed with a twin-screw microextruder. Finally, a complete characterisation was carried out by using different analytical techniques to evaluate their structural (FTIR, XRD), morphological (SEM), mechanical (tensile tests), thermal (TGA, DSC), antioxidant (DPPH, ABTS, FRAP), total polyphenolic content (TPC), barrier (WVP, OTR), overall migration (OM), disintegrability, transparency and colour properties.

RESULTS AND DISCUSSION

The optimal UAE conditions to obtain extracts rich in polyphenols provided extraction yield of 2.31 ± 0.06%, TPC value of 250 ± 27 mg_{GAE} 100 g_{dm}^{-1} and ABTS value of 12 ± 1 μmol_{Trolox} g_{dm}^{-1}. On the other hand, the optimal MAE conditions to obtain cellulose provided a crystallinity index of 53 ± 1%. Furthermore, from the results obtained from PLA-based formulations, it can be highlighted that an antioxidant effect was observed due to the incorporation of the DPE. The OM tests demonstrated that the migration levels from PLA-based formulations were below legislation limits. A reduction in OTR was obtained for films containing 1 wt.% CNCs, while WVP values similar to neat PLA were detected; as well as an excellent disintegrability at 18 days under composting conditions.

CONCLUSIONS

PLA-based films loaded with CNCs and antioxidant extracts obtained from a by-product generated in the *horchata* industry, have a potential use for the development of biomaterials, while increasing the added value of this natural waste within the circular economy approach.

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OC 15B

Chemical recycling of polyhydroxybutyrate into high added value β-hydroxy acid

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INTRODUCTION

Polyhydroxybutyrate (PHB) is a polyester produced by microorganisms that has shown great promise as a partial replacement for conventional non-degradable plastics. Along with being bio-based and biodegradable, it shows excellent barrier properties, giving a better performance like water, oxygen and carbon dioxide barrier than polyethylene terephthalate (PET)[1] and therefore it has been seen that could be a good candidate for packaging applications. However, the main disadvantage of PHB is that the production process of this bio-based polymer is expensive, more than that of conventional petroleumbased polymers, so it has been seen the need to establish a recycling process in order not to lose the material by degradation and give a new use[2]. Although PHB is a thermoplastic material, mechanical recycling is usually hindered by its lack of thermal stability. Therefore, chemical recycling, in particular hydrolysis, has proven to be the most suitable process to obtain β-hydroxy acids in a single step. Chiral β-hydroxy acids are extremely interesting monomers, mainly used in the pharmaceutical industry as precursors for the synthesis of specific chemicals such as antibiotics, vitamins, flavors, fragrances and pheromones[3]. Several authors have studied the chemical transformation of PHB into β-hydroxy acids, but obtaining high yields of hydroxy acids is hindered by the formation of the thermodynamically more stable crotonic acid. The aim of this work is to investigate different depolymerization conditions to maximize the β-hydroxy acid content from the depolymerization of PHB.

RESULTS AND DISCUSSION

The hydrolytic depolymerization reaction conditions were optimized in terms of catalyst, catalyst loading, temperature and pH. It was concluded that a naturally occurring catalyst, taurine, showed the best performance at pH 5.5, almost completely reducing the formation of crotonic acid (Figure 1). In addition, it was confirmed that the hydrolytic depolymerization process is able to preserve the R nature of the monomer, obtaining 100% R-3-hydroxybutyric acid (HBA) compound. Finally, the process was extended to PHB-based copolymers and blends with other commodity polymers, being able to selectively depolymerize PHB.

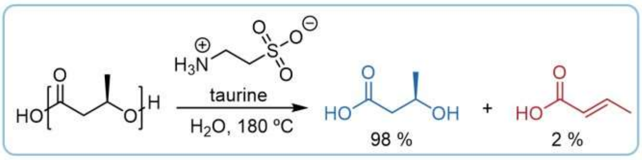

Figure 1. Hydrolytic depolymerization of PHB and recovery of β-hydroxy acid in high yield.

CONCLUSIONS

In this work, for the first time to our knowledge, the depolymerization of PHB to high yields of HBA has been carried out with almost complete reduction of CA formation. The simple one-step process makes it a suitable method for obtaining chiral 3-hydroxybutyric acid monomer in large quantities.

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OC 16B

Development of bio-based paper coatings for food packaging applications

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INTRODUCTION

Food packaging industry extensively relies on synthetic-based materials, which raises significant environmental concerns due to accumulation of plastics in landfills and waterways and resources depletion. A viable alternative is the application of improved cellulose-based materials (e.g., paper and board), which are known for their lower environmental impact [1]. However, cellulose-based materials inherently lack the performance required for food packaging applications, primarily due to their limited barrier and non-sealability. To address these performance deficiencies, coatings are frequently employed to enhance moisture, grease and oxygen resistance. Industrial applications typically use styrene-acrylic emulsions/dispersions to impart moisture and grease resistance. Alternatively, copolymers of ethylene and methacrylic acid (e.g., ionomers), are used to provide moisture barriers, grease barriers, and improved sealability [2].

The study aimed to develop a bio-based paper coating with enhanced barrier properties for food packaging, replacing conventional plastics. Experimental trials were conducted using nanocellulose with/without combination with lignin in a 1:1 ratio. Formulations had a fixed total solid content of 1% m/v. Both uncoated and coated papers were evaluated for their mechanical and barrier performance.

RESULTS

The nanocellulose coating significantly improved air and grease resistance, showing an 80% improvement on Bendtsen, Gurley, and Cobb-Unger60 tests compared to uncoated paper. However, no improvements were observed in water barrier properties. The coating with nanocellulose and lignin combined negatively affected air, grease, and water barrier performance compared to nanocellulosecoated paper alone. This suggests that lignin incorporation disrupts the nanocellulose fibre network, compromising the layered coating. The mechanical data collected from both uncoated and coated papers indicated that the coating did not impact the overall mechanical performance of the paper.

CONCLUSIONS

Despite the improvements, water vapor permeability remained high, even when adding lignin. New strategies are under study, for instance, the development of a multilayer coating comprising an inner layer of nanocellulose and an outer layer of PBAT (polybutylene adipate terephthalate) blended with lignin, to address water resistance. Esterified lignin should be used to be compatibilized with PBAT [3]. The outer layer is currently being optimized, focusing on enhancing moisture resistance.

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OC 17B

Influence of ageing in the ecotoxicity of modified hydroxyethyl cellulose polymers to freshwater biota

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INTRODUCTION

Provided its biological origin (e.g., plants, fungi) and the presence of tunable hydroxyl groups, cellulose has been reasoned as a biocompatible and biodegradable polymer, highly versatile for industrial applications. Though, its nature causes constraints in its processability, thus triggering the need to functionalize the hydroxyl groups to turn water-soluble the cellulose derivatives. The type and level of hydroxyl groups functionalization alters their physical, chemical, and mechanical properties, which may as well influence their biological activity[1]. As mentioned above, cellulose-based polymers are widely used in several consumer products, contributing to their release into the different environmental compartments, namely into freshwater ecosystems. Once in the environment, they may induce adverse effects on biota. The degree of these effects depends on their chemical composition and structure, as well as on the ageing processes it goes through once in the environment (e.g., due to its degradation and transformation because of its exposure to the action of temperature, UV-B, microorganisms). In this context, the present study intended to evaluate the influence of functionalization and ageing on the shortterm ecotoxicity of aged quaternized hydroxyethyl cellulose polymers to freshwater biota.

EXPERIMENTAL

To attain the main goal of this study, the short-term ecotoxicity of four variants of cationically-modified hydroxyethyl cellulose polymers (SoftCAT^{TM} polymers: SK-H, SK-L, SK-M and SK-MH) was characterized, before and after 1-month period of their ageing under different temperatures (15, 20 and 25 ºC). For this, the following bioassays were performed by exposing six freshwater model species to serial concentrations of the four SK polymers (before and after ageing): 72-h growth inhibition with the microalgae *Raphidocelis subcapitata* and *Chlorella vulgaris*; 48-h immobilization with the cladoceran *Daphnia magna* and the ostracod *Heterocypris incongruens*, 24-h immobilization with the rotifer *Brachionus calyciflorus*, and 96-h embryo development with the fish *Danio rerio*.

RESULTS AND DISCUSSION

Overall, the values of the hazard concentrations for 5% of the species (HC_5) revealed that the variant with medium cationic substitution (SK-M) exhibited the lowest ecotoxicity to freshwater biota, both before and after the ageing process. The 1-month ageing at 15 ºC caused a slight increase in the toxicity of the four SK variants, while at 20 ºC the observed toxicity was similar to that reported before ageing. Finally, ageing at 25 ºC caused a decrease in the toxicity of all variants by more than a 4-fold, comparatively to the corresponding non-aged variants.

CONCLUSIONS

The obtained results suggest that industry could direct the efforts to develop this type of cellulosebased polymers by tailoring its cationic substitution to moderate levels, in a way that maximizes both functionality and environmental safety.

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OC 18B

Effects of sodium sulfite on the rheological behavior of gluten plasticized with glycerol and water

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INTRODUCTION

Obtained from wheat, gluten can be shaped thanks to tools developed for plastics. The objective of the research is to define the processing window of plasticized gluten during twin screw extrusion and to enlarge these conditions with a reducing agent: sodium sulfite. The latter has already proven to be a successful candidate for sunflower protein isolate [1]. Plasticization and cross-linking are the most important aspects of protein processing. Throughout the barrel, the plastification of gluten occur and the mixture should remain inactive until it flows through the heated die where the setting of new intermolecular bonds takes place which leads to the creation of a three-dimensional network. The first need is to get a better understanding of the effect of temperature and shearing on the rheological behavior of the plasticized gluten throughout the barrel. For this purpose, the mixture viscosities have been investigated at different experimental conditions.

EXPERIMENTAL

The rheological behavior of water/glycerol plasticized gluten was investigated by means of an internal mixer equipped with a sealed chamber. Various mixtures of gluten, glycerol, water and sodium sulfite were studied. Through a proper calibration, torque measurements and rotation speeds are converted to shear stress and shear rate data and this leads to the plot of a flow curve in the 10 - 100 *s* range [2]. Sample solubility in phosphate buffer containing SDS (denaturant) was determined and changes in the molar mass distribution of the gluten proteins were characterized by SE-HPLC.

RESULTS AND DISCUSSION

The preliminary findings show that reducing agent caused a dramatic decrease in viscosity at low temperatures (20-50°C) indicating a breakdown of network structure probably due to disulfide bond reduction. It has been confirmed by the increase of protein solubility. The observed complex rheological behavior can be superposed onto a master curve by using a shift factor (aT) in the temperature range (25–50°C). SE-HPLC measurements showed that at higher temperatures the proteins cross-link.

CONCLUSIONS

This study describes the evolution of the rheological behavior of gluten plasticized with glycerol, water and sodium sulfite at different processing conditions and will help for determining the processing window.

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OC 19B

Hydrogels as promising candidates for the treatment of cutaneous wounds

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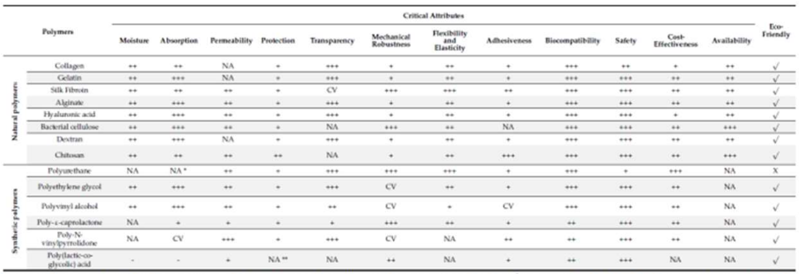
INTRODUCTION

Hydrogels are polymeric materials with characteristics that meet several requirements of an ideal dressing, making them promising for cutaneous wound care [1]. Polymers used in hydrogel formulations can be either natural or synthetic. Natural polymers are more biocompatible, while synthetic ones exhibit greater mechanical strength [2,3]. The selection of the polymer mixture should consider both wound and patient specific needs [4]. In this work [5], natural and synthetic hydrogel polymers were thoroughly explored, following the PRISMA guidelines, to understand their potential and limitations for the treatment of cutaneous wounds.

RESULTS AND DISCUSSION

In our review, we highlighted polymers' chemical structure, extraction sources, main intrinsic properties, and their roles in wound healing, providing explanations of underlying mechanisms whenever possible. Studies on the effectiveness of isolated polymers in skin regeneration were also addressed. Identifying key requirements of an ideal dressing eased the recognition of critical polymer attributes. Table I summarizes the critical analysis we conducted on polymer attributes, based on the literature.

Table I. Polymer critical analysis per critical attribute for wound healing.



	Polymers	Critical Attributes												Eco-Friendly
		Moisture	Absorption	Permeability	Protection	Transparency	Mechanical Robustness	Flexibility and Elasticity	Adhesiveness	Biocompatibility	Safety	Cost-Effectiveness	Availability	
Natural polymers	Collagen	++	++	NA	+	+++	+	++	+	+++	++	+	++	√
	Gelatin	++	+++	NA	+	+++	+	++	+	+++	+++	++	++	√
	Silk Fibroin	++	++	++	+	CV	+++	+++	++	+++	+++	++	++	√
	Alginate	++	+++	++	+	+++	+	++	+	+++	+++	++	++	√
	Hyaluronic acid	++	+++	++	+	+++	+	++	+	+++	+++	+	++	√
	Bacterial cellulose	++	+++	++	+	NA	+++	++	NA	+++	+++	++	+++	√
	Dextran	++	+++	NA	+	+++	+	++	+	+++	+++	++	++	√
	Chitosan	++	++	++	++	NA	+	++	+++	+++	+++	++	+++	√
Synthetic polymers	Polyurethane	NA	NA *	++	+	+++	+++	+++	+	+++	+	+++	NA	X
	Polyethylene glycol	++	+++	++	+	+++	CV	++	+	+++	+++	++	NA	√
	Polyvinyl alcohol	++	+++	++	+	++	CV	+	CV	+++	+++	++	NA	√
	Poly-ε-caprolactone	NA	+	+	+	+	+++	++	+	++	+++	++	NA	√
	Poly-N-vinylpyrrolidone	NA	CV	+++	+	+++	CV	NA	++	++	+++	++	NA	√
	Poly(lactic-co-glycolic) acid	-	-	+	NA **	NA	++	NA	+	++	+++	NA	NA	√

Key: "-" means "does not have"; "+" means "weak"; "++" means "good"; "+++" means "excellent"; "√" means "applicable"; "X" means "not applicable"; CV—controversial; NA—not available. * There is only information about foams/sponges. ** There is only information about nanofibers.

CONCLUSIONS

The findings of this literature review provide a solid foundation for future studies on polymers and hydrogels as dressing candidates, contributing to ongoing advancements in the development of more effective dressings. Our critical analysis is crucial for comparing properties, selecting polymers, and anticipating more suitable polymer combinations for different types of wounds. Predicting polymer combinations will optimize dressing properties, representing a significant advancement that can translate into effective and personalized solutions for wound treatment.

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OC 20B

Thermoplastic starch from avocado seed flour vs extracted avocado starch: a comparative study

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INTRODUCTION

The increased awareness about the environmental issues caused by the prolonged use of petrochemical polymers, including increased carbon footprint and residue generation, has led to a search for more environmentally friendly alternatives. Avocado seeds, frequently discarded as waste during the processing of avocado pulp, are an interesting residue for biobased packaging due to their high starch content[1]. Advantages of starch include abundance, biocompatibility, non-toxicity, low cost, biodegradability and high availability. However, starch extraction from avocado seeds requires large amounts of energy and water, and the reported yields are mostly below 20 %. This work aims to compare the properties of mold-extruded films of thermoplastic untreated avocado seed flour (A-SF) and avocado starch (A-ES), in various plasticizer concentrations. Although A-SF and A-ES presented antioxidant capacity, cinnamon essential oil (CEO) was added to amplify the active packaging properties.

EXPERIMENTAL

Avocado seeds were crushed using a grinder to produce seed flour (A-SF). Avocado starch (A-ES) was extracted from A-SF based on a modified procedure described by Chel-Guerrero[2]. A-SF and A-ES films with different glycerol (25,45,45%) content were prepared in a pilot scale twin screw extruder and directly injected molded using a pilot injector. CEO (1,3,5%) was added to the A-SF35 and A-ES35 formulations.

RESULTS AND DISCUSSION

As expected, increasing glycerol content decreased the elastic module and tensile strength, as seen in Table 1. Moreover, both A-SF and A-ES films with 45% plasticizer presented a lower elongation at break than at 35%, probably due to the anti-plasticizing effect caused by the high plasticizer content[3]. CEO also acted as a plasticizer, adding 1% of CEO decreased EM of A-SF35 by 72% and A-ES35 by 50%. However, further increasing CEO content had small impact on the mechanical properties.

Table 1. Effect of glycerol on the mechanical properties of seed flour and starch-based films.

	A-SF 25%	A-SF 35%	A-SF 45%	A-ES 25%	A-ES 35%	A-ES 45%
E (MPa)	102.3 ± 4.4	76.8 ± 6.1	9.4 ± 0.7	188.0 ± 12.5	25.1 ± 2.3	6.5 ± 0.3
ε (%)	15.4 ± 1.5	18.9 ± 1.0	11.6 ± 2.0	24.3 ± 1.9	34.3 ± 2.5	33.2 ± 2.7
Ts (MPa)	4.9 ± 0.3	4.3 ± 0.2	0.6 ± 0.1	7.4 ± 0.3	1.8 ± 0.1	0.7 ± 0.0

CONCLUSIONS

This work has proven that biobased materials can be obtained using starch-rich lignocellulosic wastes from the agricultural industry instead of native starch. Directly extruding seed flour simplifies the process and increases the usable material, increasing the revalorization value of avocado seeds.

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OC 21B

DOPA based poly(ester amide)s as a new generation of biomimetic surgical adhesives

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INTRODUCTION

Surgical adhesives (SAs) are materials that upon in situ polymerization/crosslinking are able to bind biological surfaces together, having both haemostatic and sealant properties. Nature has developed high performing protein-based adhesives in underwater environments, where α-amino acid 3,4-dihydroxy-Lphenylalanine (DOPA) is key in controlling adhesive and cohesive mechanisms. As such, the straightforward preparation of synthetic polymers able to better mimic the complex biochemistry of adhesive proteins is of utmost importance. [1]

Poly(ester amide)s based on α-amino acids (AAA-PEAs) are a thought-provoking candidate for the preparation of biomimetic SAs. This polymer family offers the possibility of fine-tuning the final properties of the material by the incorporation of different AAAs onto the polymeric backbone via straightforward methodologies, such as solution polycondensation (SP).[2]

RESULTS AND DISCUSSION

A library of PEAs was prepared from different AAA *via* SP. Liquid glues were prepared from PEAs with different structures and their adhesive performance was assessed in *ex vivo* porcine dermis and liver by tensile tests. Figure 1 presents the adhesive strength (σ_{MAX}, kPa) of different glues prepared from PEAs with DOPA/L-phenylalanine (Phe) functionality at 30/70 %mol/mol. Results show that the adhesive performance depends on the structure and molecular weight (M_w) of the PEAs.

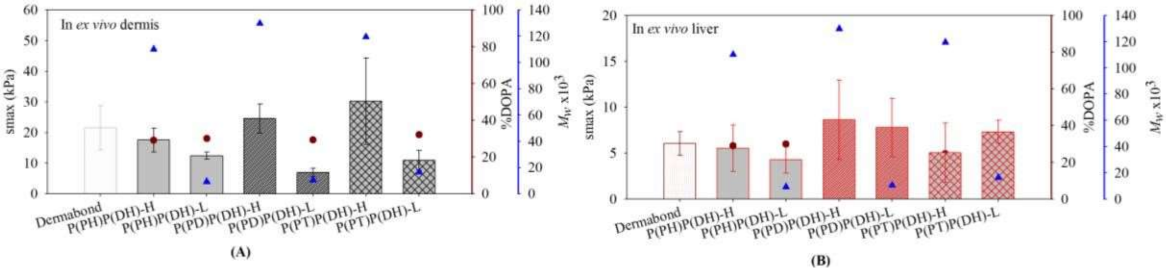

Figure 1. Influence of structural changes in maximum adhesive strength (σ_{max}) of the low and high M_w Phe/DOPAglues in *ex vivo* porcine dermis (A) and liver (B). Commercially available Dermabond® was used as reference.

CONCLUSIONS

The preparation of different DOPA-based PEAs was successfully achieved without compromising the integrity of the catechol group. The different PEA formulations tested were able to glue ex *vivo* porcine dermis and liver without the addition of an oxidizing agent with comparable and superior adhesive strength than the commercial reference Dermabond®.

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OC 22B

Accurate T_g prediction by machine learning for accelerating the development of bio-based polyester resins

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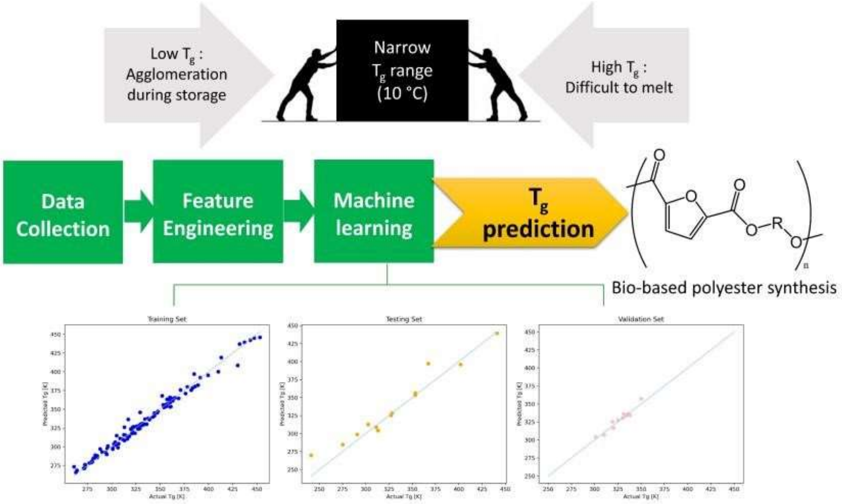

For many industrial applications, the glass transition temperature (T_g) of polyester resins is limited in a narrow range. For instance, the T_g of printing toners varies from 60 to 70 °C. Any value outside this range could lead to insufficient melting for processing or agglomeration under storage conditions. Similar principle also applies to powder coatings and heat seal adhesives. Considering T_g is correlated to many factors in the polymer composition, developing a new (co)polyester with a T_g falling in such a small range is time and labor-consuming via the conventional trial-and-error approach. Therefore, we report on a machine learning method to predict the T_g specifically for novel (co)polyesters derived from 2,5-furandicarboxylic acid (FDCA), a promising bio-based substitute for fossil-based phthalic acids as a rigid building block for producing polyesters. For training the model, a dataset encompassing 124 FDCA-based homo- and co-polyester data was collected from literature in which 36 different diols were involved. Subsequently, 32 structural, topological and electrical descriptors were calculated as features of each polyester at both monomer and polymer level. Based on this dataset, three machine learning regression models including LASSO, random forest and neural network-based multi-layer perceptron were trained. After regularization and optimization, the performance of each model was evaluated by an external validation dataset that contains 11 polyesters that we synthesized with monomers at both inside and outside the training set. Among these three models, random forest turns out to be the best performer with a R^2value of 0.91 and root mean squared error (RMSE) of 3.86 °C on the validation set. It is believed that the accuracy this model reached could facilitate the development of furanbased renewable (co)polyester resins with specific T_g requirements.

OC 1C

Synthesis of ecofriendly cationic lignin derivatives for hair cosmetics

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INTRODUCTION

The increasing interest in sustainable materials has motivated the adoption of a circular economy approach, where residues are treated as useful resources to produce new materials. In this respect, lignin, one of the main components of lignocellulosic biomass, has gained significant attention as a renewable and abundant feedstock. Although unmodified lignin can be directly used for some applications, others may require some chemical functionalization. For example, in the cosmetic industry, lignin has been investigated as a potential active ingredient for skin care, especially in sunscreens, due to the ability to absorb UV radiation, as well as other valuable properties, such as biodegradability, antimicrobial and antibacterial activities [1]. As for the development of hair conditioning agents, positively charged polymers are desired to neutralize the anionic charges of the hair fibers and to reduce the frizz effect. Thus, lignin cationization is a promising route for extending its use to the hair care sector. The study of the conditioning properties of lignin and its cationinc derivatives would contribute to the advancement and expansion of the availability of natural-based ingredients in this particular field of hair products.

EXPERIMENTAL

In this work, lignin was extracted from acacia wood and chemically modified to produce cationic derivatives that can interact with damaged human hair. Its cationization was performed via reaction with 2,3-epoxypropyltrimethylammonium chloride and the conditions (lignin/cationizing agent ratio and temperature) were optimized using a design of experiments in order to maximize the degree of substitution and zeta potential of the derivatives. They were characterized by FTIR to further identify the introduction of the cationic moieties.

RESULTS AND CONCLUSIONS

Cationic lignin derivatives were successfully obtained by grafting quaternary ammonium groups via etherification. Temperature showed a significant influence, in contrast to what was observed for the reagents' ratio. It was possible to achieve water soluble lignin derivatives with a zeta potential similar to that of a commercially available hair conditioning agent.

The new lignin-based conditioning agents are expected to efficiently repair damaged hair without compromising the environment or the consumers' health.

FUNDING

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OC 2C

Effects of grafted chitosans on the reduction of powdery mildew in wheat

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INTRODUCTION

Chitosan, a biopolymer obtained from chitin, a main component of fungal cell walls, emerges as a promising agent in controlling crop diseases. With its biocompatibility and biodegradability properties, chitosan is an attractive candidate for promoting eco-friendly agricultural practices.

Innovative research has explored enhancing the biological properties of chitosan through chemical grafting techniques. These studies focused on the grafted chitosans' ability to protect plants against foliar diseases and directly inhibit microbial growth. These studies focused on the pathosystem wheat - *Blumeria graminis* f. sp. *tritici* (*Bgt*), the fungal agent of the aerial disease powdery mildew.

RESULTS AND DISCUSSION

Wheat plantlets were sprayed with various chitosan grafts and infected with *Bgt* conidial solution for protection tests. Application of a fungal chitosan (FC) generously provided by KitoZyme and another chitosan-based commercial biofungicide (CCBF) showed an interesting reduction in the number of pustules caused by *Bgt* on wheat leaves. The protection rate was 29% for FC and 44% for CCF. Grafting succinic acid and octenylsuccinic acid (OSA) onto FC led respectively to *N*-succinyl chitosan (NSC) and octenylsuccinyl chitosan (OSC), water-soluble products at neutral pH that significantly reduced disease symptoms, with a protection rate of around 59% and 25%, respectively (Figure 1a).

The direct effects of the compounds on the germination of *Bgt* spores were also evaluated. Although functionalized FC seemed to induce a reduction of germinated spores (around 65%), FC and CCF demonstrated stronger antigerminative activities (approx. 90% of ungerminated spores) (Figure 1b).

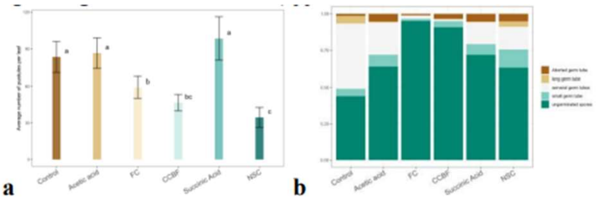

Figure 1. a) Severity of powdery mildew on wheat leaves according to treatments. b) Effects of different treatments on the germination of *Bgt* conidia.

CONCLUSIONS

First results with grafted chitosans are encouraging to develop biosourced solutions for protecting wheat against powdery mildew. Grafting other synthons onto Chitosan is investigated to improve protective properties. The eliciting properties of the most efficient molecules on the induction of the plant defense mechanisms will also be investigated.

ACKNOWLEDGEMENT

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OC 3C

Abiotic and biotic degradation of PBAT: quantification of generated products by carbon assessment

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INTRODUCTION

Plastics are ubiquitous in the environment[1], accumulating under diverse forms resulting mainly from degradation by photo-oxidation and mechanical fragmentation/abrasion of macro-plastics. These phenomena generate micro- (MP) and nano-plastic (NP) fragments, but also soluble molecules and volatile compounds. To better determine their impact, quantification and characterisation studies[2,3] are carried out. Biodegradable plastics being in a particularly close contact with micro-organisms, assessing the quantity and type of their potential degradation products seems even more important.

EXPERIMENTAL

Industrial plastic granules of Ecoflex F Blend C1200 (PBAT, BASF, Germany) and Lupolen 2420F (LDPE, LyondellBasell, Netherlands) degradation under UV and water stirring, are studied. TOC device from Analytik Jena has been used. The biodegradation has been studied by CO_2 back-titration.

RESULTS AND DISCUSSION

A protocol for the simultaneous quantification of all degradation products based on the carbon assessment and using TOC has been put in place.

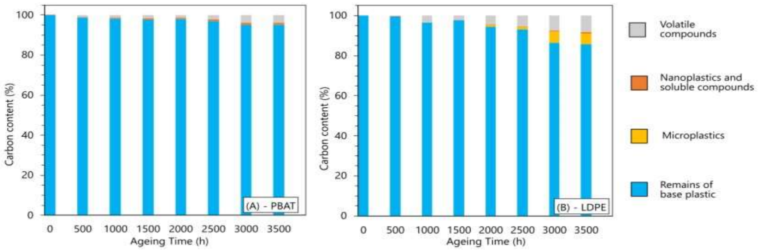

Figure 1. Carbon assessment for the abiotic degradation for PBAT (A) and LDPE (B)

Will be presented the results obtained on PBAT, whose biodegradability has been attested in industrial compost, but whose degradation products in the environment are yet to establish. LDPE will be used as reference, being a conventional plastic replaced by PBAT in some applications. Under the tested conditions as shown in Figure 1, PBAT appeared to degrade slower than LDPE and produces little or no MP, but only nanometric species, in solution or volatile, in comparable amounts to LDPE. Biodegradation of aged PBAT has been studied, showing links between biotic and abiotic degradation.

CONCLUSIONS

The carbon degradation assessment has been made successfully, allowing the quantification of degradation products and evidencing the generation of nanoplastics and/or soluble compounds, the impact of which on ecosystems is still unknown.

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OC 4C

Functional properties of hyaluronic acid-like polysaccharide produced by *Vibrio sp.* Mo245 from glycerol

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Hyaluronic acid (HA) market has grown recently due its hygroscopicity, viscoelasticity and bioactivity, rendering it interesting for medical and cosmetic applications. However, safety concerns and lack of process efficiency in producing HA using pathogens such has *Streptococcus zooepidemicus* have led to research on more sustainable approaches [1]. The production of glycosaminoglycans (GAGs) by non-pathogenic marine bacteria is being investigated due to their ability to secrete high molecular weight (Mw) polysaccharides with physicochemical and biological properties similar with HA. In particular, the strain *Vibrio sp.* Mo245 has been reported to produce a HA-like polysaccharide with potential to be an alternative to HA, due to its composition, gelling and viscoelastic properties [2]. In this study, Vibrio sp. Mo245 was cultivated, for the first time, using glycerol as the sole carbon source to produce the HA-like polysaccharide (HA-like EPS), and its functional properties were assessed. Production was conducted on a 24 h fed-batch bioreactor (2 L working volume), operated at 30 °C pH controlled at 7.20. The dissolved oxygen concentration was controlled at 40%, with a constant aeration of 1 SLPM. The high Mw HA-like EPS was recovered from the cell-free supernatant by dialysis and characterized by HPLC in terms of neutral sugars, uronic acids and hexosamines. The strain grew at a maximum specific growth rate of 0.40 h^{-1} and EPS synthesis began at the end of the exponential phase and continued throughout the stationary phase. The culture produced the HA-like EPS, attaining a final concentration of 2.71±0.03 g/L and a productivity of 0.11 g/L.h, higher than the productivity previously reported for glucose [3]. The produced HA-like EPS had a high Mw (2.01±0.01 x10^6 kDa) and was mainly composed of glucosamine and glucuronic acid, similar to HA, but also comprising rhamnose, which may confer it greater interest since the presence of this sugar monomer is associated with biological activity [4]. The HA-like EPS displayed good viscoelastic properties and formed gels in the presence of Cu^{2+} and Fe^{3+}. Furthermore, it displayed emulsifying capacity in the presence of olive, almond and sunflower oils and could form transparent, stand-alone films by casting. The suitability of the HA-like EPS produced by Vibrio sp. Mo 245 using glycerol to be developed into safe high-value biomaterials for use in areas like biomedicine and cosmetics was demonstrated, due to its valuable functional properties.

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OC 5C

High-performance, bio-based, tri-component vitrimer networks based on epoxydized vegetable oils: Control of the network synthesis and morphology.

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INTRODUCTION

Today's environmental considerations are driving the search for alternatives to petroleumbased thermoset resins based on bisphenol A, which are widely used industrially. Epoxidised vegetable oils are a promising alternative, given their biosourced origin, their widespread availability, and the simplicity of their synthesis using green, high-yield processes. However, their use as a replacement for conventional epoxy resins presents different kind of problems: Weaker thermomechanical properties [1]; Parasitic amidation reaction due to the presence of esters [2-3]; Formation of multi-phase systems when a glycidyl co-epoxy is added [4- 5].

The work presented focuses on the formation of epoxy-amine resins from epoxidised linseed oil (ELO) combined with a high level of phloroglucinol triglycidyl ether (PhGE) coming from algae to increase final properties (Tg, Young Modulus) and to use this exothermic reaction to complete conversion of ELO. These epoxies are cross-linked with 4,4 dithioaniline to form an epoxy-amine vitrimer network with disulphides bonds, which afford a high level of bio-based carbon, high thermomechanical properties and recyclability.

RESULTS AND DISCUSSION

Firstly, the amidation of these systems was controlled and strongly limited by using a crosslinking curing cycle with different steps at low and high temperatures. The conversion of these systems was carried out by ^{1}H and ^{13}C NMR throughout the cross-linking process. An original method will be presented to de-crosslinking these systems above the gel point. It allows us to well-described the crosslinking process. Secondly, the demixing process of the epoxies was controlled by an optimised compatibilization method. The network shows an homogeneous structuration at nanoscale by AFM (figure 1). DSC and DMA characterisations of the epoxies formulation show an increase of the Tg from 120 ºC to 140 ºC.

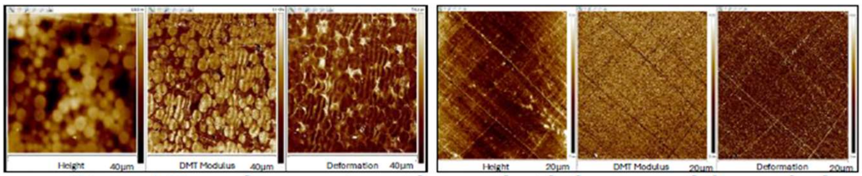

Figure 1 Network structuring without and with the compatibility method.

This work presents a method for compatibilising internal epoxy resins with more conventional glycidyl epoxies, opening up new possibilities for combining and reinforcing these resins. By controlling the amidation and structuring of these systems, superior thermo-oxidative properties can be achieved. At the same time, a new method for de-crosslinking these systems have been developed, paving the way for their characterisation using methods like liquid NMR or chromatography that are generally inaccessible to networks.

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OC 6C

Impact of the individual layers on polymer-coated cardboards properties

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INTRODUCTION

Coated papers and cardboards appear as excellent candidates for the conventional and polluting plastics' substitution in the packaging field. A polymer coating can compensate for the poor barrier properties of paper/cardboards towards gas and water vapor, and thus increase the range of application. Due to the paper intrinsic porosity, a part of the coated polymer unavoidably penetrates within the cellulosic substrate leading to a complex multi-layered structure with at least three layers, having their own properties. Understanding the relationship between this structure and the polymer-coated cardboards properties is necessary for the development of materials with tailored properties for packaging applications. While the impact of the coating weight has already been studied [1], the impact of the overall complex structure, including the impregnated layer, has never been investigated.

In this context, the aim of this study is to formalize the relationship between the structure and the properties of polymer-coated cardboards.

EXPERIMENTAL

For that purpose, a range of coated cardboards displaying contrasted structures were produced by thermocompression, using a Design of Experiment, and further characterized. Untreated blotting papers were considered to emphasize the phenomenon of polymer impregnation. PHBV, poly(3hydroxybutyrate-co-3-hydroxyvalerate), was used as polymer coating. First, the structure, i.e. thicknesses of the different layers, of the produced coated-cardboards was determined using an analytical model [2]. Then, the barrier and mechanical properties were characterized and the relationship between the structure and these properties was investigated.

RESULTS AND DISCUSSION

It has been highlighted that the properties of polymer-coated cardboards differed depending on their intrinsic structure (Figure 1).

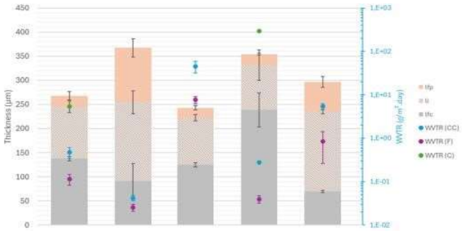

Figure 1. Comparison of WVTR for PHBV-coated cardboards depending on their structure

CONCLUSIONS

Results show the impact of the structures on the coated papers' barrier and mechanical properties, and especially the relative contribution of each layer. The barrier properties seem to be controlled by the free polymer layer. However, it is worth noting that the process used to produce coated cardboards is also impacting the properties of the materials.

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OC 7C

Monte Carlo Simulations for Screening and Optimizing Biopolymer-Based Drug Delivery Systems

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INTRODUCTION

Our group has developed effective models to describe the adsorption behaviour of charged polymers in complex systems governed by electrostatic interactions. These interactions significantly impact various aspects of biomolecule-based systems, particularly in drug delivery applications. We have employed nucleic acids, polymers, and peptides to design diverse nanosystems aimed at enhancing drug delivery for a range of diseases, including cancer. The role of electrostatic interactions varies, being either a direct determinant or an indirect but crucial factor.

Our case studies focus on DNA nanostructures, that have long been considered a cutting-edge technology with promising applications in cancer treatment and nanoparticles modified with polymers like cell-penetrating peptides with potential to enhance the efficacy of chemotherapeutic agents, improve targeting, increase biological barrier permeability, and facilitate specific cellular uptake.

EXPERIMENTAL

In this study, we explore this topic using Monte Carlo simulations and simple coarse-grained models. By focusing on a limited set of parameters, such as overall chain charge, length, and charge distribution, we aim to reduce the complexity of these systems and assess their impact on overall behaviour.

DISCUSSION

The present contribution demonstrates how computer simulations and in particular simple coarsegrained models are a valuable approach to interpreting the behaviour of these types of complex systems, in which electrostatics play a critical role.

The presented case-studies reinforces the need to carry out a "whole-picture approach" when developing biopolymer-based systems, combining experimental and in silico data.

FUNDING

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OC 8C

H-bond donor–Lewis basic anion bifunctional organocatalyst for ringopening polymerizations

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ABSTRACT

A bifunctional H-bond donor–Lewis basic anion (HBD–anion) organocatalyst manifold was proposed for ring-opening polymerizations (ROPs) of cyclic esters. A series of squaramide–phenolates (Sq–PhO) as representative HBD–anion catalysts were designed, in which the Lewis basic phenolate anion, in place of neutral bases of the Takemoto-type catalyst, activated the initiator/chain-end, while the squaramide activated the monomer by H-bonding, cooperatively. The squaramide–phenolate was generated in situ by deprotonating the phenolic hydroxyl of the counterpart squaramide–phenol with (super) strong bases. An optimal N-benzyl-N'-p-hydroxylbenzyl squaramide (Sq3-p) and the DBU base co-catalyst transformed lactides, lactones, and cyclic carbonates into the corresponding polyesters in a short time, with high conversion and a narrow dispersity (Đ = 1.06–1.19). The bifunctional activation mechanism was proposed and validated. Both the H-bond donors and basic anions are various and tuneable, which is hopefully accessible to extend this catalytic tool in wider scope of bifunctional organocatalysis.

KEYWORDS

H-bond, Lewis basic anion, phenolate, ring-opening polymerizations, squaramide.

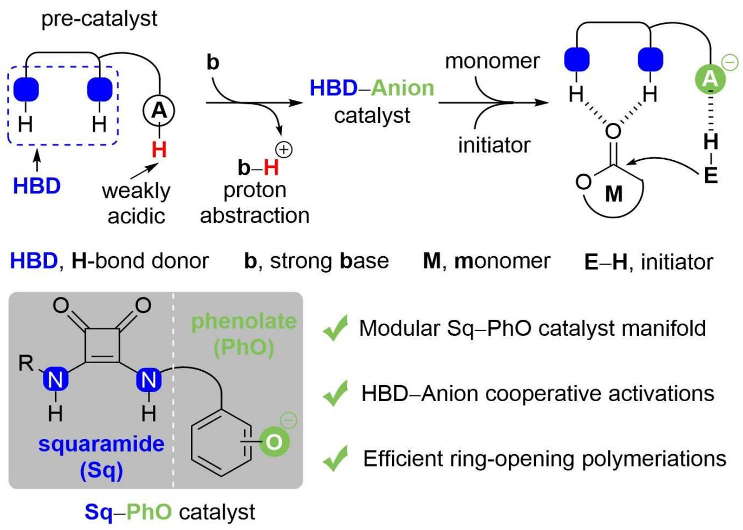

Figure 1. Design of an H-bond donor–Lewis basic anion (Sq–PhO) organocatalyst and its catalytic working model.

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OC 9C

Development of new packaging materials through novel agroindustrial valorization techniques

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INTRODUCTION

The concept of biobased materials in the field of polymers aims to use alternative sources such as biomass instead of petrol-based sources to produce new materials. Polylactic acid (PLA) is one of the most attractive biobased polymers due to its excellent strength and biodegradability. However, its brittleness and poor heat resistance restrict its use in many applications. Therefore, the use of microfillers has been proposed to obtain composites. Microfibrillated cellulose (MFC) has great potential as microfiller because of its biodegradability, as well as its good mechanical strength and high surface area. Agricultural and food wastes are becoming a major concern due to the amount generated in the whole world. Nowadays, these wastes are used for low value-added applications, such as composting, energy production, animal feed, etc. The use of lignocellulosic wastes as raw materials to extract cellulose additives will be a green shift to finish linear economy by reducing the material demand[1]. These raw materials will also offer a low-cost alternative to produce MFC compared with the current ones[2,3]. MFC is originally produced in aqueous suspension. However, nanofillers are usually desired to be in dried form for compounding processes[4]. MFC cannot be directly dried by simple evaporation since an irreversible agglomeration of the fibres, called hornification, can be occurred. Therefore, other alternatives, such as spray-drying, are proposed to preserve the fibrillar structure of MFC without hornification. Nevertheless, some issues such as the high cost of this technique have not been solved yet. The present work developed an alternative process for the production of PLA/MFC composites using an innovative processing technology such avoid the drying process of MFC and obtain in only one single step PLA/MFC composites with improved properties compared with the old processed using conventional extrusion techniques one. Wet compounding approaches have been shown very promise, but the technology is still under development. Consequently, it is needed the understanding of the interaction between MFC, water, biopolymers, and additives as well as the details of the concentration, drying, and dispersion mechanisms.

EXPERIMENTAL

The aim of this study was the use of liquid feeding as an innovative alternative to additivate the MFC during compounding processes to obtain PLA/MFC composites by avoiding drying pretreatments. MFC was obtained from wheat straw, rice husk, and broccoli. Best performance MFC was selected for composites production by Quality Index (QI) determination. The measurement of 4 parameters is required and the values obtained are introduced in an equation for obtain said Quality Index. The MFC obtained will also be characterised by means of morphological studies carried out techniques such as MorFi analyses and microscopic techniques (SEM), and thermal properties by TGA. This index allows the comparation of the MFC with a unique index representative of several tests for the control of the production quality, check the reproducibility of the results obtained at industry scale, etc.

PLA/MFC nanocomposites were obtained through compounding process. Compounding parameters were specifically adjusted for liquid additivation: MFC concentration, liquid carrier additive ratio, screw configuration for avoid thermal degradation and improve MFC dispersion. Finally, rigid packaging prototypes were obtained and characterized in terms of mechanical and barrier properties.

RESULTS AND DISCUSSION

Wheat bran MFC presents the best quality with a QI of 61.5, comparable with the quality of the commercial mechanical MFC (QI of 60)[5]. Fiber morphology was evaluated by SEM analysis and diameters of 29 ± 8 nm were determined. The results exhibit an improvement in mechanical and barrier properties, reducing the oxygen permeability up to 15% in PLA-based composites. Tensile tests revealed improvements in strength and elongation at break, with an improvement of more than 50%. These results suggest an adequate balance between mechanical and barrier properties in the evaluated formulations. Additionally, food contact analysis has been performed obtaining positive results. These results indicate the potential of these new materials with good barrier properties for packaging applications.

CONCLUSIONS

The development of improved biobased materials, such as MFC, will impact the packaging industry by giving sustainable alternatives to conventional packaging materials. Production of MFC composites involves producing good quality and low-cost MFC, removing water from MFC suspension to avoid hornification, dispersing the MFC in the selected polymer, improving the compatibility of the additives with the matrix, and adapting the process parameters to the newly developed materials. The present work covers all these points with an optimized process, avoiding high cost of MFC drying step and optimizing the properties of the final material with a specific screw configuration and the selection of the optimum additives.

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OC 10C

Development of Sustainable Cellulose-based Hydrogels for Agriculture

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INTRODUCTION

Efforts to achieve sustainable water use in agriculture are hampered by the negligence of freshwater resources, which affects crop productivity. The development of efficient and economically viable solutions for sustainable water use in agriculture is a necessity [1]. Superabsorbent polymers (SAPs), particularly hydrogels, are promising soil conditioners, capable of absorbing and gradually releasing water to plants. However, the dependence on petroleum-based monomers in their production go against sustainability goals. Recent research has emphasized the development of biodegradable alternatives that are consistent with the principles of green chemistry [2]. In this study, a sustainable and simple process for the production of cellulose-based superabsorbent materials is presented, in which salts from cellulose solvents are reused as nitrogen fertilizers.

RESULTS AND DISCUSSION

Allylic cellulose derivatives, which are known to facilitate simpler chemical processes due to their double bonds, were obtained by a homogenous modification process in a NaOH/urea solvent system. The solutions of the derivatives were neutralized with nitric acid (HNO_3), resulting in sodium nitrate ($NaNO_3$) as a nitrogen-based fertilizer, benefiting from the presence of urea, the most widely used nitrogen fertilizer [3]. The hydrogels were synthesized by UV free radical polymerization (FRP), where the cellulose derivatives were crosslinked in the presence of nitrogen-based salts. The influence of the crosslinking density of cellulose hydrogels was studied. EDS analysis confirmed the distribution of nitrogen (N) and sodium (Na) throughout the cellulose structure (Figure 1-A). The cellulose hydrogels exhibited high swelling capacity, reaching 2500%, although oven-drying reduced their reswelling capacity (Figure 1-B). However, they showed pH and salt resistance during swelling. Fertilizers release in soil tests showed a total release below 30 days. Biodegradability testing showed significant degradation within 30 days, with only 40 wt.% remaining (Figure 1-C). Ongoing studies aim to improve some properties by incorporating additional polymers into the hydrogel structure.

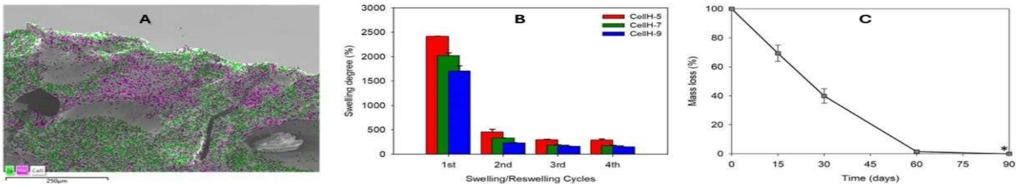

Figure 1. A-EDS analysis to fertilizers; B-swelling/reswelling capacity of hydrogels; C-Biodegradability test

CONCLUSIONS

Cellulose hydrogels were prepared using a more sustainable, simple, and straightforward method, and showed good swelling and pH/salinity resistance. As expected, they showed a rapid release of fertilizers and fast biodegradation making them suitable for use in fast growing crops such as radishes, carrots or peas which are ready for harvest within 30-60 days after sowing.

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OC 11C

Molecularly imprinted polymers for the selective elimination of aloin from *Aloe vera skin* extracts

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INTRODUCTION

Agro-food wastes and by-products are considered as promising sources of added-value biomolecules and building blocks for biomaterials formulations. In this sense, *Aloe vera* external epidermis contains active compounds with antioxidant and/or antimicrobial activities that could be potentially used in a wide range of applications once extracted from the vegetal matrix [1]. Many beneficial bio-compounds have been identified in *Aloe vera* plants. However, they also contain the anthraquinone derivatives aloin A and B. with bitter taste and powerful cathartic effect [2].

Molecularly imprinted polymers (MIPs) have attracted some attention due to their high selectivity and affinity for a specific target molecule. MIPs are stable polymers with special molecular recognition abilities that can be used for the selective extraction of specific compounds. Typically, a template molecule is self-assembled in a complex with adequate functional monomers and subsequently polymerized in the presence of a crosslinking agent. Upon the removal of the template from the crosslinked imprinted polymer matrix, tailor-made recognition cavities complementary in size, shape and chemical functionality to the template molecule are obtained [3]. In this context, this work aimed at developing MIPs for the selective extraction of aloin from *Aloe vera* skin extracts, for the first time.

EXPERIMENTAL

Aloin was used as template and β-cyclodextrin was selected as the functional monomer. Hexamethylene diisocyanate was used as the crosslinking agent. MIPs were synthesized via the bulk polymerization method. The template was removed by microwave-assisted extraction (MAE) until it was not detected by HPLC. Finally, MIPs were oven dried and stored until further analysis. Non-imprinted polymers (NIPs) were synthesized without including the template molecule and were used as control polymers.

RESULTS AND DISCUSSION

SEM was used to analyze the surface morphology of the polymers. Thermal stability and degradation processes were studied by TGA. FTIR was used to evaluate the formation of the crosslinked polymer. The surface and porous structure of MIPs were analyzed by obtaining nitrogen adsorption desorption isotherms. The adsorption performance was studied by isothermal dynamic and static binding experiments using aloin solutions at known concentration levels. Moreover, the selectivity of the developed MIPs towards aloin was determined against other analogue molecules. Finally, these polymers were applied to real samples. Faster adsorption kinetics compared to other polymers and relatively high maximum binding capacity was obtained for MIPs, according to the Langmuir model

CONCLUSIONS

Results suggested that MIPs are a suitable alternative to selectively eliminate aloin from *Aloe vera* skin extracts without producing a significant detriment in the antioxidant capacity and the total phenolic content of the extracts. More efforts are needed to decrease aloin content below regulation limits.

ACKNOWLEDGEMENTS

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OC 12C

Improving the toughness of PLA using different industrially scalable strategies

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INTRODUCTION

Polylactic acid (PLA) is a biopolymer that has become commercially popular due to its many desirable properties. Compared to other biopolymers, PLA is very easy to process, has high strength and modulus, and offers excellent clarity and barrier properties [1]. However, PLA is inherently brittle which makes it unsuitable for applications requiring high toughness and/or ductility [2]. To overcome these limitations, three simple and scalable strategies are proposed in this work. These include 1) blending PLA with core-shell rubber (CSR) impact modifiers, 2) compatibilizing PLA/polycaprolactone (PCL) blends, and 3) increasing the crystallinity of PLA in PLA/PCL blends.

RESULTS AND DISCUSSION

1) The addition of CSR is an effective strategy to increase the ductility and impact strength of PLA. The blend containing 20 wt.% of CSR displayed supertoughness (impact strength > 780 J/m) (Figure 1a). However, it should be noted that increasing contents of CSR had a negative influence on the stiffness and strength of PLA.

2) On the other hand, the addition of low concentrations of a soft polymer like PCL is enough to increase the elongation at break of PLA (Figure 1b). However, optimized contents of compatibilizers with suitable chemical structures are needed to achieve PLA/PCL blends with a good balance of high- and low-strain properties.

3) Another approach to improve the toughness of PLA/PCL blends is to increase the crystallinity degree of PLA in the blend by adding suitable nucleating agents (NA) and heat treatments. To attain supertoughness, a highly crystalline PLA matrix with numerous small crystals and a uniformly distributed PCL particle size is necessary (Figure 1c).

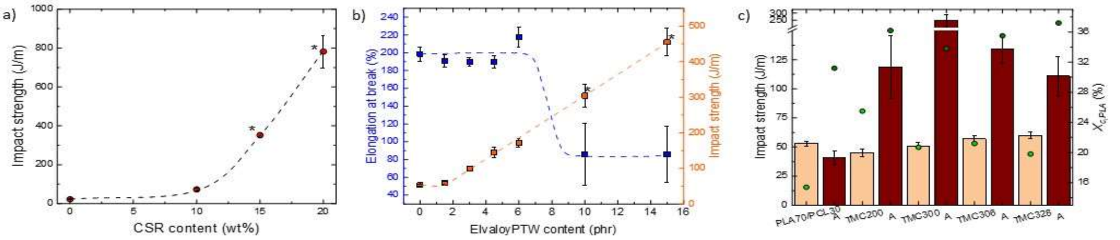

Figure 1. a) Impact strength of PLA/CSR blends as a function of the CSR content; b) Elongation at break and impact strength of PLA/PCL 70/30 blends as a function of the compatibilizer content; c) Impact strength (bars) and $X_{c,PLA}$ values (points) of un-annealed (light) and annealed (dark) PLA70/PCL30/NA blends.

CONCLUSIONS

Three different toughening strategies are proposed for PLA. All are suitable to achieve PLA-based materials with improved impact strength, but special attention has to be paid to the composition and the microstructure if a good balance of low-strain and high-strain properties is sought.

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OC 13C

Standardization of bacterial nanocellulose production from fique by-products

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INTRODUCTION

In recent years, the process to obtain bacterial nanocellulose (BNC) has focused on reducing production costs to expand the BNC applications to commodities, food, cosmetics, among others [1–2]. Therefore, alternative culture media derived from agro-industrial wastes or by-products have gained attention [2– 4]. An alternative media is the juice extracted from fique plant (*Furcraea sp*.). However, its composition is variable depending on the conditions of the land where it is grown [5], therefore, its use in BNC production can lead to heterogeneous characteristics and variable yields of the final product [1–5]. So, the aim of this study is to establish the conditions for the standardization of BNC production from fique juice looking for industrial production of this biotechnological material.

EXPERIMENTAL

Fique juice was donated by Agave S.A.S (6°54′33″N 75°04′36″W). The concentration of sugars, minerals and organic elemental analysis was determined in previous work [1]. Four juice's storage conditions (24 - 48 h and 4 °C – 26 °C) and two thermal treatments (sterilization and boiling for 5 min) were evaluated to ensure the preservation of the juice's characteristics prior to use, evaluating the process yield, microorganism's presence, and glucose concentration. The impact of adding a defoamer (DOW 1520) and an antioxidant (citric acid from a local supplier) in the process yield and the juice's processability were also analysed. Finally, fermentation kinetics were evaluated to determine film thickness over time.

RESULTS AND DISCUSSION

The optimal storage conditions were 24 h at 26°C to preserve the integrity of fique juice. However, microbiological analysis and sugar content under 48 h and 26 °C reveal the beginning of spontaneous fermentative processes [6]. Following boiling process promotes the absence of *E. coli*, fungi, molds, yeast, mesophiles, and total coliforms. Moreover, the use of additives in the juice showed that adding both a defoamer and an antioxidant reduced the process yield. Therefore, the defoamer was chosen because it improved the processability of fique juice during storage or heating. Finally, growth kinetics showed that the first day marked the beginning of exponential growth, which decreased its rate after 8 days. At this time, BNC films achieved a thickness of 6.13 ± 0.01 mm, which is desirable for industrialization

CONCLUSIONS

The processing conditions established in this research for obtaining BNC from fique juice are standardized and could be viable for industrial scalability, since they showed to be cost-efficient methods and successfully meet industrial requirements.

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OC 14C

Polycaprolactone-Based Shell Materials for Microcapsule Applications

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INTRODUCTION

Self-healing coatings are currently a highly researched topic for corrosion protection. Microcapsules are widely investigated to introduce the healing functionality in coatings, as they protect the healing agents, the core material, improving long-term efficiency and promoting stabilization against environmental degradation. [1] Urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde, and styrene coacrylonitrile are some of the most used external materials in microcapsules. However, these conventional materials used for the shells in encapsulation processes are often derived from toxic compounds, posing environmental and health risks. The growing awareness of sustainability and the environmental impact of synthetic polymers has led to an increased interest in biopolymers as alternatives. [2]

Thus, in this work, new microcapsules with polycaprolactone (PCL) were developed, using linseed oil (LO) as the core material. PCL is a biodegradable polymer, with facile processability and reduced environmental impact comparing with the traditional systems. The microcapsules were produced by solvent-evaporation method and the influence of the solvent, emulsifier, molecular weight of PCL, stirring speed, and oil/polymer ratio was studied in the efficiency of microcapsules formation and the loading content of LO.

RESULTS AND DISCUSSION

The results showed PCL microcapsules were successfully formed using dichloromethane (DCM) as a solvent, while with chloroform, aggregates were mostly formed. Microcapsules were generated with sizes ranging from 30 µm to 250 µm, depending on the type of emulsifier used (PVA, Tween 80, Tween 40, and Tween 20) and the molecular weight of PCL (25000, 50000, and 80000).

For example, using PVA as emulsifier and DCM as the solvent for PCL, the larger size of microcapsules did not imply a greater loading capacity of LO. Loading contents of about 40% were obtained for microcapsules about 70 µm diameter. Also, more than 10% oil to polymer did not improve the loading content. The results are presented in Figure 1.

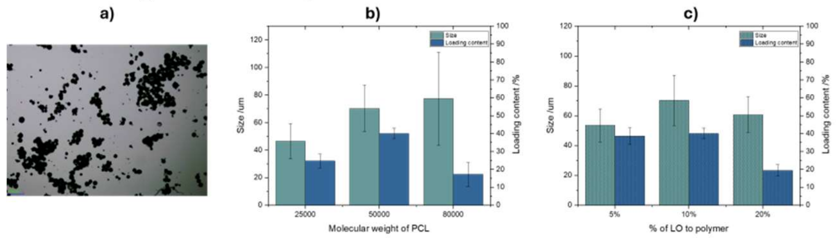

Figure 1. Microcapsules obtained using DCM as solvent for PCL, and 2% PVA as emulsifier (a). Size of microcapsules and loading capacity modifying the molecular weight of PCL (b). Size of microcapsules and loading capacity using PCL M_w=50000, and different oil/ polymer ratios (c).

CONCLUSIONS

Microcapsules were successfully produced using PCL as shell material. Dichloromethane is a suitable solvent for solvent-evaporation method, and PVA promotes higher microcapsule formation. This approach showed the high potential of polycaprolactone to encapsulate linseed oil, an important healing agent, widely used in self-healing coatings.

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OC 15C

Exploring Innovative Eutectic Systems for Enhanced Recycling of Polyesters Mixed Waste

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INTRODUCTION

The widespread use of plastics has played a major role in driving the economic progress worldwide, with an annual production exceeding 400 million tons in 2022 [1]. Nevertheless, only a small portion (*c.a.* 15%) undergoes recycling due to a myriad of constraints including the highly contaminated and mixed nature of polymer waste, leading typically to their incineration or accumulation in landfills [2]. In that regard, poly(ethylene terephthalate) (PET) have been used in the combination with other functional polymers such as PP, PE and PVC for a wide range of applications. Despite its advantages, the sorting of these polymers and the selective recycling of PET is sometimes challenging resulting in the material that is not suitable to be used for the (food) packaging applications also due to Nonintentionally added substance (NIAS). Given the imminent market introduction of poly(ethylene 2,5furandicarboxylate) (PEF) it is important to evaluate the impact on the recycling stream of PET due to their potential mixture. Very recently a few approaches using eutectic solvents (ES) have been advantageously explored for poly(ethylene terephthalate) (PET) chemical recycling, although mixpolymers waste was not assessed [3].

RESULTS AND DISCUSSION

Despite the enormous importance and impact on PET recycling, this is the first study reporting the structural, thermal and thermo-mechanical properties of the recycled copolymers rPET-co-PEF. In this work the ability of a greener chemical recycling system using ES (Urea:Zinc acetate) as catalyst was tested in the chemical recycling of commonly used PET with PEF residual molar percentages, considering 2%, 5% and 10%. The thermal and thermo-mechanical properties of the recycled rPET-coPEF, revealing very similar thermal behaviour compared to virgin PET (Figure 1).

Moreover, the depolymerization mechanism was studied trough DFT calculations, revelling that the hydrogen bond between the urea amine groups and the ester group have a major role in reducing the reaction activation energy proving the catalytic effect of used urea-based ES.

CONCLUSIONS

The characterization of recycled rPET-co-PEF reveal very similar thermal behavior in comparison with the virgin PET. Moreover, the depolymerization mechanism study proved the crucial role of urea in decreasing the depolymerization activation energy.

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OC 16C

Synthesis of novel polyesters incorporating diethylene glycol for enhanced biodegradation in soil and water

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INTRODUCTION

Many strategies have been proposed to mitigate the effects of plastic waste in the environment. A wellknown solution is the implementation of bioplastics, which has been increasing in recent years[1] with the introduction of polyesters such as poly(lactic acid) (PLA) and poly(butylene adipate-coterephthalate) (PBAT). However, their biodegradability has been proven to be quite limited[3].

Recently, Tian[4] and Hu[5] have shown that incorporating diglycolic acid into polyesters increases their degradation rate in both water and soil environments, respectively. Therefore, the goal of the present research is to produce PBAT-like polymers incorporating a ether containing diol (D) to enhance PBAT's degradability in both water and soil environments.

EXPERIMENTAL

The polyesters were synthesized in a three step polymerization in a glass reactor. The polymers contain different proportion of the monomers dimethyl terephthalate (T), adipic acid (A), 1,4- butanediol (B) and the ether diol (D): PBAT, PBD$_{10}$AT and PBD$_{20}$AT. In the first step, the reaction occurred at 180 to 210 °C for 2.5 h using titanium butoxide. Then, another dose of titanium butoxide was added and the reaction proceeded at 260 °C and 100 mbar. Finally, an acid was added and pressure reduced to under 10 mbar until Weissenberg effect was observed. The materials were characterized using proton nuclear magnetic resonance (NMR) size exclusion chromatography (SEC), thermogravimetric analysis (TGA), water absorption (WA) at 54±2 % RH (conditioned until weight stabilized) and tensile tests (specimen conditioned at 54±2 % RH until weight stabilized).

RESULTS AND DISCUSSION

NMR shows new peaks at 3.68, 3.74, 3.84, 3.89, 4.23 and 4.50 ppm. This confirms monomer D has been successfully incorporated into the polymer. Meanwhile, SEC has confirmed all reactions produced polymers with number molecular weights around 30 kDa, complementing the information gathered through NMR. The 5 % weight loss temperature was determined using TGA to assess the thermal stability of the polymers: 369.3 °C, 371.4 °C and 346.5 °C, for PBAT, PBD$_{10}$AT and PBD$_{20}$AT, respectively. This shows a decreasing thermal stability as D monomer content increases, which is a result of the ether bond present, as observed elsewhere[4,5]. PBAT, PBD$_{10}$AT and PBD$_{20}$AT showed WAs of 0.36, 0.43 and 0.48, respectively. This is in line with the increase in monomer D and, therefore, ether bonds, which in turn increases the hydrophilicity of the polymer. Tensile tests showed the increase in D monomer deteriorate the tensile properties considerably. However, the intermediate formulation PBD$_{10}$AT still retains a 329 % elongation at break and 6.4 MPa tensile strength. Degradation studies are not completed at the time of submission, but will be available at the conference.

CONCLUSIONS

NMR and SEC confirm polymers with increased D were produced. WA proves D increases the hydrophilicity of the polymers, however, the thermal stability is not severely impacted. The mechanical properties decrease considerably, but PBD$_{10}$AT still retains acceptable values. Degradation tests will hopefully show gains in degradation rates which outweigh the loss in elongation and tensile strength.

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OC 17C

Synthesis of polybutylene succinate using renewable biomass derived monomers

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INTRODUCTION

Polybutylene succinate (PBS) is a semi-crystalline aliphatic polyester, whose ester bond is susceptible to hydrolysis and responsible for its biodegradability. It shows good processability and mechanical, thermal, and vapor and gas barrier properties, which are similar to those of polyethylene terephthalate (PET), being of great interest for using in food packaging. The synthesis of PBS is carried out by polycondensation reaction from 1,4-butanediol (1,4-BDO) and succinic acid (SA). These monomers have been traditionally obtained from petrochemical substances. However, it has recently been demonstrated that these can also be obtained from renewable biomass derived feedstocks. Concretely, SA can be obtained by fermentation from monosaccharides. Meanwhile, 1,4-BDO can be synthesized by catalytic hydrogenation of SA. The polymerization of both renewable monomers results in fully biobased PBS, a thermoplastic material that can then be processed by different melt routes, such as extrusion or injection, to give rise to several products, such as films, which are biodegradable and fully recyclable by mechanical (reprocessing) or chemical (depolymerization) processes [1].

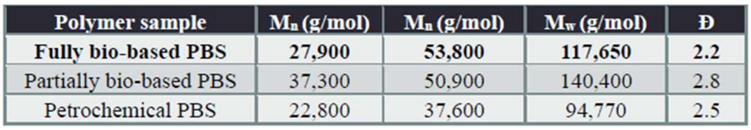
EXPERIMENTAL

Renewable SA was provided by ICP-CSIC (Madrid, Spain). 1,4-BDO was synthesized by hydrogenation process for 48 h at 160 °C and 150 bar using a palladium-based catalyst. The synthesis of PBS was thereafter carried out in two stages in a polymerization equipment [2]. During the first stage, the esterification between SA and 1,4-BDO took place at 180 °C to produce oligoesters of polybutylene succinate (OBS). In the second stage, catalytic trans-esterification (titanium-based catalyst) of OBS was carried out to obtain PBS at 230 °C and high vacuum.

RESULTS AND DISCUSSION

The molecular weight of the biopolymer was determined. This parameter is directly related to the chain length and polymer properties. Table I compares values between the synthesized PBS and its commercial counterparts obtained partially or fully from petrochemical resources.

Table I. Characterization of synthetized PBS (fully biobased) and commercial PBS (partially biobased and petrochemical)) through Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC).



Polymer sample	M_n (g/mol)	M_n (g/mol)	M_w (g/mol)	Đ
Fully bio-based PBS	**27,900**	**53,800**	**117,650**	**2.2**
Partially bio-based PBS	37,300	50,900	140,400	2.8
Petrochemical PBS	22,800	37,600	94,770	2.5

CONCLUSIONS

The molecular weight of the fully bio-based PBS is comparable to that of commercial ones, in the range of 10,000-150,000 g/mol and with a polydispersity index (Đ) between 2 and 3. Therefore, it can be concluded that the characteristics of this novel PBS, obtained entirely from renewable sources, are similar to those currently available on the market, representing an improvement in sustainability and showing great potential for developing biodegradable packaging for food preservation.

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OC 18C

Alkaline pretreatment to improve food packagings biodegradation in mesophilic anaerobic digestion

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INTRODUCTION

In order to face the problem of the inadequate end of life management of petroleum-based plastic packaging, bioplastics has been developed and are currently used in the food packaging industry[1]. As a result, the global market for bioplastics continues to expand rapidly especially for food packaging since selective biowastes collection is mandatory since January 2024. Mesophilic anaerobic digestion (AD) emerges as a promising approach to biodegrade food packaging and biowastes and simultaneously generate biogas[2]. Some food packagings degrade slowly in mesophilic condition and the application of a pretreatment can be an option to improve their biodegradability. In this study, alkaline pretreatment using KOH was explored to improve biomethane potential (BMP) and biodegradability of some food packaging items.

EXPERIMENTAL

The composition analysis of 3 coffee cups (CC) and 2 plastics bags (PB) was conducted using a combination of TGA and ^{1}H NMR. These items were composed of various polymers including PLA, PBAT, PBS, PHBV and Starch. Subsequently, thermo-chemical pretreatment was applied to these items using a KOH solution to solubilize the plastics and facilitate breakdown. The pretreated items underwent mesophilic AD to assess the impact on biodegradability and BMP compared to untreated items.

RESULTS AND DISCUSSION

2 PB and 3 CC of different compositions were pretreated to reach a significant solubilization for most items. The pretreatment led to a hydrolysis of the polymers presents in the items thus enhancing the biodegradability and the BMP of most pretreated items (Figure 1).

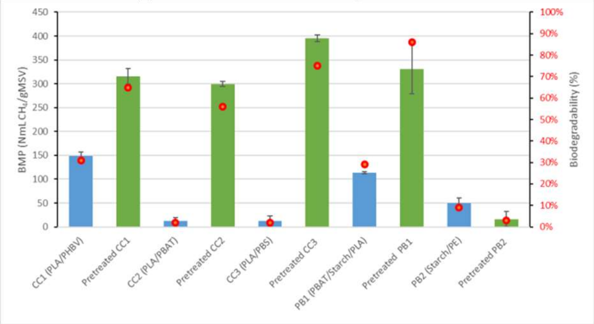

Figure 1. Biodegradability (red dot) and BMP of untreated (blue) and pretreated (green) commercial items

CONCLUSIONS

The pretreatment of commercial items significantly improved the biodegradation and biomethane potential (BMP) in mesophilic anaerobic digestion (AD) of food packaging's composed of PLA, PBAT, PBS, PHBV, and starch. This versatile and adaptable pretreatment approach holds promise as a solution to the challenge of food packaging waste, besides improving biowastes collection and reducing environmental pollution from packaging waste.

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OC 19C

Harnessing Microalgal Polymers for Cutting-Edge Tissue Engineering Applications

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INTRODUCTION

Research on biomaterials development is focusing on safer and more effective approaches for tissue regeneration [1]. A significant trend in this field is the implementation of natural materials to reduce rejections due to biocompatibility issues. Consequently, non-animal sources are being explored for the extraction of bioactive materials applicable to tissue engineering [2]. Microalgae have emerged as a promising source for extracting several compounds, including lipids, polymers, and proteins, with pharmaceutical potential [3,4]. In tissue engineering, additive manufacturing techniques, particularly 3D printing, are gaining attention. Biopolymer hydrogels, such as cellulose derived from natural resources, have attracted significant interest due to their remarkable properties, including mechanical strength, biocompatibility, renewability, and biodegradability [5]. However, efficiently using cellulose as a material source presents challenges, especially in industrial chemistry, due to poor water solubility and low thermoplasticity. Cellulose is insoluble in both typical organic solvents and water, because of its extensive hydrogen bonding network [6]. To address these challenges, the chemical synthesis of cellulose derivatives is being investigated [7]. Hence, this study aims to extract cellulose from the green microalgae *Nannochloropsis* sp. and evaluate its potential to develop an ink suitable for 3D printing applications in tissue engineering.

EXPERIMENTAL

For ten days, the microalgae *Nannochloropsis* sp. grown under optimal conditions, achieving a cellular density of 6.9×10^6 cells/ml (Fig.1a). Cellulose was extracted using a biorefinery approach, achieving a polymer yield of 20.44 g/L, and fully characterized morphologically (by Scanning Electron Microscope - SEM), thermically (by Thermogravimetric analysis), and chemically (Fourier Transform Infrared - Attenuated Total Reflectance - FTIR-ATR and gel permeation chromatography) [8]. For convenience, commercial Sodium Carboxymethylcellulose (Na-CMC) was used to evaluate the best printing parameters in an extrusion-based printer with a pressure-assisted system (BioX). As a first approach, three concentrations of Na-CMC were used (10, 15 and 20%) and two crosslinking methods were tested (ethanol precipitation and pH modification).

RESULTS AND DISCUSSION

Morphologically, the cellulose extracted presented a structure with low crystallinity, containing amorphous and crystalline regions (Fig.1b) [9]. Chemically, the absorption band at 1637cm^{-1} is assigned to C-O- group of secondary alcohols and ethers functions existing in the cellulose chain backbone. While the signal at 3011 and 1410cm^{-1} is assigned to stretching and deformation vibrations of C-H in glucose unit and the absorption band at 845 cm^{-1} is characteristic of β-glycosidic linkage between glucose units (Fig.1c) [9]. The polysaccharide extracted exhibited a molecular weight of 1147 g/mol and presented a good thermostability, since no significant weight loss occurred until 500ºC, corresponding to the cellulose pyrolysis temperature [10]. The scaffolds were best printed using a 15% Na-CMC concentration and pH adjustment for crosslinking (Fig. 1d).

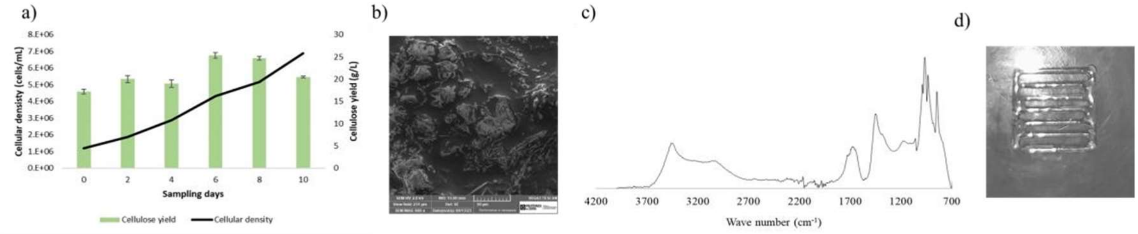

Figure 1. a) *Nannochloropsis* sp. cellulose yield during growth, b) extracted cellulose SEM image and c) FTIR-ATR spectra, d) printed carboxymethylcellulose scaffold.

CONCLUSIONS

This study shows the potential of extracting cellulose from *Nannochloropsis* sp. and to use it to create a novel ink for 3D printing for tissue engineering. This approach provides a sustainable alternative to synthetic scaffolds for medical devices.

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OC 20C

Forging sustainable pathways: advancing chemical recycling techniques to address poly(ethylene 2,5-furandicarboxylate) circularity

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INTRODUCTION

Polymers, singular materials in shaping modern society, have exceptional properties [1]. These properties which turn polymers into privileged materials also raise significant challenges, as most of them are neither biodegradable nor easily recyclable, leading to their accumulation in the environment if inadequately disposed. Hence, the development of novel technologies for polymers recycling is of utmost importance to improve circularity and to reduce the environmental burden associated with polymers use, and thus for a sustainable development of this sector.

Recent studies illustrated the potential of eutectic solvents (ES) as a *greener* approach for polyester depolymerization [2,3], where we have also showcased the recycling of poly(ethylene terephthalate) (PET) [4]. Building on these findings, the present work extends the use of terpenoid-based ES to the recycling of the PET homologue - poly(ethylene 2,5-furandicarboxylate) (PEF), achieving promising results with this innovative and environmentally friendly method.

RESULTS AND DISCUSSION

The present study presents a process involving the alkaline catalysed hydrolytic depolymerization of PEF into 2,5-furandicarboxylic acid (FDCA) using terpenoid-based ES, where the combined effect between ES components and the base was found to be essential for effective PEF depolymerization. Structural characterization confirmed the purity of the recovered FDCA. The recyclability of the ES was evaluated, demonstrating the effectiveness of the reaction media for at least 7 depolymerization cycles without a relevant loss in catalytic activity. FDCA yields exceeding 80 % were achieved at relatively mild reaction temperature, room pressure and not exceeding 5h of reaction. Green metrics were determined, with E-factors akin to those found in the fine chemicals industry [5]. Finally, the feasibility of using the recycled FDCA for repolymerization into PEF was also proven successful.

CONCLUSIONS

This work demonstrates the potential of terpenoid-based ESs combined with sodium carbonate for PEF depolymerization, enabling efficient FDCA recovery in high yields.

ACKNOWLEDGEMENTS

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OC 21C

Active polylactic acid-based films with encapsulated lemongrass essential oil for fresh-cut apples packaging

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INTRODUCTION

The search for sustainable and innovative solutions for food preservation is a top priority for food industry. Biodegradable active packaging is a promising solution to these challenges, meeting both consumer and environmental needs (1). The incorporation of active components to packaging materials, while providing a physical barrier to protect food, is a significant advancement in food preservation. One crucial aspect of active packaging is its ability to maintain the food quality and integrity without altering taste, odour, or appearance (2). Encapsulation of essential oils (EOs) offers an effective way to preserve food's sensory characteristics and extend shelf life due to their antimicrobial and antioxidant properties. This study aims to develop and characterize active PLA-based films containing encapsulated lemongrass essential oil in cyclodextrins as well as the evaluation of their antioxidant and antifungal effectiveness on 'Fuji' apples packaging.

EXPERIMENTAL

EOs were encapsulated in γ-cyclodextrin by Spray drying. Five films were processed using a twin-screw microextruder: neat PLA as control and four films with increasing concentrations of encapsulated lemongrass oil (1, 3, 5, and 7 wt%). Thermal (DSC and TGA), optical (transparency, UV-blocking, colour change), barrier (WVP), antifungal, antioxidant, mechanical, FTIR, and SEM properties were determined for all films. The active films efficiency (up to 5 wt% lemongrass EO) was evaluated on minimally processed apples stored for 15 days at 4 °C, with evaluation of their colour, weight loss, acidity, soluble solids, bioactive compounds, enzymatic browning, and membrane damage every 5 days.

RESULTS AND DISCUSSION

Minimal variations in colour, transparency, thermal properties, and UV-blocking ability between neat PLA and active films, up to 5 wt% additive concentration, were noticed. Antifungal and antioxidant activities were more prominent at higher EO concentrations. However, despite the higher antioxidant and antimicrobial potential of the 7 wt% EO film, losses in other properties significantly compromised its performance. Consequently, films containing 1, 3, and 5 wt% encapsulated lemongrass EO were chosen for in vivo testing. These films exhibited a slowdown in maturation reactions, reduced sugar increase, and higher organic acid levels. Additionally, samples with active films exhibited limited carbon dioxide production, better preservation of bioactive compounds, and reduced activity of enzymes responsible for apple browning and membrane damage.

CONCLUSIONS

Lemongrass EO microcapsules were successfully incorporated into PLA to produce biodegradable active films. These additives demonstrated good compatibility with the polymer matrix, resulting in minimal changes in thermal and UV barrier properties, while providing antifungal and antioxidant activities to the film. Moreover, when applied to minimally processed fresh fruit, these films slowed down fruit ripening processes, weight loss, respiration rate, enzymatic browning, membrane damage, and loss of bioactive components. Therefore, these films could be considered as potential formulations adequate for storing highly perishable foods, such as fruits.

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OC 22C

A new family of bio-based polyurethanes for cosmetic use

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INTRODUCTION

The cosmetics industry is rapidly shifting towards replacing fossil fuel-derived polymers[1,2] and materials with bio-based alternatives to reduce environmental impact and promote sustainability. Anhydrous products play a primary role in make-up, especially for the decoration of lips and eyes, where they can deliver special effects and textures able to create peculiar sensory responses. However, the historical period dictates that materials are easily available and a plus is represented by natural derivation using agricultural by-products containing precious building blocks otherwise wasted. In this regard, the versatility of polyurethane chemistry was adopted to develop unique raw materials, tuned to the need of giving structure, shape, and improved cosmetic performance to new and more sophisticated anhydrous formulations.

In the present work, the focus was the obtainment of a family of materials with vegetable origin, exploiting polyurethane chemistry. Succinic and azelaic acids are precursors conveniently sourced from nature and used in the synthesis. These organic diacids where esterified with naturally derived glycerin and bio-based short chain acids (C8-C10, e.g. from coconut oil) to obtain pre-polymer macro-diols that were further copolymerized with isophorone diisocyanate (IPDI) and lineseed oil-derived hydrogenated dilinoleyl alcohol[3,4].

RESULTS AND DISCUSSION

The polyurethanes were successfully synthesized. The introduction of derivates of succinic acid or azelaic acid as a macro-diol in the polymer structure was modulated together with an alkyl diol (hydrogenated dilinoleyl alcohol), and physico-chemical characterization (ATR-FTIR, DSC, SECGPC) was performed on the synthesized polymers to determine their structure, thermal behavior and molecular weight.

CONCLUSION

The materials presented in this work are the first born of a new bio-based polyurethanes family. Conceived to improve skin adherence, shiny appearance, long-lasting and good sensory properties, they also boast high Natural Origin Index. The lip fluid containing bio-based polyurethanes displays a very glossy finish, and its principal characteristics is naturality, due also to the wise choice of co-ingredients in the formulation. The ongoing research on the design of polyurethanes for cosmetics is consolidating the knowledge on their structure-property relationships, making the way towards high performance biobased products increasingly viable.

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OC 23C

Development and Evaluation of Eco-Friendly Plastic Films with Nano-TiO_2 for Ethylene Scavenging: Characterization, *in vivo* Evaluation, and Compostability Analysis

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INTRODUCTION

Ethylene (C_2H_4) is a gaseous hormone responsible for the ripening and senescence of fruits and vegetables, especially during storage [1]. To control the ethylene levels around this kind of food, titanium dioxide (TiO_2) has been studied as a possible active agent for the development of ethylene scavenger films due to its photocatalytic capacity against organic molecules. Thus, the aim of this study was to develop active nanocomposites based on poly(lactic acid)-(PLA) and MaterBi-(MB) with nanoTiO_2 able to be ethylene-active and to environmentally friendly.

EXPERIMENTAL

PLA/TiO_2 and MaterBi/TiO_2 nanocomposites were prepared using different contents of nano-TiO_2 (0, 5 and 10 wt. %) through an extrusion process [2]. The different nanocomposites were characterized by a structural analysis (FTIR), morphological (SEM), thermal (DSC and TGA), dynamic (DMA) and mechanical properties. On the other hand, the ethylene removal capacity was determined by gas chromatography using ultraviolet (UV) and visible light (VIS) application on the plastic materials. In addition, an *in vivo* study was conducted on bananas over a 9-day period at 25 °C to assess the impact of films on the physiological aspects of the fruit. Finally, in order to evaluate the effect of nanoparticles on the compostability of the different materials, disintegration and ecotoxicity testing were conducted.

RESULTS AND DISCUSSION

All nanocomposites showed ethylene removal capacity. However, the materials exhibited the highest activity against the olefin when UV light was used to activate them. It was observed that agglomeration of the TiO_2 in the materials was a critical factor in ethylene removal. Consequently, it was demonstrated that films made with 5 wt. % presented a higher ethylene removal capacity than those made with 10 wt. %. Based on these findings, films with 5 wt. % were selected for evaluation in *in vivo* tests. Figure 1 shows the ethylene removal capacity of bananas packed with this active material during 9 days at room temperature, and the effect on ripening of banana fruit.

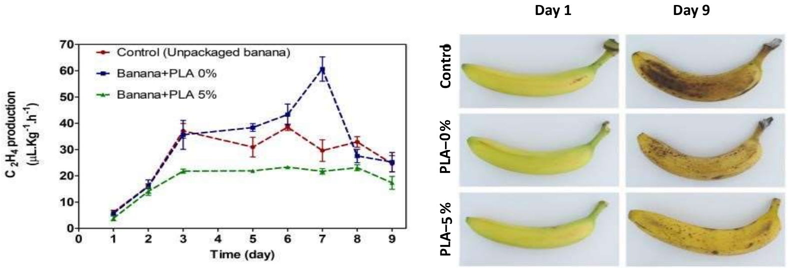

Figure 1. Evolution of ethylene production (left) and ripening of banana packed in PLA active material.

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4.

POSTER COMMUNICATIONS

P1.1

Alginate/Chitosan nanocomplexes for p53 encoding plasmid DNA delivery

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INTRODUCTION

The tumour suppressor p53 remains one of the most interesting therapeutic targets in cancer gene therapy due to its consistent mutation in numerous cancers (1). Polymeric nanocarriers have offered an ideal platform for incorporating all the desirable characteristics (like a targeted delivery, controlled release, among others) into a single gene delivery system (2).

By modifying the surface properties, nanocarriers can achieve better biocompatibility, controlled release, and precise interaction with biological targets (3). Moreover, positively charged nanoparticles can easily interact with the negatively charged cell membranes of cancer cells resulting in a higher uptake and enhanced therapeutic efficacy (4).

Align with this, the work aimed to develop biopolymer nanocomplex based on a core of alginate and a surface layer of chitosan. To achieve this, chitosan with different molecular weights was used to cover alginate nanoparticles. Moreover, smaller nanoparticles (produced with low molecular weight chitosan) was loaded with p53 encoding plasmid DNA (pDNA) and its cytotoxicity was evaluated

EXPERIMENTAL

Alginate-Chitosan nanoparticles were formulated using chitosan of different molecular weights and characterized for size, PDI, and zeta potential. The optimized nanoparticles were loaded with p53 encoding pDNA. These nanoparticles were characterized by FTIR, SEM and EDX analysis, always comparing with the uncoated nanoparticles. Release kinetics were evaluated, and the nanocarriers were tested on CaCo-2 (p53 down-regulated cells) and healthy fibroblast cells.

RESULTS AND DISCUSSION

Chitosan led to a decrease in particle size and to positive zeta potential when compared with alginate nanoparticles. This occurs for any kind of molecular weight chitosan tested. Also, through FTIR was possible to see some differences between the spectra of the particles produced with different molecular weight Chitosans. The pDNA encapsulation efficiency was around 96% and the cytotoxic effect of these particles was also assessed.

Table I – Nanoparticles size, PDI and zeta for different tested formulations.

Sample	Mw	Size nm (Mean)	PDI (Mean)	Zeta mV (Mean)
Alginate	-	269 ± 29.2	0.288 ± 0.019	- 2.863 ± 1.821
Alginate + Chitosan	High	189.8 ± 9.1	0.195 ± 0.061	23.387 ± 5.407
Alginate + Chitosan	Medium	175.4 ± 14.5	0.212 ± 0.082	19.817 ± 4.291
Alginate + Chitosan	Low	161 ± 16.8	0.284 ± 0.023	19.623 ± 1.341

CONCLUSIONS

By adding chitosan to the alginate nanoformulations, some physical changes were observedbeing the nanoconjugate size smaller than the alginate nanoparticles which could lead to an easier internalization. Notably the major changes were seen in the zeta potential, shifting from negative to positive charges, reflecting the success of the Chitosan coating. They also presented a good ability to transport high amounts of pDNA.

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P2.1

Effect of processing conditions on Supercritical Foaming of caffeic acid-loaded PLA/PBAT blends for the development of sustainable materials

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INTRODUCTION

In recent years, PLA foams have emerged as a promising alternative to traditional polyolefin-based polymeric foams, such as polystyrene (PS) [1]. However, PLA has some limitations that are important for its application and foam production. Considering these disadvantages, several alternatives have been studied, such as its blending with other polymers. Among the polymers used, PBAT stands out as a commercially available copolymer with excellent mechanical properties, characteristics that make it an ideal candidate for blending with PLA to increase its crystallinity and overcome its brittleness and low toughness [2]. In this work, the effect of pressure on the supercritical foaming of PLA/PBAT blends impregnated with caffeic acid (CA) has been analysed.

EXPERIMENTAL

Supercritical foaming of PLA/PBAT blends with impregnated caffeic acid was performed at 130 ºC, pressures of 15 and 25 MPa, for 30 min. The morphologies of the different foam samples were analyzed by scanning electron microscopy (SEM) using a Scanning Microscope (Tokyo, Japan) with accelerating voltage at 20 kV. Cell size was measured using ImageJ 1.53t software and was obtained by measuring the maximum diameter of each cell. To determine the cell size distribution, the size of at least 75 cells in the central part of the cryofracture cross-section was analyzed.

RESULTS AND DISCUSSION

PLA polymeric foams and PLA-based blends were developed with and without impregnated CA at different processing conditions. SEM micrographs of foams showed significant differences due to the presence of PBAT (Figure 1). PLA and blends produce microcellular foams, and the increase in pressure conditions caused a decrease in pore diameter for all foams.

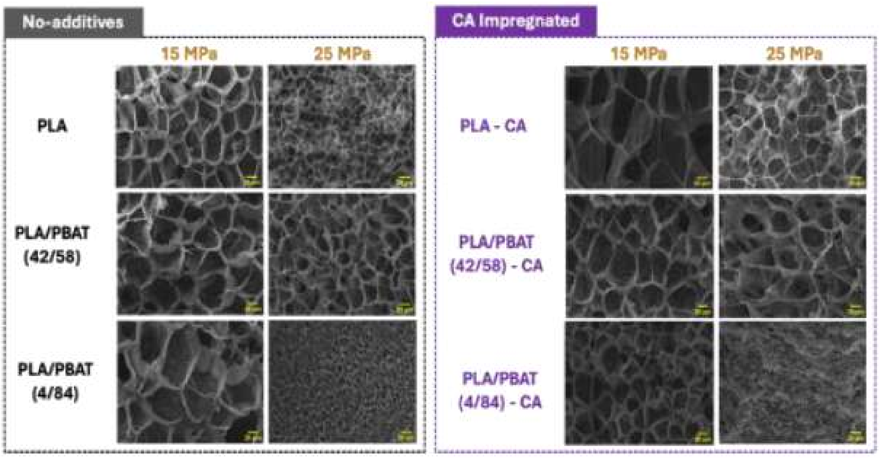

Figure 1. SEM micrographs of PLA and PLA/PBAT foams at different pressures.

CONCLUSIONS

SEM images of both films and foams showed significant differences due to the presence and amount of PBAT and the low miscibility between the polymers.

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P3.1

Ecodesign and processability assessment of novel furan-based biopolymers for innovative applications

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INTRODUCTION

In this study, we exploited the effectiveness of polymer chemical modification to ecodesign biopolymers with target properties for innovative applications: a flexible and transparent film for biomedical and electronic packaging, an antibacterial car filter and a transparent screen for the automotive sector, by acting on polymer chemical structure, copolymerization and molecular architecture. Poly (trimethylene 2,5-furanoate) (PTF), poly (butylene 2,5-furanoate) (PBF) and poly (pentamethylene 2,5-furanoate) (PPeF) are three furan-based polyesters known for their excellent gas barrier properties [1-3]. The last one is rubbery at room temperature with limited crystallization capacity [3]. Starting from these well-known homopolymers, a series of copolymers have been obtained through a solvent-free melt polymerization, aiming to tune flexibility, crystallization capacity, degradability/resistance in different conditions and hydrophilicity/hydrophobicity ratio. Lastly, ionizable functional groups and aliphatic side chains have been used to promote interaction and denaturation of bacterial cell membranes [4].

EXPERIMENTAL

Each obtained polymer (Figure 1) has been molecularly characterized through GPC, NMR and FT-IR. DSC analysis helped to determine the useful window for thermal processing via compression molding, while WCA analysis allowed the evaluation of the hydrophilicity of all the produced systems.

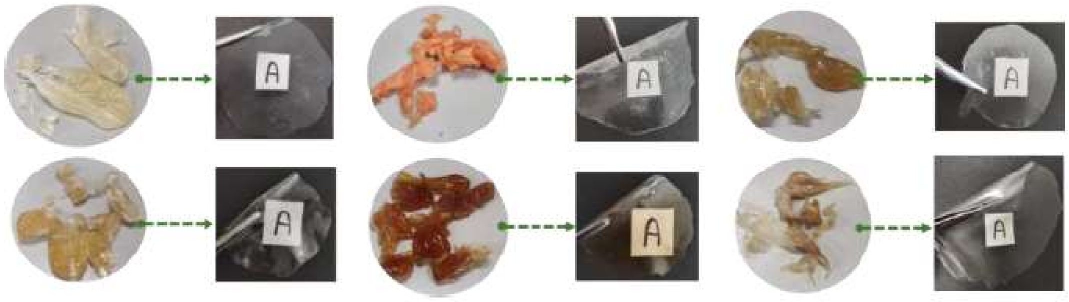

Figure 1: Some polymers synthesized and processed via compression molding

RESULTS AND DISCUSSION

The inclusion of comonomers like 1,6-hexanediol, 1,8-octaneidol, 2-butyl-2ethyl-1,3-propanediol and triethylene glycol has limited the crystallization capacity of the final materials, ensuring transparency and flexibility. Also, the hydrophilicity and degradation kinetics have been altered. Finally, a series of copolymers have been synthesized using monomers derived from fatty acids (such as Pripol 1009-LQ and

PriamineTM 1075), these last have great potential in imparting intrinsic antibacterial properties to the polymer.

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P4.1

Valorisation of date seeds for the production of oil-rich formulations based on maltodextrin and casein

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INTRODUCTION

Date seeds are residues, rich in bioactive compounds, which are obtained during the fruit manufacturing [1]. However, these compounds are prone to thermal degradation and they should be protected in some way during materials processing. In this sense, encapsulation is commonly used to protect these sensitive compounds. The barrier provided by the encapsulation agent protects bioactive compounds from oxidation, light, and temperature, avoiding interaction with other components and also controlling, in some cases, the release of the active compounds to the environment [2]. Biopolymers, including starches, gums, gelatins, and others with hydrophilic or hydrophobic character, are used as wall materials for encapsulation. This study aimed to assess the potential of a combination of maltodextrin (MD) and sodium casein (CS) for microencapsulating oil extracts from date seeds obtained by microwave-assisted extraction (MAE). Different formulations were obtained by spray-drying and were fully characterised.

EXPERIMENTAL

Oils extracts from date seeds were encapsulated by using spray-drying with MD and CS (1:1). Two ratios for encapsulation were evaluated (1:2 and 1:3 extract:polymer). The obtained microcapsules were characterised, and the microstructure (SEM and XRD), thermal behaviour (TGA), encapsulation yield and efficiency were used.

RESULTS AND DISCUSSION

Encapsulation efficiencies (EE) ranging from 48.3% to 80.7% (w/v) for oil in the MD/CS formulations were obtained, and microparticles showed spherical shape and smooth surfaces (Figure 1a). The maximum degradation temperature was around 300 ºC, and the XRD spectra showed the predominance of amorphous regions in the materials structure (Figure 1b). The FTIR spectra corroborated the presence of oil in the capsules. Finally, the thermal stability, based on tocopherols composition, indicated that the microcapsules remained stable even at temperatures higher than 130 °C compared with the non-encapsulated oil.

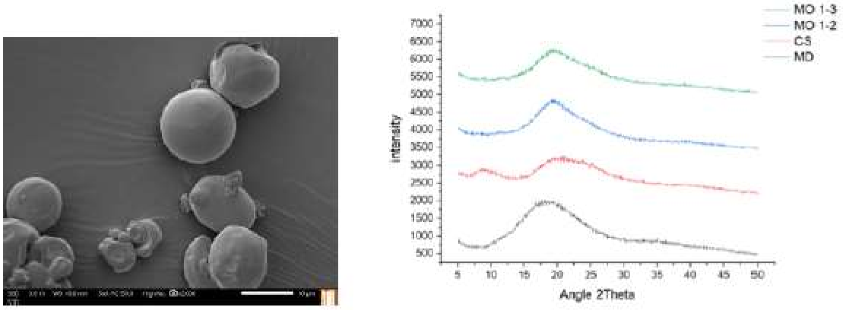

Figure 1. (a) SEM image of the spray-dried powder date seed oil; (b) XRD patterns of materials

CONCLUSIONS

The oil extracted from date seeds can be efficiently protected by encapsulation in MD and CS (1:1) materials. In conclusion, the valorisation of date seeds results in biomaterials by the application of oils and tocopherols into biopolymer matrices and can be used as food additives and functional ingredients.

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P5.1

Coupled diffusion of salts and sodium hyaluronate in aqueous solutions

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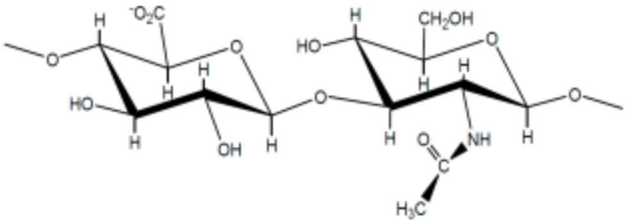
INTRODUCTION

Hyaluronan (sodium salt of hyaluronic acid, (NaHy) consists of a disaccharide repeating sequence of d-glucuronic acid and N-acetyl-d-glucosamine, linked via alternating β-(1→4) and β-(1→3) glycosidic bonds bonds (Figure 1)



For most of these applications, the knowledge of the transport properties ofNaHy in aqueous solutions plays a key role. Furthemore, it is known that Hofmeister or specific ion effects affect some physicochemical properties of aqueous and nonaqueous (e.g., [1,2]) systems. Other example are studies made by Mráček et al. [3] about the influence of Hofmeister series ions on HyA behaviour and HyA film-swelling. Mráček et al. [4] also showed, by using viscosity measurements, that the presence of specific ions such as sulphate anions, affects the behaviour of NaHy in aqueous solutions due to its ability to act as “structure making” and “structure breaking”, leading to the expansion or contraction of the NaHy coil. Following this work, and given its importance, the present work focuses on the investigation of the effect of different salts (Crcl3 and Cocl2), on the mutual interdiffusion coefficients of NaHy, at 25.00 °C. Thees parameters were measured by using Taylor Technique.

RESULTS AND DISCUSSION

Tracer diffusion coefficients obtained from the Taylor dispersion technique at 25.0 °C were measured to study the influence of cobalt and chromium salts at 0.01 mol dm−3 on the transport behavior of sodium. Table 1 summarizes the mean values of the Dik diffusion coefficients for the solutions of different compositions and concentrations for six aqueous systems, involving two salts (CoCl2 and CrCl3) and NaHy with different molecular weight (124 kDa and 245 kDa).

The values were calculated by fitting Equation (1) to dispersion curves; the number of replicas is always greater than four. The main diffusion coefficients (D11 and D22) have an uncertainty value smaller than

(±0.015 × 10−9 m^2 s^{-1}), whilst the cross-diffusion coefficients (D12 and D21) have an uncertainty value smaller than (±0.050 × 10−9 m^2 s^{-1}).

From this table, it is note that $D_{12} < 0$. That is, the gradient in the concentration of produces counter-current coupled flows of these salts. These observations can readily be explained by the following two phenomena: the hydrolysis of cobalt and chromium ions and association between $CoCl_2$ (or $CrCl_3$) and these NaHy entities, leading to the formation of supramolecular complexes in solution. This phenomenon will lead to a decrease in free cobalt (or chromium ions), and, consequently, to compensate for that loss, a counterflow of these salts will occur.

$D_{12} < 0$, that is, the gradient in the concentration of produces counter-current coupled flows of these salts. From these data, it can been that there are interaction of these solutes (NaHy and Salts).

Table 1 Tracer diffusion diffusion coefficients $^{a)}$ for NaHy in aqueous CoCl2 and CrCl3 solutions at 25.00 ºC

Sal	**Molecular weight/kDa**	D_{11}**± SD**^{d}	D_{12}**± SD**^{d}	D_{21}**± SD**^{d}	D_{22}**± SD**^{d}
$CoCl_2$ 0.010 M a) (NaHy pure 1 %)	124	1.215±0.010	−0.205±0.050	0.010±0.019	0.192±0.013
$CrCl_3$ 0.010 M b) (NaHy pure 1 %)	124	1.137±0.012	−0.182±0.040	−0.050±0.020	0.302±0.017

^{a} https://doi.org/10.3390/pr11061701

CONCLUSIONS

Based on these measurements of diffusion coefficients of systems containing sodium hyaluronate and electrolytes in aqueous solutions, we conclude that the diffusion of this polysaccharide in aqueous solutions is strongly affected by the presence of the electrolytes. The behaviour of diffusion of NaHy in aqueous solutions changes in the presence of the salts as a result of the salting-in effect.

Diffusion coefficients measured for aqueous solutions of systems containing sodium hyaluronate and salts, provide transport data necessary to model the diffusion in pharmaceutical and engineering applications. The most relevant contributions of the study should be summarized in this section.

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ACKNOWLEDGMENTS

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P6.1

Chemically functionalized starch as a multifunctional material in bio-based food packaging

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INTRODUCTION

In the last few decades, there has been a significant increase in demand for sustainable materials due to their advantages compared to plastics from fossil sources, such as biodegradability, lower operating costs, and less environmental impact. Starch is a well-known bio-based polymer widely used in the pharmaceutical, cosmetic, and food industries. It can be modified to enhance its physical properties and extend its applications[1].

Our goals in this work are (1) to obtain the functionalization of potato starch with antimicrobial agents[2], in a controlled and reproducible manner, using a simple and environmentally friendly methodology; (2) to collate mechanical properties in both pristine and modified starch material, as well as their antimicrobial activity; and (3) to apply this chemical procedure to starch obtained from other sources (cereals, fruits and other vegetables) in order to generalize its use for food packaging regardless its origin.

EXPERIMENTAL

Potato starch was modified using a one-pot reaction, wherein an isocyanate derivative carrying the antimicrobial agent in bulk is prepared (figure 1), which reacts with starch dispersed in methyl-THF (solvent from renewable sources) at 70ºC, and using K_2CO_3 as a base. The products were analyzed by FTIR-ATR, ^{1}H-NMR, and TGA. Afterwards, films were prepared, mixed with glycerol and water as well as neat starch in different percentages to facilitate processing. Films were studied by tensile testing.

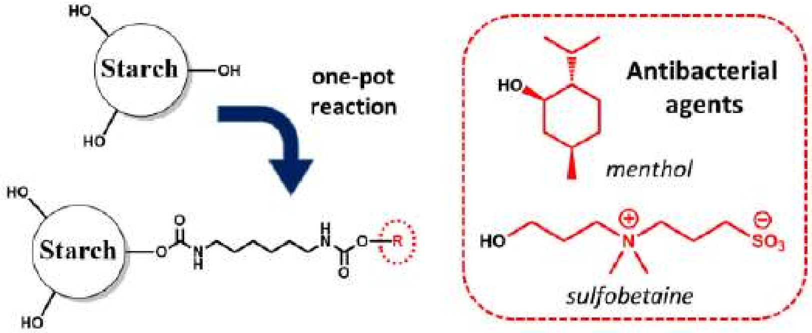

Fig. 1: Scheme of starch functionalization via urethane linker with antibacterial agents.

RESULTS AND DISCUSSION

The chemical modification was achieved successfully, obtaining up to 15 mol% of the antibacterial agent. As expected, the higher the menthol content the more hydrophobic behavior of the starch, in contrast to sulfobetaine when anchored. However, this functionalization had small impact on the mechanical properties.

CONCLUSIONS

The results suggest that the chemical modification of starch with bioactive compounds, containing nucleophilic groups, can be achieved using a linker such as diisocyanate. Additionally, it is possible to process such materials by solvent casting, maintaining mechanical properties similar to those of the unmodified starch. In the future, antibacterial behavior of these materials will be analyzed in order to achieve optimal bio-based materials for food packaging.

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P7.1

Edible films based on sheep's second cheese whey and whey protein isolate incorporating oregano essential oil

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INTRODUCTION

The addition of essential oils to films manufactured with whey protein concentrates or isolates has been investigated due to their antimicrobial and antioxidant effects. However, their incorporation in films produced with second cheese whey (SCW) has not been studied. Sheep´s SCW is an important byproduct obtained in the ovine whey cheese production. The aim of this work was to study the properties of films obtained with sheep's SCW and whey protein isolate (WPI) incorporating oregano (Origanum compactum) essential oil (EO) in two different proportions.

EXPERIMENTAL

WPI (NatWPI90, with 90% w/w protein) supplied by InLeit Ingredients S.L.U. (Curtis, Spain) and sheep's SCW powder obtained after ultrafiltration/diafiltration and drying (with 55% w/w protein) were used to prepare the films with a final concentration of protein in film-forming solution of 8% (w/v), using glycerol as plasticizer. Six different films were prepared with the addition of oregano (Origanum compactum) essential oil (Plena Natura, Amadora, Portugal). The films were prepared in the following way: after heat treatment and cooling, the WPI film-forming solution added with plasticizer was separated into six equal portions; then, the corresponding amounts of SCW powder and the EO were incorporated to prepare films containing three proportions of WPI-SCW (2:1, 1:1 and 1:2) and two different concentrations of oregano EO (1 and 2% of the powder weight in solution). Water vapor permeability, thickness, dry matter content, solubility, density, color parameters and opacity, mechanical properties and antioxidant activity of the films were determined according to Cobos and Díaz [1].

RESULTS AND DISCUSSION

The films produced with the addition of 2% of oregano EO showed lower values of water vapor permeability (WVP) than the corresponding films with the incorporation of 1% of oregano EO. No important effects of the addition of oregano EO were found in thickness, dry matter content, solubility, and density of the films. The color parameters of the films (L*, a*, b*) and their opacity were not influenced by the proportion of oregano EO.

Regarding the mechanical properties, the most remarkable result is that the films with 2% of oregano EO showed higher values of tensile strength than the corresponding films with 1% of oregano EO. The addition of oregano EO increased the antioxidant activity of the films.

CONCLUSIONS

The addition of oregano EO to the SCW-WPI films increased the antioxidant activity of the films. It also modified other characteristics of the films such as the WVP and the tensile strength.

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P8.1

Dynamic chitosan based shell for alginate microparticles obtained by microfluidics

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INTRODUCTION

Largely due to their microsize, hydrogel microparticles have attracted significant attention as a promising functional platform in tissue engineering and drug delivery. Droplet microfluidics provides meticulous management of fluid flows at the microscale, facilitating the creation of sophisticated microparticles with finely adjustable structures and compositions. These microparticles hold immense promise across diverse bio-related domains, encompassing drug delivery, cell-laden matrices, biosensors, and potential applications as synthetic cells. [1,2].

EXPERIMENTAL

Alginate microparticles cross-linked with Ca^{2+} by internal gelation were produced using droplet-based microfluidics. 2 wt% alginate aqueous solution containing Ca-EDTA was used as dispersed phase, and mineral oil containing Span 80 (0.1 wt%) was the continuous one. Microparticles were collected in acidified continuous phase to obtain the crosslinked alginate microparticles, whereas alginate-chitosan core-shell microparticles were obtained in a biphasic solution of acidified continuous phase and chitosan (1 wt% in HAc 1 wt%). Finally, the alginate-chitosan core-shell microparticles were incubated in a PEG-dialdehyde solution (0.5 wt%) in order to form the dynamic shell. All the microparticles were characterized by OM, FTIR, and SEM.

RESULTS AND DISCUSSION

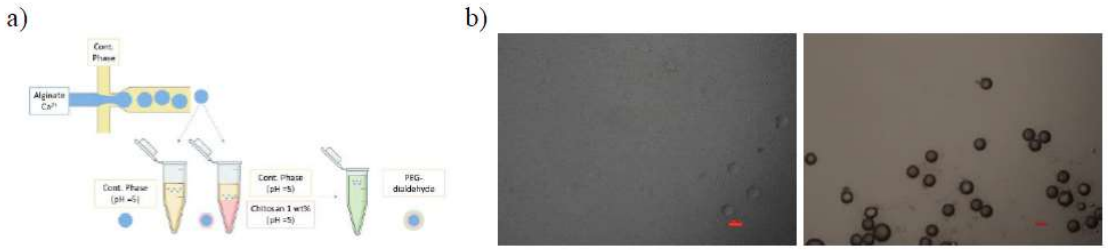

Figure 1. a) Schematic experimental procedure, and b) OM images of alginate microparaticles (left) and alginate-chitosan core-shell microparticles (right). Scale bar 100 µm.

CONCLUSIONS

Alginate microparticles decorated with chitosan/PEG Schiff base dynamic shell as pH-responsive drug delivery systems were successfully prepared by microfluidics. The microparticles showed good dimensional stability and homogeneous final morphologies.

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P9.1

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/chitosan bilayer membrane as magnetically responsive bioactive wound dress

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INTRODUCTION

Electrospinning is an adaptable method for the production of polymeric nanofibers [1] with enormous potential for their use in biomedical applications, mainly in wound dressing and drug delivery. In the search of materials for this field of application, chitosan (Cs) is one of the most commonly used polymers, thanks to its biocompatible and antimicrobial character [2]. Moreover, recently, in the biomedical field, the use of magnetite (Fe3O4) has gained great popularity [3], owed to its proven potential in wound dressing. In this context, the main objective of this research was to produce and characterize magnetically responsive bilayer membranes composed of outer magnetite nanoparticles (MNPs) loaded poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) layer and inner Cs/polyether oxide (PEO) bioactive nanofibers. The good spinnability and mechanical resistance of PHBV confers stability to the wound dressing, maintaining the biodegradable character of the material, while acting as a matrix for the MNPs.

EXPERIMENTAL Commercial PHBV (ENMAT Y1000P, Tianan Biologic Materials (Ningbi, China)) with a HV fraction of 2-3 mol%, according to the manufacturer, low molecular weight Cs and PEO (600kDa) (both from Sigma-Aldrich) were employed for the preparation of electrospun nanofibers, using a Fluidnatek LE-10 equipment (Bioinicia S.L.). MNPs coated with oleic acid were incorporated to the PHBV electrospinning solution, while silver sulfadiazine (SSD, Thermo Fisher Chemicals), curcumin or eugenol (Sigma-Aldrich) were mixed with that of Cs/PEO. Tetrafluoroethanol and deionized water:acetic acid (1:1 v/v) were used as solvents of each layer.

RESULTS AND DISCUSSION

The morphology of each side of the bilayer membrane was analyzed by SEM (Figure 1B,C). Both showed homogeneous defect-free nanofibers, presenting average diameters of 0.6 ± 0.1 µm and 0.2 ± 0.1µm for the PHBV/MNP and Cs/PEO/drug layers, respectively. The magnetic responsiveness of the outer layer conferred by MNPs increased with the nanoparticles content (Figure 1A).

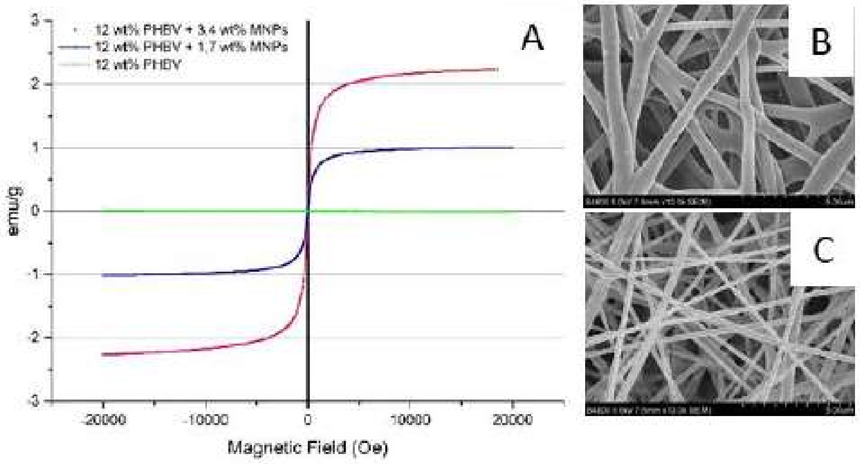

Figure 1. A) Magnetic properties of PHBV/MNPs mats with different MNP contents. SEM images of B) PHBV/MNPs and C) Cs/PEO nanofiber membranes.

CONCLUSIONS

MNPs loaded PHBV and drug containing Cs/PEO solutions were successfully electrospun one on top of the other, obtaining a defect-free nanofiber bilayer membrane as promising magnetically responsive active wound dressing.

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P10.1

Advancements in Thermally Shaped Polymer Sutures for Microsurgery: From Synthesis to Biocompatibility

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INTRODUCTION

Traditionally, sutures used in ophthalmology are made from materials such as prolene or nylon [1]. However, these sutures have limitations such as poor handling and the need for removal after healing. To overcome these limitations, researchers started investigating the use of biodegradable and thermally memory-shaped polymers. To obtain a memory shaped material, copolymers containing a hard segment (an aliphatic highly semicrystalline polyester) (A), and a soft one (an aliphatic ether oxygen atom-containing polyester) (B), should be used. Indeed, the hard part provides the necessary mechanical strength and stability, while the soft part allows for easy manipulation and shaping of the suture [2].

EXPERIMENTAL

A and B were synthesized by melt polycondensation. A physical blend and various copolymers were synthesized by solvent casting and reactive blending at different times, respectively, starting from the same weight amount of the two homopolymers. Molecular characterization was performed by means of NMR and GPC, while thermal properties were analysed by DSC and TGA. In addition, the crystallinity was determined by WAXS, and SEM was used to determine the compatibility of the two homopolymers inside the blend. Tensile and cyclic mechanical tests, contact angle measurements and qualitative evaluation of shape memory were conducted. In vitro cytotoxicity was evaluated using a primary culture of corneal fibroblasts. Finally, hydrolytic degradation tests were also performed.

RESULTS AND DISCUSSION

The chemical structure and the molecular architecture of the copolymers were determined, confirming a good control over polymerization. In terms of thermal behaviour, the blend reproduces the behaviour of the two homopolymers, with a low melting crystalline phase typical of B and a high melting one of A. For the copolymers, the higher melting phenomenon becomes less intense and shifts towards lower temperatures as the mixing time increases. Crystallinity also decreases as the length of the copolymer sequences decreases. After that, the physical blend and a block copolymer were selected for further characterization, as the more promising for the intended application. These materials were characterized by high molecular weights and high thermal stability. Although A exhibits contact angle values typical of hydrophobic materials, the blend and the copolymer are more hydrophilic, thanks to the presence of ether oxygen atoms in B moieties. Both the blend and the copolymer exhibit also a thermoplastic elastomeric and a shape-memory behaviour. In vitro cytotoxicity tests showed very good cell viability and the materials turned out to be also biodegradable in physiological environment.

CONCLUSIONS

The appropriate choice of starting homopolymers, as well as the proper chemical design, made possible to obtain suitable materials for a potential use in ophthalmic microsurgery as shape memory sutures.

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P11.1

Cross-linking of chitosan-lignin biocomposites for fuel cell applications

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INTRODUCTION

Chitosan has emerged as a promising material for fuel cell applications, despite its low durability in humid environments. Covalent and ionic cross-linking can enhance the dimensional stability and mechanical strength of chitosan [1]. In addition, the use of lignin has been shown to improve the mechanical properties, thermal stability, and water absorption [2]. In this study, two different covalent cross-linking agents (glutaraldehyde (GP) and genipin (GP)) and two different types of lignin (organosolv-acid (OL) and kraft (KL)) are used to prepare chitosan-lignin biocomposites. Finally, the cross-linked composites are sulfonated to improve their conductive properties for fuel cell applications.

EXPERIMENTAL

Cross-linked chitosan-lignin composite membranes were prepared by solvent casting. First, chitosan was dissolved in acetic acid and lignin (OL and KL) in ethanol. Then, the solutions (10wt% lignin) were mixed together and the covalent cross-linking agent (GA or GP) added before being placed in an incubator. Sulfonation was achieved by post-immersion in sulfuric acid (1M) at 30 °C for 1 hour.

RESULTS AND DISCUSSION

FTIR studies show that the covalent cross-linking with GA and GP disrupts the chain arrangement resulting in a less crystalline structure with weaker hydrogen bonding which is promoting water penetration. The effects of cross-linking in the swelling studies show higher water uptake for the membranes cross-linked with GA than with GP and that dimensional swelling can be reduced adding lignin to the composites. As a result, the membranes cross-linked with GA show increased proton conductivity in dielectric thermal analysis, due to elevated water absorption and incorporation of sulfate groups. Ultimately, fuel cell performance improves due to covalent cross-linking but worsens with increased water uptake, because high amounts of water can saturate the pores of the membrane.

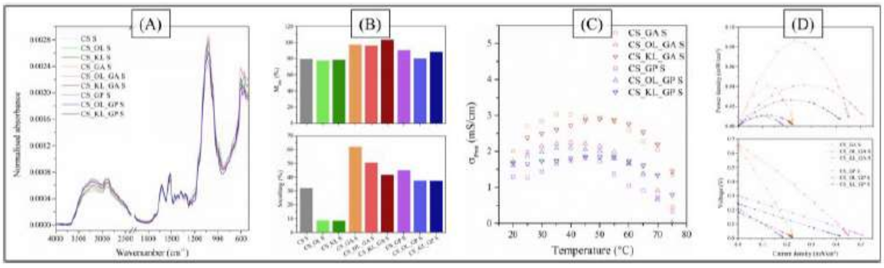

Figure 2. Results of the cross-linked chitosan-lignin biocomposites: (A) Infrared spectroscopy, (B) water uptake & swelling studies, (C) proton conductivity assessment, (D) H2/O2 fuel cell performance tests.

CONCLUSIONS

The cross-linking of chitosan with genipin and glutaraldehyde provides a simple method for modifying the structural and conductive properties. Furthermore, the incorporation of lignin into this modification results in cheap, waste-derived biocomposites with high variability. The correct selection of lignin filler and cross-linking process can influence the composite structure and improve fuel cell performance.

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P12.1

Study of Polyvinyl Alcohol Composite Membranes for Fuel Cells

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INTRODUCTION

Fuel cells are a critical technology in order to mitigate global greenhouse gases emissions. In particular Proton Exchange Membrane Fuel Cells (PEMFCs) are becoming increasingly important [1]. In this study, different percentages of cellulose nanofibers (CNF) are added into a PVA matrix. Furthermore, the composite membrane is crosslinked with sulphosuccinic acid (SSA), and graphene oxide (GO) is incorporated as filler. The composite membranes are characterized by means of Fourier transformed infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dielectric broadband spectroscopy (BDS), proton diffusion, and fuel cell tests. The addition of CNF nanofibres, in the appropriate percentage, enhances structural integrity, and optimises the performance of the electrolyte in operative conditions contributing to develop more effective and sustainable PEMFCs.

EXPERIMENTAL

The novel polyelectrolyte membranes consist of polyvinyl alcohol (PVA) cross-linked with sulfosuccinic acid (SSA) with graphene oxide (GO) as filler. Cellulose nanofibres (CNFs) were incorporated into these membranes in varying percentages (5% and 15%). The membranes obtained were compared with a commercial reference material, Nafion® 115.

RESULTS AND DISCUSSION

FTIR results showed that GO, and CNFs were successfully integrated into the polymer matrix (Figure 1A). No significant degradation was observed up to 200°C (Figure 1B). Regarding proton conductivity, the structural differences, obtained above 70ºC, show that PVA-SSA-GO and PVA-SSA-GO-CNF-5% exhibit similar results (Figure 1C). Fuel cell test (Figure 1D) corroborated the results provided by BDS.

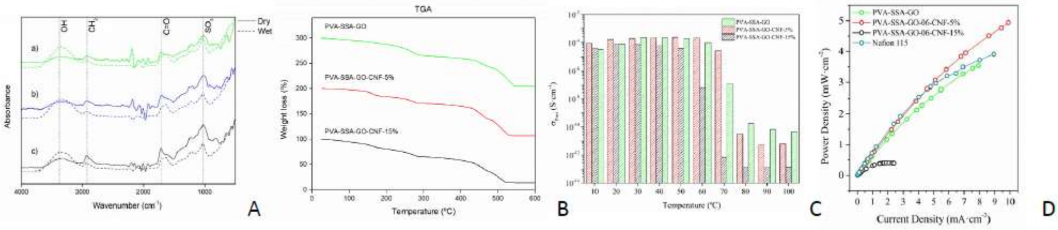

Figure 1. (A) FTIR spectra in dry and wet states; (B) Thermogravimetric curves; (C) Proton conductivity ranging from 10 to 100 °C; (D) Power density vs Current density curves for all the studied membranes.

CONCLUSIONS

Membranes incorporating 5% CNF display a good performance due to CNF's hydrophilicity which increases water uptake and retention within the membrane. Moreover, the employed methodologies provide profound insights into the molecular-level mechanisms, and the consistency across various tests underscores the efficacy of the approaches.

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P13.1

Bilayer films based on PLA and gelatin/sodium caseinate activated with rutin and carvacrol in Pickering emulsion

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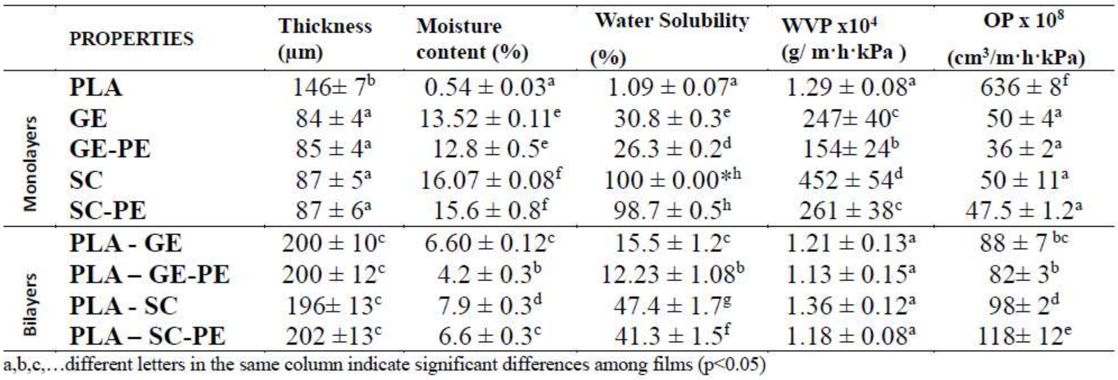
INTRODUCTION

Protein-based films are capable of acting as carriers of bioactive compounds, but in turn present limitations of brittleness, high permeability to water vapor and low resistance to prolonged processing operations strongly limiting their applications [1]. On the other hand, PLA is also a biodegradable polymer, highly flexible, easy to process and with excellent physical and functional properties but exhibited low barrier to oxygen. The combination of biodegradable polymers with complementary barrier properties loaded with active agents (antimicrobial and/or antioxidant) allows us to obtain multilayers films with an extra functional properties than conventional packaging materials.

The objective of this study was the development and characterization of enhanced biodegradable bilayers films based on PLA and gelatin/sodium caseinate obtained by hot-compression molding and activated with rutin and carvacrol encapsulated in Pickering emulsion as active agents.

RESULTS AND DISCUSSION

Table 1. Physicochemical properties of monolayer and bilayer films without and with emulsion (PE).



	PROPERTIES	Thickness (μm)	Moisture content (%)	Water Solubility (%)	WVP x10^{4} (g/ m·h·kPa)	OP x 10^{8} (cm^{3}/m·h·kPa)
Monolayers	**PLA**	146 ± 7^{b}	0.54 ± 0.03^{a}	1.09 ± 0.07^{a}	1.29 ± 0.08^{a}	636 ± 8^{f}
	GE	84 ± 4^{a}	13.52 ± 0.11^{e}	30.8 ± 0.3^{e}	247 ± 40^{c}	50 ± 4^{a}
	GE-PE	85 ± 4^{a}	12.8 ± 0.5^{e}	26.3 ± 0.2^{d}	154 ± 24^{b}	36 ± 2^{a}
	SC	87 ± 5^{a}	16.07 ± 0.08^{f}	$100 \pm 0.00^{*h}$	452 ± 54^{d}	50 ± 11^{a}
	SC-PE	87 ± 6^{a}	15.6 ± 0.8^{f}	98.7 ± 0.5^{h}	261 ± 38^{c}	47.5 ± 1.2^{a}
Bilayers	**PLA - GE**	200 ± 10^{c}	6.60 ± 0.12^{c}	15.5 ± 1.2^{c}	1.21 ± 0.13^{a}	88 ± 7^{bc}
	PLA – GE-PE	200 ± 12^{c}	4.2 ± 0.3^{b}	12.23 ± 1.08^{b}	1.13 ± 0.15^{a}	82 ± 3^{b}
	PLA - SC	196 ± 13^{c}	7.9 ± 0.3^{d}	47.4 ± 1.7^{g}	1.36 ± 0.12^{a}	98 ± 2^{d}
	PLA – SC-PE	202 ± 13^{c}	6.6 ± 0.3^{c}	41.3 ± 1.5^{f}	1.18 ± 0.08^{a}	118 ± 12^{e}

a,b,c,…different letters in the same column indicate significant differences among films ($p<0.05$)

As expected, the bilayers exhibited the same WVP values ($p>0.05$) and enhanced OP values ($p<0.05$) than PLA monolayer. The incorporation of phenols (rutin and carvacrol) on the monolayer films led to lower solubility values and greater barrier capacity to water vapor and oxygen (lower WVP and OP values). This is surely due to the establishment of interactions between proteins and phenols (mainly hydrogen bonding, hydrophobic bonding and van der Waals forces) [2], thus contributing to the development of a tighter polymer matrix with reduced mobility. This effect was not observed in the bilayers films, as the improvement in the permeabilities when combining the monolayers with complementary barrier properties was greater than the effect of incorporating the phenolic compounds.

CONCLUSIONS

The incorporation of phenolics compounds enhanced the water vapor and oxygen permeability values of protein-based monolayers, but this effect was not observed in the bilayers, in which the barrier properties were already enhanced. The PLA-gelatin bilayer incorporating the active agents (rutin and carvacrol) presented the best barrier properties, regardless the phenolic compounds incorporation.

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P14.1

Chemical Characterization of Locust Bean Gum (LBG) Derivatives For Hydrogel Production

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ABSTRACT

Locust bean gum (LBG), derived from the endosperm of carob tree (Ceratonia siliqua) seeds, holds promise as a versatile biopolymer due to its abundance and diverse applications in industries, such as food and pharmaceuticals. However, its poor water solubility has hindered its widespread industrial utilization. To address this limitation, our study focused on chemically modifying LBG to enhance its solubility. We synthesized two anionic (sulfate and carboxylate) and one cationic derivative (trimethylammonium) through sulfation, alkylation, and carboxylation reactions, respectively. Fourier transform infrared (FTIR) spectroscopy and elemental analysis were employed for chemical characterization of the derivatives. These modified derivatives were then utilized for the development of new hydrogels, intended for agricultural applications. By enhancing the solubility of LBG through chemical modification, we aim to unlock its potential for broader industrial use, contributing to sustainable solutions in various sectors.

ACKNOWLEDGMENTS

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P15.1

Optimization of physical-crosslinked silk sericin-based membrane for advanced applications

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INTRODUCTION

In recent years, materials derived from silk sericin have garnered significant interest across diverse fields, such as biomedical applications and, more recently, controlled-release transportation [1]. Despite this, the strength and durability of sericin-based membranes remain inadequate, limiting their widespread use. Previous efforts to enhance the mechanical properties of sericin materials involved blending with natural or synthetic polymers and employing chemical cross-linking methods [2]. However, this final approach often presents challenges such as resource wastage and environmental pollution. In this study, a simple and eco-friendly method is proposed for forming membranes with useful properties for use as bioactive dressings, promoting physical cross-linking in two phases: the manufacturing process from a polymer mixture and post-treatment with water vapor. The process involves drying a pre-gelled mixture comprising sericin (SS), gelatin (G), and polyvinyl alcohol (PVA), and implementing an experimental design to evaluate the effect of the concentration of the mixture, the addition of glycerol (Gly) to the mixture, and the cross-linking time with water vapor on the absorption capacity in phosphate buffer saline (PBS), weight loss in PBS, and Young's modulus. A response surface experiment was performed to obtain an optimal membrane.

EXPERIMENTAL

A high-temperature and high-pressure degumming method and a spray drying process were used to extract SS and obtain SS powder, respectively. Subsequently, aqueous solutions of SS, G, and PVA (each at 2% w/v) were mixed at a 1:1:2 v/v ratio (SS/G/PVA). In the first phase, the mixture was concentrated by evaporation of the solvent to 6, 8, and 10% w/v, and different percentages of Gly were added to the mixture (0.5, 1.0, and 1.5% Gly v/solution v). The obtained solutions were stabilized overnight and dried in an oven at 40 °C for 24 h, followed by lyophilization to obtain the porous membranes. In the second phase, cross-linking with water vapor was performed at 60 °C and -0.6 bar (0, 8, and 24 h). The effects of these factors were evaluated using a Box-Behnken design with a total of 15 runs. The optimal membrane with the highest PBS absorption capacity and Young's modulus, and minimum weight loss in PBS was selected using a numerical method based on desirability functions.

RESULTS AND DISCUSSION

The manufacturing process of the sericin-based membranes revealed a porous, ordered, and interconnected morphology, as confirmed by Scanning Electron Microscopy. Membranes with higher PBS absorption capacity after 24 hours of immersion (500%) had lower mixture concentrations (6%) and higher glycerol contents (1.5%). Moreover, the cross-linking process had no significant influence on this parameter. The

Gly content notably affected the weight loss of the membranes in PBS after 24 h of immersion, with the lowest observed weight loss (3.2 ± 0.92%) in membranes containing 1.5% Gly, a concentration of 6%, and an 8-hour treatment. Conversely, the samples with 1% Gly and no treatment exhibited a weight loss of 20 ± 1.4%. The Young's modulus was significantly influenced by all three factors evaluated. The optimized membrane conditions were as follows: concentration of 6%, 1.5% Gly, and treatment time of 3 h and 30 min. The membrane exhibited high absorption rates while maintaining its structural stability and high elasticity.

CONCLUSIONS

The comprehensive results demonstrate the effectiveness of the response surface in optimizing membrane formation and understanding the underlying mechanisms. Furthermore, the successful implementation of a novel processing technique involving physical cross-linking processes for fabricating porous membranes could boost the development of sericin-based dressings.

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P16.1

Processing of 3D printed PLA-based composites foams by Supercritical CO_2 process for sustainable food contact material

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INTRODUCTION

3D printing has attracted significant interest for new product development because of its ability to produce customized and low-cost plastic items with ease [1]. PLA foaming can be achieved through several methods, including chemical blowing agents, batch processing with supercritical CO2 ($scCO_2$) in an autoclave, foam injection molding, and extrusion foaming [2]. The impact of scCO2 foaming on 3D-printed PLA/$CaCO_3$ parts was investigated for the production of sustainable single-use food contact materials.

EXPERIMENTAL

3D-printed PLA/$CaCO_3$ parts were printed with a 20% and 80% infill, with rectilinear and triangular infill patterns and then foamed with $scCO_2$ (25 MPa, at 130 °C for 23 min, and depressurization for 1 s).

RESULTS AND DISCUSSION

Foam samples with 80% infill were successfully obtained (Figure 1-A) and they were thermally stable up to ~300 °C, while they showed closed-cell foams. Moreover, tensile test analysis showed that the 80% infill and triangular pattern foams showed better mechanical performance (Figure 1-B).

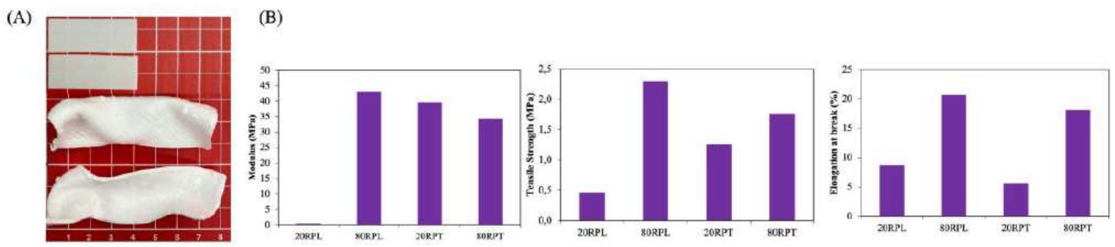

Figure 1. Results of (A) 3D-printed PLA/CaCO3 parts and foams and (B) mechanical properties.

CONCLUSIONS

The potential of the scCO2 process for the efficient production of foams from 3D-printed components was highlight by means of the results. These materials offer a sustainable alternative to non-biodegradable materials like EPS (Expanded Polystyrene) and show promise for various industrial applications.

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P17.1

Exploring the potential of bacterial cellulose films from SCOBY in Green Tea Kombucha

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INTRODUCTION

Cellulose is the most abundant biopolymer on Earth, present in large amounts in plants and algae. It is renewable, sustainable, as possesses good chemical stability, as well as being non-toxic.

Also, some bacteria can also produce cellulose, referred as "bacterial cellulose". Bacterial cellulose is described as having higher purity, crystallinity, water holding capacity, and biological adaptability than plant cellulose, as it does not have lignin and hemicellulose. [1]

Bacterial cellulose films are synthesized during the fermentation process of manufacturing the beverage Kombucha by the symbiose of bacteria and yeasts (SCOBY). The function of these films is to protect the beverage from external competitors or contaminants, and they are considered a byproduct of this industry. [2] Nevertheless, they represent numerous opportunities in a large range of areas.

In this work, bacterial films were obtained from the fermentation process of green tea by SCOBY, adding two different amounts of sugar (50 or 30 grams) and using the inoculum at room temperature and 38 ºC. The films were removed, dried using three different methods, and then characterized by refractive index, FTIR-ATR, water contact angle, swelling index, water vapor transmission rate, among other parameters. The scheme of the process is depicted in Figure 1. Commercial celluloses were also characterized for comparison.

RESULTS AND DISCUSSION

The preliminary results showed the formation of multilayered films, obtained from SCOBY. With 50 grams of sugar, films were thicker and with 30 grams the films were more homogeneous. Using the inoculum at 38 ºC, the films were also more homogenous and easily handled. The films could absorb more than 100% of their weight of water, varying their contact angles between 20 and 70 ºC, and with a lower water vapor transmission rate.

CONCLUSIONS

The amount of sugar added to SCOBY, the temperature of the inoculum, and the drying process influenced the appearance of the final films. The better film properties were obtained using 50 grams of sugar and the inoculum at 38 ºC.

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P18.1

Crosslinked poly(hydroxyurethanes) films from biobased carbonates: Structure-properties relationships and the influence of moisture in the mechanical properties

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INTRODUCTION

In recent years, intensive research has been carried out to obtain polyurethane (PU) based materials, by green routes, using renewable and non-hazardous reagents. This has led to the development of non-isocyanate PUs (NIPUs), particularly poly(hydroxyurethanes) (PHU), which are obtained by the reaction of cyclic carbonates and amines. PHUs have hydroxyl groups in their structure, which contribute to an increase in the hydrophilicity of the material, resulting in higher water absorption values. This fact can be particularly detrimental if PHUs are to be used as coatings.

In this work, various cyclic carbonates based on renewable resources (adipic, azelaic and sebacic acids) were successfully synthesized in high yields, and reacted with hyperbranched PEI, to form crosslinked PHU films without catalysts. The films were characterized with respect to their mechanical behavior, before and after exposure to a humid environment. In addition a simple strategy to reduce the hydrophilicity of the films was developed.

RESULTS AND DISCUSSION

The PHU films had a gel content close or higher than 99% indicating that the precursors were effectively incorporated into the crosslinked networks. Both the glass transition temperature (Tg) and the mechanical properties of the films were found to be dependent on the chain length of the cyclic carbonate; the shorter the chain length, the more rigid was the film. The PHU films were found to be susceptible to moisture, and a significant decrease in mechanical properties was observed after the films were subjected to humid environments (HR=56%), and subsequently dried. In an attempt to reduce the susceptibility of the films to moisture, their surface was modified with a fatty acid derivative. It was found that even the modified films exposed to an environment of HR=56% showed a loss of their mechanical properties. However, after a drying process, the mechanical properties of the films were restored. This result indicates that the hydrophobization of the surface, can also be effective inside the samples, preventing the damaging effect of water or by helping to restore the hydrogen bonds between the PHU chains.

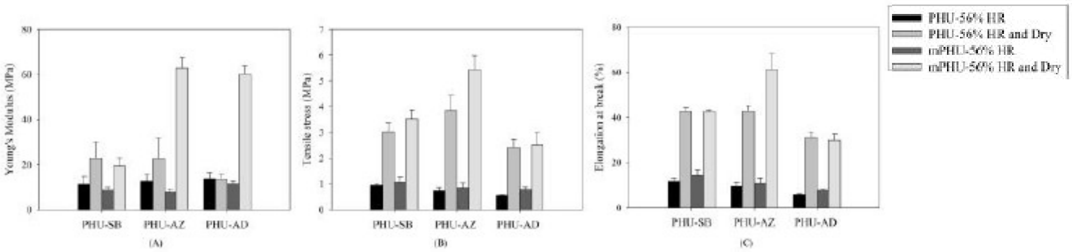

Figure 1. Mechanical properties of the PHU films after the modifications. Young's modulus (A), Tensile stress (B) and Elongation at break (C).

CONCLUSIONS

Different biobased crosslinked PHU films were prepared, and their properties were shown to depend on the chain length of the bio-based cyclic carbonate. The mechanical properties of the films decreased significantly when exposed to a humid environment. Modification of the film surface with a fatty acid derivative resulted in films that were able to restore the original mechanical properties after exposure to a humid environment and subsequent drying.

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P19.1

Antioxidant-releasing system based on the post-consumer PLA from water bottles

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INTRODUCTION

The detrimental impact on the environment derived from the wrong management of residues of conventional plastics is promoting the market entry of biobased and biodegradable food packaging materials. They guarantee greater sustainability since they come from renewable sources, in addition to maintaining the quality and safety of its products. Specifically, poly(lactic acid) (PLA) is characterized by its compostable nature, its availability and its easy processing by melt extrusion, becoming one of the most used biopolymers in the industry. In this regard, Cabreiroá company has recently launch water bottles made of PLA. Because PLA is a valuable polyester, its recyclability should be an alternative in addition to its compostability. Beyond that, the upcycling is presented as an innovative alternative where post-consumer plastics are upgraded in order to achieve similar or superior properties [1]. Thus, in this work, the use of the post-consumer PLA from these water bottles will be used to developed novel antioxidant-releasing systems to be further applied as active packaging or drug-delivering systems.

EXPERIMENTAL

Commercial PLA-water bottles were subjected to a prior accelerated aging and washing process to simulate real post-consumer mechanical recycling conditions, obtaining "recycled" PLA, RPLA [2]. Blends of RPLA with polycaprolactone (PCL) at two different ratios: RPLA/PCL 85/15 and 70/30 were extruded in order to mitigate the deterioration of this biopolymer during its recycling thanks to the excellent deformability of PCL. PCL can improve the loss of mechanical properties of RPLA, modifying aspects as its crystallinity. Likewise, the addition of quercetin (Quer), a natural polyphenolic antioxidant, to the polymeric blends intrinsically increased the interaction between both polymers and will allow greater preservation of food sensitive to oxidation through its progressive release. Q was incorporated at 3 %wt. and blends were extruded and thermopressed. Structural (FTIR), thermal (DSC and TGA), optical and morphological (SEM) properties were analysed in order to study the effect of recycling process and the addition of PCL and Querc. In addition, the antioxidant activities of developed films and the release profiles of Querc in two food simulants were studied.

RESULTS AND DISCUSSION

Microscopical images evidenced the lack of miscibility between polymers and the homogeneity dispersion of the phenolic compound. The incorporation of PCL and Quer slightly modified structural and thermal properties. Blends of RPLA with PCL evidenced different release profiles and partition coefficients of quercetin when compared to active films based on RPLA. PCL boosted the release of the antioxidant compound in both food simulants.

CONCLUSIONS

The design of delivering systems of active compounds can be an interesting upcycling process of post-consumer PLA.

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P20.1

Development of smart materials based on blood orange juice, alginate and lignin nanoparticles

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INTRODUCTION

Despite major technological efforts, changes in consumer habits and modifications in current food legislation, problems related to food waste and food-borne diseases are raising worldwide. Several studies to produce smart materials were developed to control food contamination and spoilage [1]. In this study, the combination of natural anthocyanins derived from blood orange with lignin nanoparticles has been evaluated to produce smart materials with possibilities to act as biosensors in food packaging. Alginate was selected as the polymer matrix.

EXPERIMENTAL

Smart materials were processed by casting. Alginate was dissolved in distilled water and different amounts of blood orange juice were incorporated (10, 30 and 50% (v/v)). Then, solutions were maintained for 2 hours under magnetic agitation and $CaCl_2$ 0.1M was added as crosslinking agent. Finally, 15 mL of each formulation was introduced into Petri dishes until complete dryness. To evaluate the effect of lignin nanoparticles, different concentrations (1 and 3 wt% respect to the polymer matrix) were introduced simultaneously to the blood orange juice. 10 formulations were studied using TGA, FTIR, SEM, and their functional properties were also tested.

RESULTS AND DISCUSSION

Results showed that the incorporation of all concentrations tested of blood orange juice, rich in anthocyanins, lead to materials that change their colour depending on the pH. In addition, these materials showed high antioxidant properties, increasing with the concentration of blood orange juice. However, the thermal stability of these smart materials, decreased slightly at high concentrations of anthocyanins but in all cases, these materials were thermally stable up to 150 ºC. The addition of lignin nanoparticles reduced transparency of films, but increased the antioxidant activity. The compatibility with alginate and good dispersion of lignin nanoparticles into the films were confirmed by SEM.

CONCLUSIONS

The combination of lignin nanoparticles and blood orange juice has great potential to develop new smart food packaging materials based on alginate. These materials can prevent food waste and help to improve food safety. They are able to extend food shelf life due to their antioxidant activity while monitoring degradation related to pH changes in food.

ACKNOWLEDGEMENTS

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P21.1

Natural hair cosmetics: development of hair conditioner formulations using lignin from acacia wood

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INTRODUCTION

The use of cosmetic products is a highly popular practice. However, the increasing use of these products has raised concerns about their environmental impact. For example, some compounds commonly found in hair care formulations, such as cationic conditioning agents, are reported to be toxic to aquatic organisms [1]. The rinsing of hair care products results in their entry into wastewater systems ending up in rivers and oceans. These problems, and the increasing preference for natural products with low environmental impact, have motivated the research on renewable feedstocks for the development of cosmetic formulations [2]. Natural biomass-derived compounds, such as lignin, have a great potential as future efficient and sustainable ingredients due to their high abundance, biodegradability, and low toxicity. Lignin's hydrophobic nature can help to restore the hydrophobic barrier characteristic of healthy hair. Also, the presence of functional groups allows for its chemical modification, namely by introducing cationic groups, which will enhance the interactions with hair.

EXPERIMENTAL

In this work, lignin extracted from acacia wood was chemically modified to prepare two cationic derivatives with different degrees of substitution. They were fully characterized, and their physicochemical properties compared to those of a commercial cationic polymer commonly used in cosmetic formulations (PQ-11). The conditioning properties of lignin derivatives and PQ-11 were evaluated by studying their adsorption onto biomimetic model surfaces by AFM and ellipsometry. Additionally, hair conditioner formulations were prepared containing either the lignin derivatives or PQ-11, and then characterized regarding their stability, viscosity, and sensory evaluation.

RESULTS AND CONCLUSIONS

Two cationic lignin derivatives were successfully obtained with different degrees of substitution via different cationization reaction conditions. The zeta potential of lignin derivatives was similar to that of PQ-11. AFM results show the effect of surface treatment with aqueous solutions of the different polymers. In addition, results from ecotoxicological tests showed that the cationic lignin derivatives present a significantly lower risk to the aquatic organisms than the commercial polymer. Thus, lignin derivatives appear as more environmental benign alternatives to the highly toxic cationic polymers that are currently used in cosmetics.

FUNDING

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P22.1

Polymeric Nanoparticles for Drug Delivery: An *In Vitro* Study Using Bovine Serum Albumin for Prostate Cancer Treatment

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INTRODUCTION

Prostate cancer (PCa) is the second most incidence type of cancer in the male population worldwide.[1] The current treatments face many limitations, such as low specificity and drug resistance, with serious consequences for the body. To address these challenges, researchers are focused on developing advanced drug delivery systems. Polymeric nanoparticles (NPs) have been proposed as valuable drug delivery systems, with promising in vitro results in cancer cell lines. Bovine serum albumin (BSA) NPs represent a promising and eco-friendly approach for targeted drug delivery, with reported biocompatibility, stability, and biodegradability.[2] This study aimed to synthesize BSA NPs using a genipin (GNP) based cross-linking method to act as carriers for cancer treatment potential agent, the antidepressant sertraline (STR), that demonstrated potential efficacy in prostate cancer treatment.

EXPERIMENTAL

BSA NPs were synthesized using an emulsion method and characterized by Dynamic Light Scattering (DLS). After selecting the most adequate method of synthesis, the procedure for STR encapsulation was tested. Then, the NPs were characterized by DLS and the encapsulation efficiency was assessed using HPLC. The PNT-2 cell line (normal prostate cells) and 22Rv1 cell line (prostate cancer cells) were used in in vitro assays to evaluate their potential efficacy. These cell lines were exposed to BSA NPs with and without STR and cytotoxicity was assessed.

RESULTS AND DISCUSSION

BSA NPs were successfully synthesized, presenting a hydrodynamic size distribution (200 to 400 nm) and a polydispersity index of 0.183. The STR was effectively encapsulated (82% efficiency) in the BSA NPs, which maintained good stability and monodispersity despite the formation of some aggregates. Exposure to BSA NPs slightly decreased the viability of PNT-2 and 22Rv1 cells, with no GNP toxicity. BSA NPs loaded with STR demonstrated ability to affect cell viability.

CONCLUSIONS

This study demonstrated that BSA NPs have good encapsulation efficiency and act as effective STR carriers. BSA NPs loaded with STR caused a slight reduction in cell viability, which increased over time. This is a promising approach for treating prostate cancer due to the less toxicity of BSA NPs loaded with STR when compared to direct STR exposure. Further studies should extend the exposure time to assess the effects of BSA NPs loaded with STR and study their release mechanism.

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P23.1

Aromatic copolyesters containing furan and isophthalic rings for vascular applications

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INTRODUCTION

The impact of cardiovascular diseases (CVDs) on the world's population appears to be increasing year after year, due to the aging of the population, together with its increase [1]. As to the possible treatments, autologous blood vessels, allogenic, or artificial ones are the most used. In the latter case, the implementation of tissue engineered vascular grafts (TEVGs) is considered a new cutting-edge frontier, in particular when the diameter of vessels is lower than 6 mm [2]. The TEVGs can be obtained from polyesters, thanks to their high versatility, easy processability and tunable properties. Among this wide family, bio-based aromatic polyesters containing both furan and isophthalic rings [3,4] along their main chains have been chosen: as known, the aromatic character warranties high stability over time, necessary requirement for the long-term success of the graft.

EXPERIMENTAL

Poly(butylene 2,5-furanoate) (PBF), poly(butylene isophthalate) (PBI) and two random copolymers, containing different molar ratios between the two co-units, were synthesized through two-step melt polycondensation. All the polymers were subjected to molecular, thermal, mechanical, and diffractometric characterization. Water contact angle measurements and in vitro cytotoxic assay, using human umbilical vein endothelial cells (HUVECs), were also performed. Last, hydrolytic degradation tests were carried out at 37 and 70 °C, to mimic physiological and accelerated conditions, respectively.

RESULTS AND DISCUSSION

From molecular characterization, it was possible to confirm the chemical structure and composition of all the materials, as well as their high and comparable molecular weights, proving a good control over the synthetic process. A high thermal stability was observed in all cases, thanks to the aromatic nature of the polyesters. From calorimetric and diffractometric measurements, the as-synthesized materials turned out to be semicrystalline, becoming amorphous or only slightly crystalline after processing into compression-molded films. As shown by tensile tests, copolymerization is responsible for a good modulation of the mechanical properties, maintaining at the same time high resistance to break, which is a key feature for the intended application. All the materials also show a hydrophobic character, with a high resistance to hydrolytic degradation under both physiological and accelerated conditions. Last, preliminary in vitro cytotoxic assay indicated promising results in terms of cells' viability.

CONCLUSIONS

The polyesters herein investigated turned out to be valuable candidates for the treatment of pathologies of small diameter vessels. According to all the above-mentioned results, future promising scenarios can be hypothesized, such as the fabrication of tubular scaffolds, which mimic the real shape of the vessel.

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P24.1

Mushroom waste biomass utilization for development of sustainable food packaging materials

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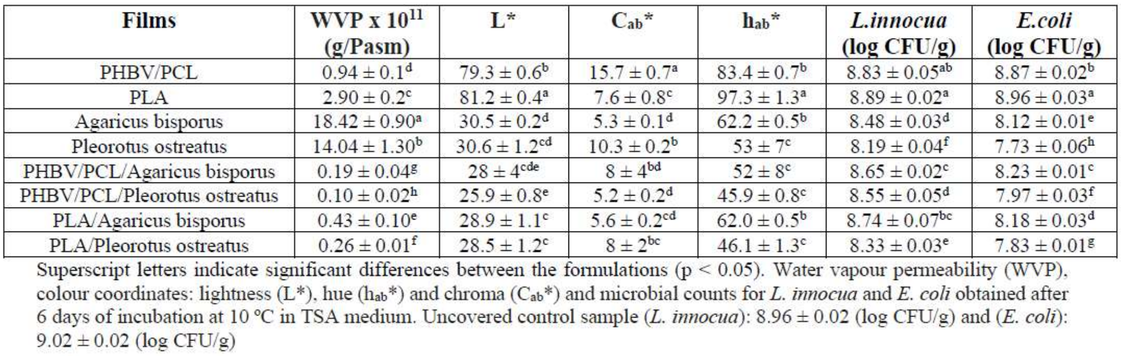
INTRODUCTION

Synthetic polymers derived from petroleum are widely used as packaging materials. However, most of these polymers are neither biodegradable nor recyclable, which causes a serious environmental pollution problem [1]. Therefore, there is a need to develop sustainable packaging materials to reduce the use of conventional plastics. As an alternative, agri-food waste and by-products are being explored as a source of new packaging materials. For example, the use of mushroom waste biomass to develop sustainable food packaging materials is a little explored area, but with great potential from an economic and environmental point of view following the principles of the Circular Economy [2]. Hence, the aim of this work was to valorize mushroom waste biomass of two different species (*Agaricus bisporus* and *Pleorotus ostreatus*) to produce biopolymeric films by melt blending-compression molding. Then, bilayer films based on mushroom-based monolayers and PHBV/PCL and PLA films were obtained. The resulting films were evaluated as to their water vapour permeability, color and the antibacterial properties against *Listeria innocua* (Gram-positive) and *Escherichia coli* (Gram-negative).

RESULTS AND DISCUSSION

Pleorotus-based monolayer and bilayer films presented lower WVP values compared to Agaricus-based films ($p<0.05$), both values being better than starch based films. On the other hand, the bilayer films showed lower WVP values than the pure films while the PHBV/PCL/Pleorotus formulation showed the lowest WVP value. Regarding the color, mushroom waste based films, both monolayer and bilayer, exhibited darker (lower L* values), less saturated colors (lower C_{ab}* values) with more brownish/reddish appearance (lower h_{ab}* values) than pure PLA and PHBV/PCL films. They also showed antimicrobial activity against *Listeria innocua* and *Escherichia coli*.

Table I. Physicochemical and antimicrobial properties of mono and bilayers. Mean values ± standard deviation.



Films	WVP x 10^{11} (g/Pasm)	L*	C_{ab}*	h_{ab}*	*L.innocua* (log CFU/g)	*E.coli* (log CFU/g)
PHBV/PCL	0.94 ± 0.1^{d}	79.3 ± 0.6^{b}	15.7 ± 0.7^{a}	83.4 ± 0.7^{b}	8.83 ± 0.05^{ab}	8.87 ± 0.02^{b}
PLA	2.90 ± 0.2^{c}	81.2 ± 0.4^{a}	7.6 ± 0.8^{c}	97.3 ± 1.3^{a}	8.89 ± 0.02^{a}	8.96 ± 0.03^{a}
Agaricus bisporus	18.42 ± 0.90^{a}	30.5 ± 0.2^{d}	5.3 ± 0.1^{d}	62.2 ± 0.5^{b}	8.48 ± 0.03^{d}	8.12 ± 0.01^{e}
Pleorotus ostreatus	14.04 ± 1.30^{b}	30.6 ± 1.2^{cd}	10.3 ± 0.2^{b}	53 ± 7^{c}	8.19 ± 0.04^{f}	7.73 ± 0.06^{h}
PHBV/PCL/Agaricus bisporus	0.19 ± 0.04^{g}	28 ± 4^{cde}	8 ± 4^{bd}	52 ± 8^{c}	8.65 ± 0.02^{c}	8.23 ± 0.01^{c}
PHBV/PCL/Pleorotus ostreatus	0.10 ± 0.02^{h}	25.9 ± 0.8^{e}	5.2 ± 0.2^{d}	45.9 ± 0.8^{c}	8.55 ± 0.05^{d}	7.97 ± 0.03^{f}
PLA/Agaricus bisporus	0.43 ± 0.10^{e}	28.9 ± 1.1^{c}	5.6 ± 0.2^{cd}	62.0 ± 0.5^{b}	8.74 ± 0.07^{bc}	8.18 ± 0.03^{d}
PLA/Pleorotus ostreatus	0.26 ± 0.01^{f}	28.5 ± 1.2^{c}	8 ± 2^{bc}	46.1 ± 1.3^{c}	8.33 ± 0.03^{e}	7.83 ± 0.01^{g}

Superscript letters indicate significant differences between the formulations ($p < 0.05$). Water vapour permeability (WVP), colour coordinates: lightness (L*), hue (h_{ab}*) and chroma (C_{ab}*) and microbial counts for *L. innocua* and *E. coli* obtained after 6 days of incubation at 10 °C in TSA medium. Uncovered control sample (*L. innocua*): 8.96 ± 0.02 (log CFU/g) and (*E. coli*): 9.02 ± 0.02 (log CFU/g)

CONCLUSIONS

It was possible obtain films (monolayers and bilayers) using only mushroom-waste with proper water vapour permeability and antimicrobial capacity. Thus, this vegetal residue has a great potential to be used as packaging material for food preservation.

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P25.1

Migration of phenolic compounds from active films based on poly(3-hydroxybutyrate-co-3-hydroxyvaterate) (PHBV)

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INTRODUCTION

PHBV is a biosynthesised and biodegradable material that could be used to obtain more sustainable an active food packaging material by incorporating compounds with antioxidant/antimicrobial activity into the polymeric matrix, such as phenolic acids or plant phenolic extracts [1]. One important aspect of novel biodegradable and active materials designed for food packaging application is the migration of both passive components and active compounds in the food systems, in order to ensure food safety and preservation capacity of the packaging material. The standards UNE-EN 1186-1:2002 and UNE-EN 1186-3:2022 specify both the test conditions and the overall migration limit to food (OML=10mg/dm^2), while Regulation No 450/2009 stablishes that active compounds should not be considered in the determined MO values, as they should be delivered into the food substrate to exert active action. This study aimed to analyse the migration behaviour from PHBV films of non-intentionally added polymeric components and intentionally added active compounds, such as ferulic and p-coumaric acids (FA and PCA at 3, 6 and 9%) or active rice straw extracts (at 6%), obtained at 160 and 180 ºC (RSE160 and RSE180) by subcritical water extraction. The films were obtained by melt blending and compression moulding and migration tests were carried out according to the above mentioned standards, using the methanolic extraction of the migrated dry residue to determine the release of the phenolic compounds.

RESULTS AND DISCUSSION

The migration of non-intentionally added compounds was below the OML (10 mg/dm2) in all cases, while the release of active compounds depended on their concentration in the film and the food simulant. The greater the active concentration in the films and the ethanol ratio the food simulant, the higher the release ratio of the phenolic compounds. Their release was practically complete in the 95% ethanol system for both, films containing pure phenolic acids and rice straw extracts (RSE160 and RSE180). In contrast, very low OM values were observed in the fatty simulant (isooctane).

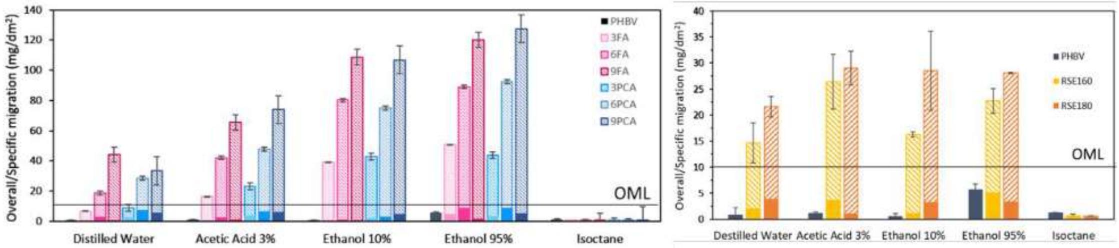

Figure 1. Overall and specific migration from PHBV films containing ferulic and p-coumaric acid (left) and rice straw extracts (right). Non-solid bars: active compounds, solid bars: passive material.

CONCLUSIONS

Developed PHBV materials with pure phenolics or phenolic rich extracts meet the migration requirements stablished in the standards while allowing the selective migration of active compounds to exert active action, depending on the nature of the food substrate (simulant). Therefore, these biodegradable films could be used as food packaging materials, contributing to extend the shelf life of food while reducing the environmental impact of non-degradable plastics. Nevertheless, the use of phenolic acids or rice straw extracts as active compounds for food contact materials needs to be authorised by the European Food Safety Authority (EFSA) according to Regulation (EC) No 1935/2004. Likewise, validation of these materials in real food is necessary to assess their potential to prevent oxidative and microbial spoilage and to extend food shelf life.

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P26.1

Development of poly(alkylene 2,5-furandicarboxylate)s *via* ring opening polymerisation – the poly(hexylene 2,5-furandicarboxylate) case

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INTRODUCTION

The increasing concerns, regarding the massive use of polymers and materials and the associated environmental pollution, green-house gas (GHG) emissions and non-circularity, have stimulated considerable research efforts and technical advancements to deliver polymers from renewable resources as alternatives to overpass the use of fossil-based counterparts in a variety of commodity applications, including packaging, textiles, coatings, among others. However, in addition to the biobased origin of the monomers, from a sustainability perspective, the development of *greener* strategies for polymers synthesis is absolutely fundamental. In this context, the Ring Opening Polymerization (ROP) of macrocyclic esters to yield the corresponding polyesters can be considered as a greener synthetic route since all reactants used are incorporated into the final polyesters (atom-economic) and, in general it requires less severe reaction conditions than the conventional melt polycondensation [1].

RESULTS AND DISCUSSION

The aim of this work involved first, the use of ROP to synthesize synthesis of two 2,5-furandicarboxylic acid-based macrocycles, namely macrocyclic ethylene 2,5-furandicarboxylate (CEF) and macrocyclic hexamethylene 2,5-furandicarboxylate (CHF) via cyclodepolymerization of the corresponding low molecular weight linear polyesters species under high dilution conditions. Secondly, we studied the ROP of those macrocyclic oligoesters using several metal catalysts using different time and temperature conditions leading to high molecular weight polyesters. Both the macrocyclic and their related polymers were in-depth characterized by FTIR, ^{1}H and ^{13}C NMR, Intrinsic Viscosity, DSC and TGA.

CONCLUSIONS

The present work is a contribution to the development of greener routes towards more sustainable poly(alkylene 2,5-furandicarboxylate)s. The dimethyl derivative of the 2,5-furandicarboxylic acid was used to prepare two cyclic furanic oligoesters using ethylene glycol (EG) and hexanediol (HD) as comonomers and their subsequently ROP affording the corresponding polyesters poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(hexamethylene 2,5-furandicarboxylate) (PHF) with high molecular weights.

ACKNOWLEDGMENTS

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10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). The FCT is acknowledged for the research contract under Scientific Employment Stimulus to AFS (CEECIND/02322/2020, DOI 10.54499/2020.02322.CEECIND/CP1589/CT0008). FCT and CICECO are also acknowledged for a doctorate grant under LA/P/0006/2020 to FA (BI/UI89/117032/2023) and a research contract to PSSL.

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P27.1

Cardboard packaging enhanced with Chitosan and Beeswax Biocoatings

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INTRODUCTION

Plastic waste is reaching alarming levels, making the search for sustainable packaging solutions a critical priority [1]. In response, the packaging industry is shifting towards alternatives like paper and cardboard. However, these materials are porous and hydrophilic, requiring coatings to enhance performance [2]. Chitosan exhibits antimicrobial and barrier properties similar to PET, while beeswax enhances the physical and mechanical properties of polymeric films [3,4]. Moreover, the coating method, flexography, significantly impacts the quality and durability of the coating2. This project aims to develop and optimize a biodegradable coating based on chitosan and beeswax, applied through flexography. The coating will be characterized and evaluated concerning its application as cardboard biocoating.

EXPERIMENTAL

Several chitosan and beeswax formulations were applied on cardboard through flexography (Figure 1). Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX), Water Contact Angle, Fourier-transform infrared spectroscopy (FTIR) and Viscosity were used to evaluate the properties of coated cardboard.

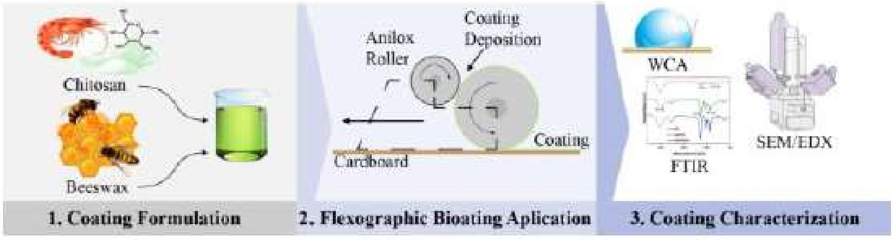

Figure 1 - Overview of the chitosan and beeswax bioacoating production and characterization methodology.

RESULTS AND DISCUSSION

The chitosan beeswax biocoating was sucessfully developed presenting hydrophobic properties. Furthermore, the application of the biocoating didn't change the visual appearance of the cardboard (Figure 2).

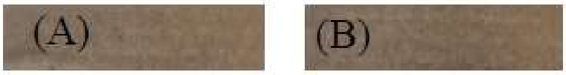

Figure 2 - Visual comparison between chitosan beeswax coated cardboard (A) and uncoated cardboard (B).

CONCLUSIONS

It was developed a hydrophobic biocoating that can be applied through flexography, enabling the industry to profit from its existing technology (flexography). Additionally, this developed chitosan beeswax biocoating does not change the visual appearance of the coated cardboard.

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P28.1

Wheat straw lignin as active filler in thermoplastic starch packaging films

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INTRODUCTION

Lignin is an interesting candidate as an additive in biopolymer composites in order to confer anti-oxidant, UV-shielding, and antimicrobial properties in packaging films made from biopolymers such as thermoplastic starch (TPS) [1]. As the second most abundant biopolymer after cellulose, lignin is produced as a side stream in biorefineries or the pulp and paper industry in vast amounts. In contrast to lignin deriving from wood, lignin from herbaceous biomass such as wheat straw is characterized by additional structural features like p-hydroxycinnamic acids, which can be present either incorporated into the lignin macromolecule or as pendant groups on lignin side-chains [2]. These structural features could promote interactions between the active filler and the biopolymer matrix during film formation providing improved thermal and mechanical properties.

EXPERIMENTAL

Two different non-wood lignins were utilized as active fillers in TPS films. Organosolv wheat straw lignin was prepared using ethanol-water for Organosolv extraction and separated by precipitation after evaporation of ethanol, followed by repeated washing with acidified water (pH 2), centrifugation and freeze-drying. For comparison, commercially available wheat straw lignin from alkaline pulping (Protobind 1000, PLT Innovations AG, Rüschlikon, Switzerland) was used. Biocomposite films were realized by using a twin-screw microextruder (DSM Xplore 5&15 CC Micro Compounder/Film Device). During the mixing/plasticization, the screw speed was set at 60 rpm, with a temperature profile of 135-140-145 °C for 180 s.

RESULTS AND DISCUSSION

The wheat starch matrix was amended with lignin nanoparticles before mixing with glycerol and eventual film extrusion. SEM analysis showed two distinct particle size fractions of wheat starch granules. Wheat starch granules were covered and held together by phases of agglomerated lignin nanoparticles. Extruded films were analysed regarding their UV-light blocking capacity, antioxidant activity and their degradation behaviour in composting conditions. Mechanical properties were investigated using tensile tests.

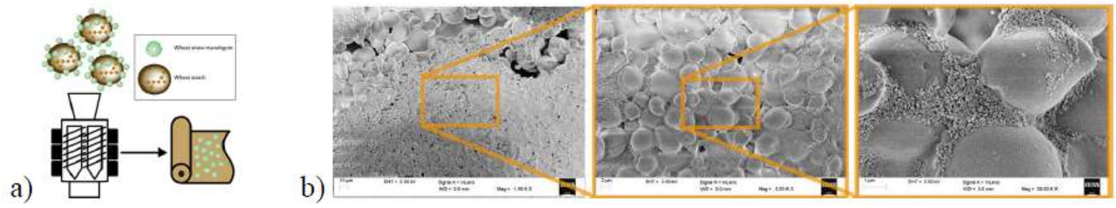

Figure 1: a) Scheme of the experimental set-up b) SEM images of prepared hybrid starch-lignin particles.

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P29.1

Effect of a phenolic-rich extract from chestnut wastes (CSW) on thermal, mechanical, antioxidant and antimicrobial properties of polylactic acid films

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INTRODUCTION

This research activity proposes the development, production, and characterization of PLA films for food packaging sector. In this work, chestnut extract at 1, 3 and 5 wt % was used as active ingredient. The effects of content on optical, morphological, thermal and mechanical properties of PLA based films have been investigated. In addition, migration and radical scavenging activity, antimicrobial and antifungal, disintegration in compost studies were performed, with the aim of evaluating the effect on structural and functional properties of realized food packaging systems [1].

EXPERIMENTAL

A phenolic fraction (CSW) was obtained by water-ethanol extraction and purification/concentration by membrane technology. CSW was characterized by a total polyphenol content of 260 ± 3 mg/g, while the most representative phenolic compounds were hydrolysable tannins, such as vescalagin (47.6 ± 0.5) and castalagin (97.7 ± 0.9) [2]. Poly(lactic acid) (PLA, 4032D) was purchased from NatureWorks. Neat PLA, PLA_1CSW, PLA_3CSW and PLA_5CSW films were realized by using a twin screw microextruder (DSM Explore 5&15 CC Micro Compounder/Film Device). During the mixing, the screw speed was set at 60 rpm, with a temperature profile of 170-175-180 °C and a die temperature of 180 °C. The films obtained by this process have a nominal thickness between 30-50 μm.

RESULTS AND DISCUSSION

Results from overall migration tests (EN 1186) for simulant C evidenced that all PLA based formulations were well below the allowed migration limit of 10 mg/dm^2. Tensile test (ISO 527-3) show that strength values and elastic moduli of films were not affected by the presence of CSW, while a reduction of elongation at break was registered. Full disintegration (ISO 20200) was reached in two weeks. The use of CSW induced antioxidant activities, inhibitions on fungal growth, suggesting the practical and possible applications in the food and biomedical packaging industrial sector.

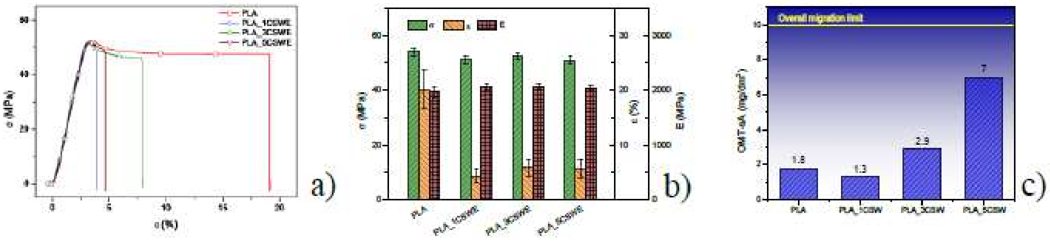

Figure 1: PLA/CSW films: a) stress-strain curves and b) mechanical test values; c) results of migration test.

ACKNOWLEDGMENTS

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P30.1

Development of an active, biodegradable mulch film for sustainable agriculture

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INTRODUCTION

As the environmental impact of conventional plastics becomes increasingly evident, exploring sustainable alternatives for agricultural applications is crucial[1]. This work proposes the development of an active, biodegradable mulch film that decouples agricultural productivity improvements from negative environmental impacts[2]. This innovation uses a multilayer structure that releases bioactive substances—such as organic acids—in a controlled manner to induce the plant immune system without soil deterioration.

EXPERIMENTAL

The film is manufactured using conventional extrusion for the structural layer. This layer is mainly based in polyhydroxyalkanoates and micronized nut shells[3]. The active layer is processed using electrospinning technology allowing for the formation of nanometric fibers and layers at low energy cost. The encapsulated bioactive substances are integrated both into this layer and the structural layer, designed to degrade at different rates in soil.

RESULTS AND DISCUSSION

Preliminary results demonstrate the effectiveness of malic acid as the bioactive substance in the protection of *Solanum lycopersicum* from *Botrytis cinerea*. The mulch films displayed rapid biodisintegration in soil which aligns with environmental sustainability goals. The rapid absorption and non-accumulation of malic acid in plants highlight an efficient integration of this compound into the biodegradable matrix, indicating effective delivery mechanisms.

CONCLUSIONS

This work confirms the feasibility of using malic acid-enhanced, biodegradable mulch films to support plant health and reduce environmental impact. The outcomes suggest that such films can significantly contribute to sustainable agricultural practices, promoting both environmental protection and enhanced crop resilience. Further research will focus on optimizing the formulation and delivery of the bioactive substances in the mulch films to maximize both protective efficacy and environmental benefits.

ACKNOWLEDGMENTS

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P31.1

High protein content nanofibers as novel platforms for antibody and antimicrobial peptide loading

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INTRODUCTION

The desirable characteristics of nanomaterials such as nanofibers (NFs) make them suitable for implementation in biomedical applications [1]. Protein NFs provide properties such as biocompatibility, biodegradability or intrinsic functions to nanofibrous mats. However, the electrospinning of natural molecules can be challenging, and, on many occasions, it is necessary to resort to blending with other polymers [2]. Moreover, the incorporation of bioactive compounds with specific functions can produce specialized NFs. This study aimed to fabricate NFs with high content of one of two model proteins: bovine serum albumin (BSA) or lysozyme (LYZ). Following the optimization of these base NFs, small quantities of the AMP piscidin (PIS) or the Ab horse radish peroxidase (HRP)-conjugated Anti-Mouse IgG, were added as proof of concept.

EXPERIMENTAL

NFs were synthesized via electrospinning by using polyethylene oxide (3% w/w) and large quantities of one of two proteins BSA or LYZ (5-20% w/w). To further functionalize these materials, an AMP (piscidin, PIS) or an antibody (Ab, HRP-IgG) were added at 0,1% w/w to the protein NFs, producing BSA/PIS, LYZ/PIS and BSA/Ab NFs.

RESULTS AND DISCUSSION

The NFs presented an average diameter ranging from 301 to 752 nm, and those obtained from 15% and 20% solutions were smooth and uniform, as determined by FESEM (Figure 1). The SDS-PAGE and FTIR assays showed that the proteins maintained their integrity and structure after the electrospinning process. In addition, no toxicity of NFs was found up to 5 mg/mL in human epidermal keratinocytes. The antibacterial assays showed that LYZ NFs were only effective against *Bacillus circulans*, while BSA/PIS and LYZ/PIS NFs were highly effective against all tested bacteria. Furthermore, HRP-IgG incorporation maintained activity within the NFs, with enhanced preservation observed in BSA/Ab NFs.

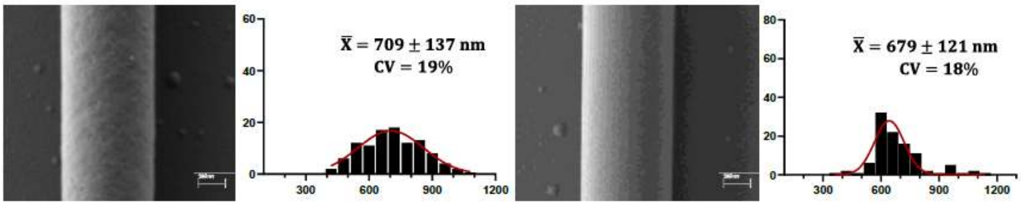

Figure 1. FESEM images and diameter frequency histograms of electrospun NFs containing PEO and 15% w/w of BSA (left) or LYZ (right).

CONCLUSIONS

These findings suggest the promising potential of these functionalized NFs for a range of biomedical applications.

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P32.1

Renewable aliphatic/aromatic furan-based copolymers for high-performant food packaging

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INTRODUCTION

Considering that the global production of plastic reached about 400.3 million tonnes in 2022 and, among them, about the 39% is used only for packaging [1], reuse and recycling should be maximized, in order to reduce plastics waste and to fulfil the requirements of circular economy. Moreover, to reduce the volumes of plastics and to save energy, flexible packaging should be chosen instead of rigid one [2]. A further challenge is related to the use of renewable sources to produce sustainable materials with the same properties as their fossil-based counterparts. For example, 2,5-furandicarboxylic acid is being attracting considerable attention among bio-based building blocks, since it can be derived from cellulosic non-food crops and wastes. According to this scenario, new aromatic/aliphatic random copolymers poly(trimethylene 2,5-furandicarboxylate-co-trimethylene suberate) (PTFcoPTSub) have been investigated for potential applications in food packaging (Figure 1).

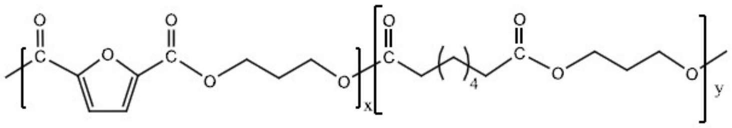

Figure 1. Chemical structure of (PTFcoPTSub) copolymers.

EXPERIMENTAL

The starting homopolymer poly(trimethylene 2,5-furandicarboxylate), PTF, has been chosen due to its high thermal stability, chemical resistance and good barrier properties. To overcome its main drawback, i.e. the high mechanical stiffness, copolymerization was carried out, by inserting different molar amounts (5, 15 and 25 mol %) of aliphatic poly(trimethylene suberate) (PTSub) co-units. All the polymers were synthesized by solvent-free melt polycondensation. Films were obtained by compression moulding and then chemical, thermal, mechanical and gas barrier properties were investigated. Labscale composting experiments have been also carried out.

RESULTS AND DISCUSSION

All the materials are characterized by high molecular weight, high thermal stability and tuned crystallinity. The introduction of aliphatic co-units also allowed to improve the mechanical flexibility and to maintain, or even improve, the already good barrier properties, reaching performances close to those of EVOH, commonly used in multilayer packaging films. Last, the presence of at least 25 mol% of PTSub co-units makes the copolymers degradable in compost.

CONCLUSIONS

According to the results obtained, copolymerization of PTF with PTSub was a successful tool to obtain sustainable and very performing materials, with high potential for flexible food packaging applications.

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P33.1

Blown films of PLA/PBSA blends: effect of composition on processability and thermal, mechanical, and barrier properties

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INTRODUCTION

The environmental problems arising from the massive use of polymers are well-known. Polymers produced for packaging and single-use applications are one of the main contributors to these issues, since a large volume of post-consumer plastic waste comes from these products. Substituting the commonly used petrochemical and non-degradable polymers for the aforementioned applications with bio-based and biodegradable ones would highly contribute to the sustainability of polymers. In this context, polylactic acid (PLA) and poly(butyl succinate-co-adipate) (PBSA), are biodegradable and biocompatible aliphatic polyesters fabricated from renewable resources, showing very interesting properties. While PLA is a stiff and strong biopolymer, featuring good barrier properties [1,2], PBSA is ductile and tough [3]. Therefore, blending them would allow obtaining new multiphasic materials combining the excellent properties offered by each component. Here, we propose a simple melt-blending fabrication process to obtain bio-based and biodegradable PLA/PBSA films.

EXPERIMENTAL

Blending of PLA and PBSA was carried out in a twin-screw extruder and films were obtained in a second processing step by blown film extrusion. The microstructure and the thermal, mechanical, and barrier properties of the PLA/PBSA blends were characterized.

RESULTS AND DISCUSSION

Dynamic mechanical thermal (DMTA) analysis showed that PLA/PBSA blends are immiscible, since the Tgs of the pure components barely changed when blended. Insignificant changes in the crystalline phase of the components were detected by differential scanning calorimetry (DSC). The immiscibility of the system was confirmed by transmission electron microscopy (TEM) observations. In blends with compositions up to 40/60 PLA/PBSA, PLA formed the continuous phase while PBSA appeared dispersed as elongated particles. On the contrary, at higher PBSA contents, the latter formed the matrix and PLA was dispersed as spherical particles displaying a significant size distribution. The ductility of the blends increased with increasing the PBSA content, while the stiffness decreased. The tear strength showed a negative deviation from linearity. The permeability of the blends was mainly influenced by the component forming the continuous phase, showing a discontinuous behaviour: while PLA-matrix blends showed values close to the ones featured by pure PLA, PBSA-matrix blends showed permeability values similar to the ones of the neat PBSA.

CONCLUSIONS

The addition of a small concentration of PBSA (10%) to PLA allows obtaining PLA/PBSA films with increased ductility while the stiffness and good barrier properties of PLA are maintained. On the contrary, the barrier properties of PBSA can be improved by adding 20% of PLA without its high ductility and tear strength being compromised.

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P34.1

The influence of mixing pressure in spray gun on application of bio-based rigid polyurethane spray foam

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INTRODUCTION

Rigid polyurethane spray foam is a major insulation material in housing industry. Due to its great insulation properties and application efficiency. There are over 1000 companies in Poland spraying polyurethane foam.

World trends tend to be more into bio-based materials, repelling fossil-based polymers. This approach generates many difficulties for producers and suppliers which researchers tries to overcome.

EXPERIMENTAL

Poster presents the analysis of the influence of the mixing pressure in spraying gun on the parameters and structure of the polyurethane rigid foam based on tall-oil polyols.

A simple method of SEM Images analysis using freeware software ImageJ [1] was used to analyze batch of images. Over 70k of pores were taken into account observed on 136 images, form which a statistical analysis is performed, based on literature [2,3]. Mechanical analysis such as compression and friability tests were done, also properties like lambda, and water absorption were analysed.

RESULTS AND DISCUSSION

The increase of mixing pressure increased the cell density NA at almost 20%. The amount of closed cell increased from 89,6% up to 93,5% which provided better insulation properties, remains the same foam density.

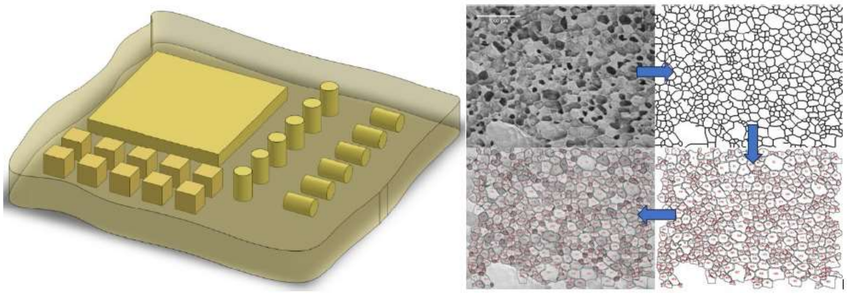

Figure 1. Sample extraction and SEM analysis steps.

CONCLUSIONS

SEM batch analysis provides an easy way for image statistical analysis. A mixing pressure parameter adjusted properly may provide a positive effect on application of bio-based polyurethane spray foam.

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P35.1

Use of natural additive in biodegradable thermoplastic materials for food preservation

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INTRODUCTION

Developing polymeric materials with specific characteristics is necessary to face the growing competitive market. For instance, there is a need for polymeric materials capable of releasing active components interacting with food. In this sense, different research studies are conducted in which polymeric matrices are provided with antioxidant properties to offer greater effectiveness when preserving food [1]. Oxidative reactions, microbial growth and metabolism are the main factors leading to quality loss and food spoilage. Food deterioration due to oxidative processes occurs when foods are exposed to air, heat, or light, producing free radicals that damage proteins, lipids, and vitamins, causing a decrease in their nutritional value and generating odors and unpleasant flavors [2].

RESULTS AND DISCUSSION

The antioxidant activity of films made of polylactide polymer and solid fractions of pine tree exudation (SFPT) was monitored using 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging, following the methodology reported by Łopusiewicz Ł. et al. [3]. The control film (F8.0, polylactide polymer) showed low scavenging activity. In contrast, the films containing different concentrations of SFPT showed profound, radical scavenging activity, and the activity was found to increase significantly ($P<0.01$ vs. F8.0). Therefore, the presence of SFPT in the films significantly increased the antioxidant activity of all formulations. The highest antioxidant activity was recorded for films F8.2 and F8.6. Furthermore, using this natural additive is a valuable strategy to reduce the stiffness of F8.0-based blends and increase their renewable content. For this reason, the potential application of films in the food packaging sector can be confirmed by the analysis of the scavenging activity produced to slow down the decomposition of the food. The statistical significance was analyzed by t-test, $p<0.01$ vs. control (F8.0).

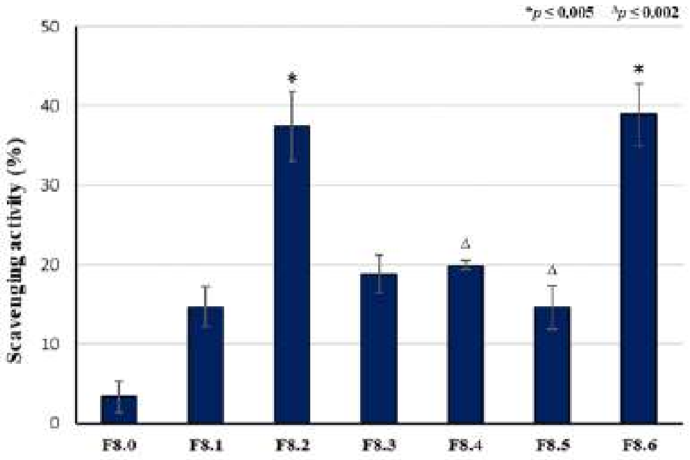

Fig. 1. Antioxidant activity of all films.

CONCLUSIONS

Incorporating the solid fraction of pine tree exudation into Polylactide polymer significantly increased the formulated materials' antioxidant activity. This additive could potentially be used as an active component for food preservation.

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P36.1

Harnessing surfactants produced by microorganisms as eco-friendly constituents for polyurethane synthesis

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INTRODUCTION

Surfactants produced by microorganisms are increasingly recognized as promising resources for the development of innovative polymeric materials. In this research, esterified 3-(3-hydroxyalkanoyloxy)alkanoates (HAAs) and polyol lipids (PL), primarily composed of a mannitol head group linked to three or four 3,5-dihydroxydecanoic acids (DDA), were explored as sustainable building blocks for polyurethane (PU) synthesis. The aim of our study was to capitalize on the potential of HAAs and polyol lipids as renewable sources in crafting pioneering PU membranes, aiming to foster a more sustainable era of PU generation aligning with the principles of the circular bioeconomy. Comprehensive evaluations were conducted to assess the structural, thermal, and mechanical properties of the PU membranes prepared using with aromatic (MDI) and aliphatic (PDI) diisocyanates [1,2].

RESULTS AND DISCUSSION

The structural characteristics and properties of the resulting macromolecular architectures were significantly influenced by the composition of these polyol lipids. Our findings indicate that a higher HAA content leads to a slight increase in hard segments (HS) due to the asymmetrical arrangement of aliphatic branched chains, thereby impeding regular organization. While the entanglement of aliphatic branched chains contributed to network cohesion through physical crosslinking, HAA-based PU remained entirely amorphous. Surprisingly, chemically crosslinked PL-based PU produced a meltable membrane, also fully amorphous. Nevertheless, the PL-based membrane exhibited superior mechanical properties on average, despite having lower HS as compared to HAA-based membranes.

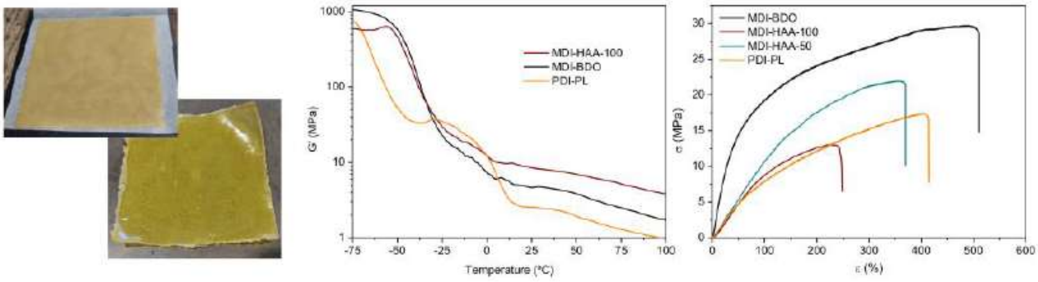

Figure 1. PU membranes referred to MDI-HAA-100 (top) and PDI-PL (bottom). Storage modulus G' and stress-strain curves profiles of these membranes compared to the reference MDI-BDO.

CONCLUSIONS

Careful selection of each building block and synthesis pathway, in addition to HAAs and PL, was crucial for ensuring the feasibility and conducting relative performance evaluations of the final products. Our research outcomes have laid the groundwork for potential opportunities, potentially broadening the utilization of HAAs and polyol lipids for various industrial PU applications.

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P37.1

PHBV-based Materials for Food Packaging Applications

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INTRODUCTION

The transition of society to a more sustainable way of living is of crucial importance to guarantee the well-being of the next generations. Currently, most plastics are produced from non-renewable sources. Some are biobased however, not all are recyclable, reusable, or biodegradable. The progressive substitution of consumer products derived from fossil fuels is crucial to decarbonise our society, especially in short shelf-life packaging.[1]. In this context, biobased polymers have gained attention from both academia and industry in the last decades. They are proposed as a real sustainable alternative to fossil-based plastics. Within this family, one of the most promising biopolymers for food and drink packaging manufacturing is the biopolyester poly (3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) due to its excellent properties such as complete biodegradation in different environments (soil, water, home composting), non-toxic, barrier properties, flexibility (that can be modulated according to 3-HV content) and mechanical resistance [2].

EXPERIMENTAL

Haloferax mediterranei was the halophile of choice for the production of PHBV.

Different organic wastes (lemon extract, apple and grape pomace, and residues from the candy industry) were used as carbon sources for microorganism growth.

The physicochemical properties of the PHBV produced were determined; hydroxyvalerate comonomer content by NMR, tensile properties, thermal properties by DSC, and molecular weight distribution by GPC.

PHBV based formulations were prepared and their mechanical properties investigated.

PHBV based formulations were transformed into packaging (films and trays) to evaluate their processibility and weldability.

RESULTS AND DISCUSSION

PHBV was produced with high content in the comonomer 3-hydroxyvalerate (between 10 and 14 %; ten times higher than the commercial PHBV, and up to 30% when using precursor. The 3-HV richest material (PHBV 30) behaved as a ductile material as opposed to PHBV 10 and the commercial one.

Six PHBV formulations were prepared and successfully processed into packaging with good weldability behaviour.

CONCLUSIONS

The valorization of residues from the food sector have been achieved through a biotechnological process to afford a range of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with different content in the comonomer 3-hydroxyvalerate. Six different PHBV-based formulations were investigated. Four of them (T1-PTA1, T1-PTA2, T1-PS1, and T1-PS2) were used in flexible packaging (blown films) for lemon concentrate and apple & pear cream. The other two (T1-PA1 and T1-PA2), were employed in the production of rigid trays for cured meat and cheese.

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P38.1

DNA-containing PVA-based hydrogels for application in gene therapy

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INTRODUCTION

The use of polymeric matrices for genetic material delivery and treating genetic disorders signifies a significant advancement in biotechnology [1]. Poly(vinyl alcohol) (PVA) has emerged as an effective non-viral vector owing to its favorable physical, chemical, and biological attributes. Moreover, enhancing PVA properties is achievable by incorporating it with other polymers such as cellulose, chitosan, starch, or nanotubes [2]. Hence, this study focuses on developing various hydrogel systems comprising PVA associated with different polymers and loaded with DNA for gene therapy applications.

EXPERIMENTAL

Equal volumes (1 mL) of 20% PVA were added aseptically to each well of a 24-well plate. Subsequently, 200 µL of 1% (w/v) PLA, 1 mg/mL chitosan (CH), or 0.1% (v/v) PEG 10000 were added to their respective wells to create PVA-PLA, PVA-CH, or PVA-PEG blends. The hydrogels underwent a freeze-thaw cycle, consisting of overnight freezing followed by twelve hours of thawing, repeated three times. Various characterization methods were employed on the materials.

RESULTS AND DISCUSSION

The swelling test revealed that adding different polymers increases hydrogel water absorption. Infrared spectra indicated characteristic PVA and polymer bands in the hydrogel matrix, along with DNA bands. Fluorescence spectra confirmed DNA presence. Thermogravimetric tests improved PVA hydrogel thermal properties with polymer addition. SEM images displayed surface and interior changes with polymer and DNA incorporation. DNA release kinetics demonstrated PEG and PLA addition to hydrogels results in controlled DNA release, potentially beneficial for gene transfection (Figure 1).

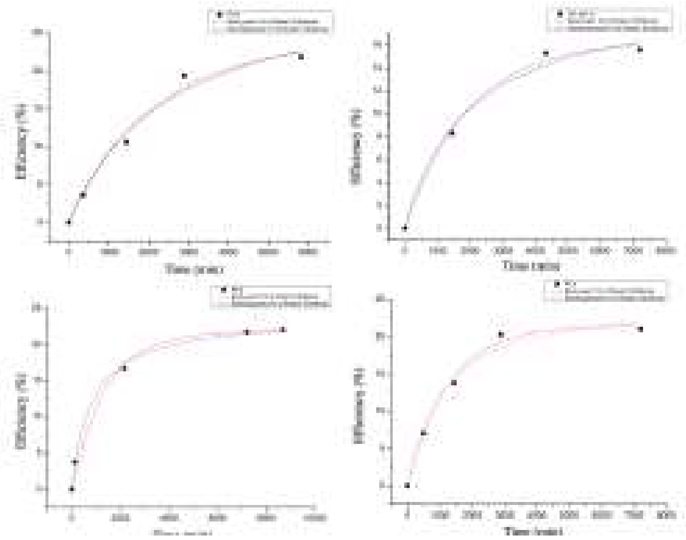

Figure 1. DNA release from PVA/DNA hydrogels.

CONCLUSIONS

It has been demonstrated that the addition of different polymers affects the neat PVA hydrogels' properties. Both PEG and PLA play an important role in the efficiency and control of DNA release, making it a promising material for applications in future gene therapy trials.

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P39.1

Use of natural resin to produce water soluble thermoplastic starch-injected molded materials

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INTRODUCTION

Peach gum (PG) is a natural gum produced by peach trees (Prunus persica, family Rosaceae) that is insoluble in aqueous solution. [1] Nonetheless, peach gum contains water-soluble polysaccharides made of arabinogalactans and galactose than can be extracted by hydrolysis. [2] Thermoplastic starch (TPS) is a promising bioplastic because starch is available, affordable, and biodegradable. However, TPS materials suffer from two primary drawbacks: low mechanical performance and susceptibility to moisture absorption. [3] Nonetheless, this susceptibility to water can be used to produce soluble materials and increase the TPS range of applications. The current work attempts to create water-soluble thermoplastic starch-injected molded specimens using raw peach gum (PG) and peach gum polysaccharide (PGP) as additives without reducing TPS mechanical properties.

EXPERIMENTAL

Native rice starch was supplied by Manuel Riesgo S.A. (CAS: 9005-25-8). Distilled water and glycerol were used as plasticizers. The raw peach gum (PG) samples were purchased from Plant Gift (China). Peach gum polysaccharide was extracted using the thermal hydrolysis. Mechanical characterization specimens were prepared by injection molding in a in a micro-compounder Xplore MC 15HT.

RESULTS AND DISCUSSION

Table 1 presents the tensile properties and the water sensitivity of TPS, TPS-PG, and TPS-PGP. It is observed that the tensile parameters did not change significantly with the addition of 10 phr of PG and PGP. PG and PGP are compatible with starch; PG does so because of its hydroxyl groups and their similarity in structure in its polysaccharide and monosaccharide composition, [4] whereas PGP is a polysaccharide. [2] As the two additives are compatible with starch, when added at 10 phr, they are solubilized in the matrix, producing no significant differences ($p > 0.05$) in the tensile properties of TPS.

Table 1. Tensile properties and water sensitivity (%) of TPS and TPS-PG and TPS-PG formulations

Material	σ_y (MPa)	ε_b (%)	E_t (MPa)	Water Sensitivity (%)
TPS	4.35 ± 0.06^a	57.89 ± 0.44^a	36.00 ± 3.50^a	38.3 ± 1.47^a
TPS-10PG	4.51 ± 0.05^a	56.94 ± 2.85^a	39.71 ± 5.17^a	69.2 ± 2.33^b
TPS-10PGP	4.61 ± 0.51^a	55.96 ± 3.63^a	38.92 ± 7.07^a	68.1 ± 4.69^b

Moreover, water sensitivity tests were conducted on the injected molded specimens; the results in Table 1 show that both PG and PG increase TPS water sensitivity by 80 %; however, contrary to the film behavior, no significant differences ($p > 0.05$) were noticed between TPS-10PG and TPS-10PGP water sensitivity, which could be related to the low contact area compared to the films.

CONCLUSIONS

The use of PG and PGP allow to boost TPS water solubility keeping its mechanical performance.

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P40.1

Use of machine learning models for forcasting polylactic acid properties after reinforcement

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INTRODUCTION

Artificial intelligence is increasingly applied across various domains, while in materials science, traditional trial-and-error experiments are time-consuming.[1] Several algorithms can be distinguished for training regression models, among others, linear and boosted decision tree algorithms.[2] Environmental consciousness and sustainable practices have driven increased interest in developing green composites, leveraging biobased materials like wool fibre due to their significant advantages over fossil-dependent or inorganic alternatives in terms of reduced greenhouse gas emissions throughout their life cycle.[3] This study aims to develop regression models to predict the tensile strength and 5% mass loss temperature of unmodified and modified wool-reinforced PLA composites using machine learning algorithms.

EXPERIMENTAL

Machine learning methods were employed to preprocess and analyse the collected data of modifying polylactic acid (PLA) with maleinized linseed oil (MLO) and reinforcing it with sheep wool fibres treated with various coupling agents.

RESULTS AND DISCUSSION

The linear regression model for tensile strength shows that an increase in coupling agent concentration, coupled with a decrease in wool concentration, generally leads to an increase in tensile strength, especially notable at lower coupling agent concentrations up to 0.5 phr. Conversely, the boosted decision tree regression model for tensile strength reveals that the addition of coupling agents generally enhances tensile strength across all concentrations, with changes in coupling agent concentration not affecting this property, and even low concentrations of coupling agents proving beneficial improvement.

For the 5% mass loss temperature, the linear regression model predicts an initial increase followed by a decrease in temperature at coupling agent concentrations higher than 0.5 phr. While the boosted decision tree model predicts temperature stabilization between 0.5 and 1.5 phr of coupling agent concentration before a decline associated with decrease in predicted temperature, indicating as well varying effects of coupling agents on thermal behavior.

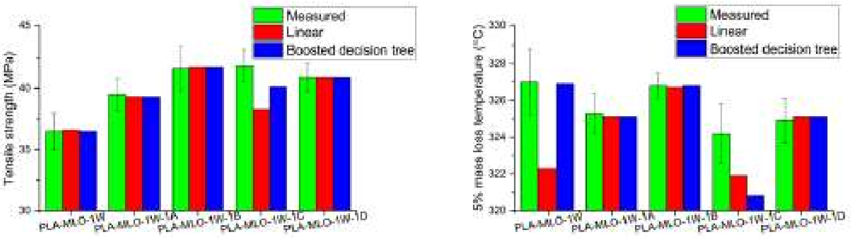

Figure 1. Example of an image inserted on the text.

CONCLUSIONS

Comparing actual and modeled data from five representative formulations revealed that boosted decision and linear regression models generally produced predictions closely approaching actual outcomes. However, the differences with measured values revealed limitations in model accuracy.

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P41.1

Ultraviolet irradiation effect at dry and water-immersion conditions on poly(lactide) commercial films

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INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic widely employed in diverse applications, spanning from packaging to biomedical devices. Understanding degradation is crucial for assessing material durability during operation and its post-use changes. This study aims to investigate UVC irradiation, both at dry ambient and under water immersion, as a potential strategy to enhance the degradation of commercial PLA films.

EXPERIMENTAL

PLA commercial films supplied by Prime Biopolymers SL (Spain) were exposed in a dark chamber equipped with four 15W UVC lamps, providing an irradiance of 0.90 mW/cm² at 254 nm wavelength. Films were subjected to both dry conditions (UVC) and immersion into 20 mL of distilled water, (UVC + H2O) with time exposure 24 h, 48 h, 72 h, and 96 h. Characterization techniques including FTIR, SEM and DSC were used to analyze the bulk and surface property modifications induced in the plastics.

RESULTS AND DISCUSSION

Significant variations have been observed in the characteristic peak (Figure 1a) of carbonyl groups in ester linkage of PLA backbone (1748 cm^{-1}). After 48 hours, a notable decrease in the intensity of this peak is recorded, suggesting the formation of shorter polymeric chains. A reduction in glass transition temperature ($Tg_{pristine} = 55.02$ºC, $Tg_{48h} = 51.57$ºC, $Tg_{96h} = 47.91$ºC) as well as variation in melting peaks and temperature cristalization (Figure 1b) of the PLA films was observed. Additionally, a 24 hour irradation under dry conditions induced an apparition of holes on the surface' films (Figures 1c, 1d).

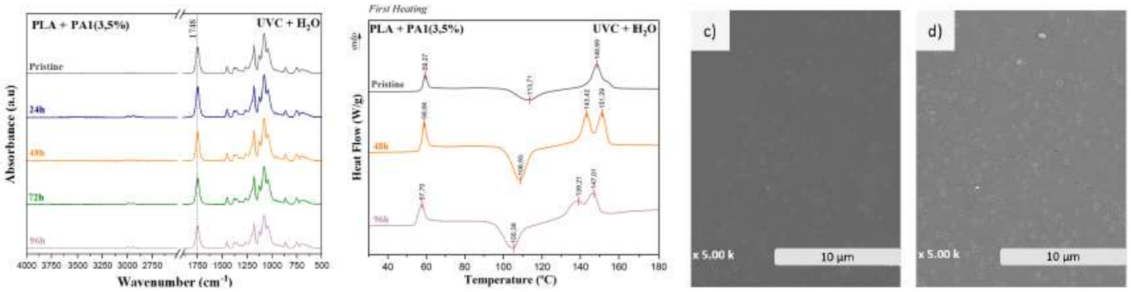

Figure 1. a) FTIR spectra, b) DSC thermograms of PLA samples after UVC + H2O pretreatment, and c) SEM microscopies of pristine film and d) after 24 hours of UVC pretreatment.

CONCLUSIONS

The reduction in the intensity of the C=O groups suggested reduction of carbonyl groups during photodegradation [1] as a result of cleavage of ester bonds in PLA. These changes occurred in both conditions. Additionally, an increase in porosity may served as a medium to assess biodegradation, as it enhances water absorption, thereby accelerating the breakdown of the PLA films.

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P42.1

An interdisciplinary approach for the enzymatic degradation of plastics

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INTRODUCTION

As plastic waste accumulation continues to surge uncontrollably, a planetary crisis is unfolding beneath our feet. Despite plastics' durability and resistance to degradation, recent emphasis has shifted towards enzymatic breakdown, the ability of enzymes to target and shatter polymer bonds, leading to breakdown into oligo- and monomers. The main purpose of our research was to discover novel enzymes and develop systems aiming to degrade PET and other polymer materials. Hereby, a detailed path starting from the selection of candidate enzymes to the development of a microbial-cell-factory for plastic degradation and monomer upcycling is described.

EXPERIMENTAL

The discovery of candidate enzymes was achieved mainly by genome mining using bioinformatic tools (e.g., BLAST and HMMER). The selected genes were synthesized, heterologously expressed in *E. coli* and purified. The most promising PET hydrolases were distinguished utilizing a high-throughput screening methodology, developed based on novel fluorescent labelled PET model substrates. These enzymes were biochemically characterized and tested on other polyester materials such as PBS, PCL, PHB, PLA as well as polyether PU and a variety of virgin or pretreated PET samples of varying crystallinity grades. Following, protein engineering methodologies, based on rational design and AI prediction tools, were applied for the enhancement of their polyesterase activity and thermostability. Ultimately, different bacterial species, including *Pseudomonas* and *Streptomyces*, initially characterized as promising biopolymer and biopigment producers, were genetically modified by transformation and introduction of the most prominent polyesterases.

RESULTS AND DISCUSSION

Following the aforementioned methodology, the degradation potential of more than 15 hydrolases, from different families, was assessed, leading to some significant findings. A novel thermotolerant cutinase, *Dm*PETase, was capable of degrading crystalline compartments of PET bottles, as well as semicrystalline PET powder at the same level as LCC^{ICCG} [1], an industrially relevant enzyme, while getting less affected by PET crystallinity grade, while a lipase-like enzyme, *Se*1JFR, was discovered, presenting promising results in polyester degradation. Through protein engineering more than 15 variants were expressed. A single mutation (G122S), of FoFaeC, a feruloyl esterase from *Fusarium oxysporum*, increased the activity on MHET by 30%, compared to the WT. Synergistic action of FoFaeC with MoPE [2], an esterase from

Moraxella sp. with polyester depolymerase action, led to the development of an efficient dual system for PET degradation. Ultimately, combining the results of our approach, the design of a consolidated bioprocess through the development of a biorefinery with plastic waste as feedstock was accomplished.

CONCLUSIONS

The fields of chemistry, biotechnology and polymer science cooperated to the development of a complete methodology for the discovery and utilization of novel plastic degrading enzymes and enzyme systems, which could possibly offer a vital solution controlling plastic's accumulation.

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P43.1

Deep eutectic solvent (DES)-extracted lignin hydrogels as a platform for drug delivery systems

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INTRODUCTION

Climate change and scarcity of resources are forcing a transition towards a bioeconomy and the search for eco-friendly renewable resources [1]. In this context, lignocellulosic biomass (LB) is deemed as available, ubiquitous and carbon neutral source. For instance, *Paulownia elongata x fortunei* is a fast-growing dihybrid species with high biomass production (50 t/(ha·year)) and low growing requirements, with high potential within biorefinery [2]. The fractionation of LB implies a pretreatment, and the use of deep eutectic solvents is considered as a low-cost eco-friendlier alternative to other delignification processes [3]. Although cellulose and hemicelluloses have been widely employed, lignin is usually underutilized, although presenting potential for biomaterials production, such as hydrogels [1].

EXPERIMENTAL

This study comprises (i) the delignification of Paulownia wood by DES (either with a previous hydrothermal treatment or not) and the isolation of lignin, (ii) the cast (40% lignin content, lignin-crossliker ratio of 1:0.5 to 1:1 w/w) of lignin-based hydrogels chemically crosslinked by polyethylene glycol diglycidyl ether -PEGDE, and their structural (ATR-FTIR), morphological (SEM), and thermal (TGA-DTG) characterization, besides studying the swelling capacity and rheological behavior, and (iii) the evaluation of hydrogels as controlled drug delivery systems for paracetamol.

RESULTS AND DISCUSSION

The delignification of Paulownia wood was optimized for choline chloride:lactic acid-DES(1:9) at 130 °C for 60 min, recovering up to 89-94% of initial lignin (average purity of 85%). The synthesized hydrogels were subjected to rheology evaluation, resulting in a solid/gel-like behavior. The SEM demonstrated the formation of higher surface pores in hydrogels with lower PEGDE, which also enabled higher swelling capacity (up to 217%) and higher thermogravimetric stability. Hydrogels synthesized with lower PEGDE content were subjected to paracetamol delivery, resulting in 57-91% of cumulative release after 7 h.

CONCLUSIONS

Choline chloride:lactic acid-DES exhibited selective effect to recover high-purity lignin from Paulownia wood, and the obtained lignins showed potential as source for hydrogels as platform for controlled paracetamol release.

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P44.1

Advancing Biodegradation of Bioplastics: Strategies for Isolating Microbial Degraders and Accelerating Biotechnological Solutions

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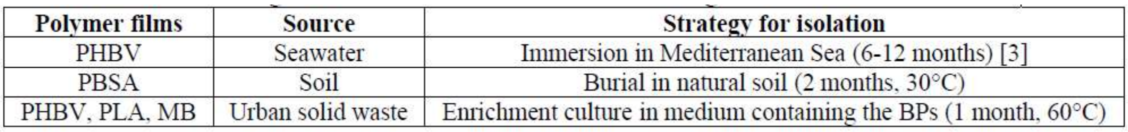
INTRODUCTION

Bioplastics (BPs) have gained attention as eco-friendly alternatives to conventional plastics. Forecasts predict global BPs production to rise from 2.2 MT in 2023 to an estimated 7.4 MT in 2028 [1]. Understanding the ability of microorganisms to degrade BPs is crucial for the development of innovative biodegradation formulations, applicable in both laboratory and industrial settings [2]. This study aims to present diverse strategies for isolating bacterial BPs degraders from various sources, facilitating their use as biotechnological tools to promote their biodegradation in the *in vitro* assessment of their biodegradation kinetics, and in *in vivo*, including environmental and industrial applications.

EXPERIMENTAL

The polymers used were: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), Poly(butylene succinate-co-adipate) (PBSA), Poly(lactic acid) (PLA), and Mater-Bi (MB). Table I summarizes the strategies applied for the isolation of BPs bacterial degraders. After purification, bacterial strains were plated on solid media incorporated with the BPs. The appearance of clear zones around colonies, indicating polymer degradation, was monitored. For soil and urban solid waste strains, biodegradation extent was assessed by film specimens mass loss.

Table I. Strategies for the isolation of BPs bacterial degraders from various sources



Polymer films	Source	Strategy for isolation
PHBV	Seawater	Immersion in Mediterranean Sea (6-12 months) [3]
PBSA	Soil	Burial in natural soil (2 months, 30°C)
PHBV, PLA, MB	Urban solid waste	Enrichment culture in medium containing the BPs (1 month, 60°C)

RESULTS AND DISCUSSION

Bacterial strains degrading PHBV, PBSA, and PLA were isolated from all sources, with soil being the main source. Urban solid waste yielded fewer strains, possibly due to the incubation at 60°C, suitable only for thermophiles. An isolate from soil demonstrated the capability to degrade PBSA by up to 38% over 41 days in liquid media, while PLA experienced a mass loss over 80% when incubated with a thermophilic consortium from urban solid waste.

CONCLUSIONS

Several BPs microbial degraders have been isolated from various sources. Studying microbial BPs degraders is vital for environmental conservation and sustainable technology development. Future research should focus on innovative, rapid screening methods to handle large strain numbers.

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P45.1

Effect of maleinized borage seed oil as an additive in PLA and PHB blends

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INTRODUCTION

Renewable and biodegradable materials are increasingly importance in different research and industry areas. These biomaterials need an investment on research to be economically competitive, and expand applications, achieving new biomaterials with interesting properties. For this reason, research on developing biomaterials to increase the possibilities of these materials.

EXPERIMENTAL

In this work was study a formulation based on a matrix of poly (lactic acid) 75%PLA (PLA L130 (Total Corbion)), with an incorporation of polyhydroxybutyrate 25%PHB (Biomer P226E), initial blend. The development of plasticizer was following the previous work [1], maleinization process of borage seed oil (MBSO), and incorporated into the initial blend on different percentages, 1, 3, 5, 7, and 10 %wt, to increase the miscibility and properties. The formulations were developed by extrusion, and then were injected in shape of standardised traction and flexibility test specimens.

RESULTS AND DISCUSSION

The incorporation of plasticizer achieves a reduction in tensile strength properties, comparing with PLA's values, typical of fragile material. Mechanicals properties showed that MBSO's values increased ductility behavior represented on elongation at break, and impact absorbed energy. These results achieved an increase on the synergy between biopolymers, performing as a compatibilizer, and a reduction of glass transition temperature caused by plasticizer effect increasing mobility of the polymeric chains.

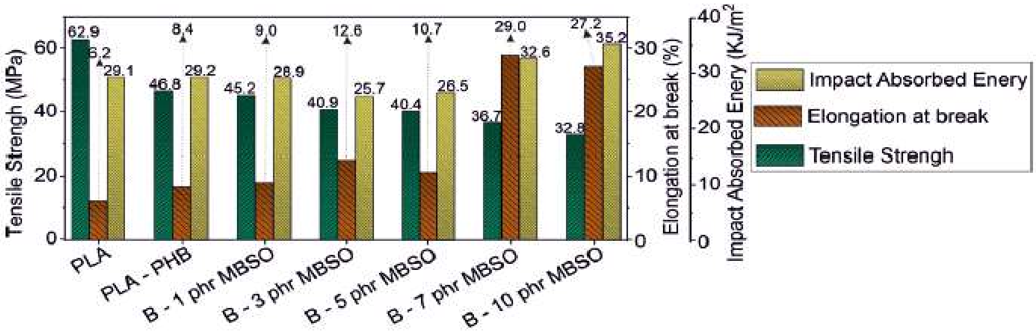

Figure 1. Mechanical properties, and glass transition temperature.

CONCLUSIONS

Plasticizer obtain of MBSO showed mechanical properties behaviour interesting to increase the ductility of PLA, such as create a great synergy between both biopolymers causing an increase on miscibility.

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P46.1

Furan-based thermoplastic polyesters: a short overview of their physical properties

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The number of research papers and patents highlighting how interesting are the properties of furan-based polyesters has been skyrocketing in the last years. Indeed, furan-based derivatives can be used to obtain a variety of polymers, both thermosetting and thermoplastic. 2,5-furandicarboxylic acid (2,5-FDCA), in particular, has been recently listed among the top 12 platform molecules to produce biobased polymers as a potential replacement for polyethylene terephthalate (PET) [1]. Unsurprisingly, the thermoplastic homopolyester poly (ethylene 2,5-furandicarboxylate) (2,5-PEF) has raised much attention, especially since it was proven to be particularly suitable for packaging applications due to its superior barrier properties [2]. Although the research efforts have mainly converged on the homopolyester obtained with 2,5-FDCA and ethylene glycol (EG), other possibilities exist, and a careful selection of the initial building blocks could help in tuning the properties, whilst attempting at reducing the time and costs for biomass valorisation. In fact, the microstructure and molecular mobility of furan-based thermoplastic polyesters can be controlled by varying the nature and proportion of the selected monomers. To begin with, the assortment of diols capable of reacting with FDCA for the synthesis of polyesters is quite large [3], not to mention that different positional isomers of FDCA are obtained during the Henkel-type disproportionation reaction [4], and that two of them (2,5- and 2,4-FDCA) are obtained in yields that are sufficient to synthesize PEF. But what makes furan-based thermoplastic polyesters so competitive compared to other polyesters?

This communication will give a short overview of the physical properties of furan-based thermoplastic polyesters, based on the latest experimental results obtained by advanced thermal analysis techniques (modulated-temperature differential scanning calorimetry MT-DSC, fast scanning calorimetry FSC, dielectric relaxation spectroscopy DRS, thermally-stimulated depolarization currents TSDC) on selected systems (homopolyesters based on 2,5-FDCA and different diols, random co-polyesters based on 2,5-/2,4-FDCA and EG). Their ability to crystallize and their glass-forming behaviour will be discussed, along with the inevitable consequences on free volume and molecular mobility [5-8].

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P47.1

PLA blended with recycled PHBV reinforced with functionalized bacterial cellulose obtained from kombucha fermented in coffee waste

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INTRODUCTION

Poly(lactic acid) (PLA) and polyhydroxyalcanoates (PHAs) are biobased and biodegradable polymers that can be mechanically recycled. Thus, they have gained interest in short-term applications such as food packaging [1,2]. At the industrial scale, several defective plastic parts are rejected from the production line, that can be easily reprocessed avoiding aggressive washing steps since these plastics do not come from waste streams and are of well-known origin. The strategy to blend PLA with PHAs allows for obtaining a fully biodegradable material with improved properties since PHAs enhance PLA crystallinity and PLA improves PHAs' processability [1]. It has been observed that cellulosic particles improve the compatibility between PLA and PHAs [1]. Although cellulose is mostly extracted from plants, the process is quite complex and needs the removal of lignin and hemicellulose by acid hydrolysis. But cellulose can also be obtained from microorganisms by fermentation, such as in the case of bacterial cellulose from kombucha beverages (KBC) [3]. KBC is a by-product from the kombucha beverage industry, produced by a symbiotic community of bacteria and yeast (SCOBY) in a sugared infusion. Additionally, KBC can be obtained from waste such as spent coffee grounds (SCG).

EXPERIMENTAL

KBC was fermented in an infusion of SCG to revalorize this waste from the HoReCa (Hotel, Restaurant and Catering) sector [3] and it was further functionalized by an esterification process with a fatty acid derivative (palmitoyl chloride) [2] (kCf) to reduce the hydrophilicity. PLA was blended with 30 wt.% of reprocessed PHBV (rPHBV), to simulate the revalorization of industrial plastic waste of PHBV, and the blend was further plasticized with 15 wt.% of OLA and reinforced with the obtained functionalized kCf at 1 and 3 wt.% as well as with 1 and 3 wt.% of functionalized SCG (Cf) for comparison.

RESULTS AND DISCUSSION

The PLA-30PHBVr-OLA15-Cf and PLA-30PHBVr-OLA15-kCf films were successfully produced by melt-extrusion into transparent films with more hydrophobic surfaces than films with non-functionalized particles. Films were subjected to a specific migration test to determine their antioxidant activity by 2,2-diphenyl-1-picrylhydrazyl (DPPH)-method. The biocomposite films showed antioxidant activity. Those films with 3 wt.% of the Cf or kCf showed a Radical Scavenging Activity of around 40 %.

CONCLUSIONS

KBC was fermented in a sugared infusion of SCG and further successfully functionalized with palmitoyl chloride (kCf). The obtained particles were used to reinforce PLA and reprocessed PHBV blend (PLA-30PHBVr) into sustainable active films with interest in the antioxidant active food packaging sector.

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P48.1

Isolated environmental microorganisms with biodegradative activity on polyurethane

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INTRODUCTION

Polyurethane (PU) is a versatile and widely used material in industry. However, there are no sustainable solutions for waste management, with landfill burial and incineration being the most common destination at the end of its useful life. Several studies were carried out to find novel solutions for its efficient degradation and recycling. Some strategies are based on the isolation of new degradative microorganisms from soil [1], plants [2] or various sources [1]. The objective of the present study was to identify new PU-degradative microorganisms from environment, accessing waste accumulation areas to isolate efficient strains in the PU foam recycling.

EXPERIMENTAL

Two waste accumulation areas were accessed, taking soil samples and PU foam waste. The samples were cultured in a saline medium supplemented with an aqueous PU dispersion (MM-PU) and incubated at 30ºC with shaking for 7 days. Next, serial dilutions of the cultures were inoculated in MM-PU agar plates and incubated until growth was observed. The colonies presenting a halo around them, evidencing the degradation of the PU present in the medium, were selected to obtain pure cultures. The PU degradation capacity of the isolates was evaluated using an absorbance measuring method.

RESULTS AND DISCUSSION

A total of 32 isolates were obtained that showed a PU degradation halo. After the establishment of pure cultures, the isolates were categorized as bacteria or fungi and morphologically and biochemically characterized. Eleven isolates stood out for their PU biodegradation capacity when cultured in liquid MM-PU (Figure 1), being three filamentous fungi and seven bacteria.

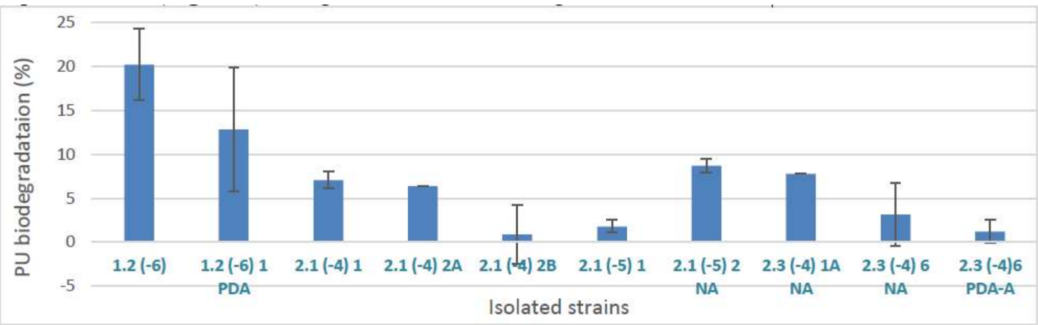

Figure 1. Biodegradation percentage of PU of isolates.

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P49.1

Physical Recycling of ABS: Leveraging Renewable Solvents for Circular Economy Solutions

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INTRODUCTION

Approximately 85% of end-of-life acrylonitrile-butadiene-styrene (ABS) plastic is commonly used in durable products such as electrical and electronic equipment and other quotidian items, and often ends up in landfills or incineration [1]. However, mechanical recycling of ABS does not allow for full circularity of this thermoplastic because of challenges such as diverse compositions and loss of properties over time [1]. A promising solution to this issue involves the utilization of physical recycling processes. Recently, *greener* and renewable-based solvents have attracted attention for various purposes, owing to their potentially low toxicity, as well as their cost-effective synthesis [2]. Thus, this work aims to develop a technology for physically recycling ABS based on the use of renewable solvents, including eutectic solvents (ESs) and biosolvents, in alignment with circular economy principles.

RESULTS AND DISCUSSION

In this work, an extensive *in-silico* screening of benign and suitable renewable-based solvents for selectively dissolving the styrene acrylonitrile/polybutadiene of ABS was performed using the COndutor-like Screening Model for Realistic Solvents (COSMO-RS). This thermodynamics method was used to calculate the activity coefficient of polymers in solution for the combinations of 185 HBA and 164 HBD, totalizing 30340 eutectic mixtures. Results suggest that esters-based solvents are the most promising for the dissolution of ABS terpolymers. Subsequently, wet tests confirmed that the identified ester family of solvents was the most promising. The waste and recycled ABS products were characterized using various spectroscopic techniques, including Fourier transform infrared spectroscopy (FTIR) and ^{1}H and ^{13}C nuclear magnetic resonance (NMR), for structural analysis.

CONCLUSIONS

In summary, this study suggests that careful selection of appropriate renewable solvents for the efficient and selective dissolution and recovery of complex terpolymers, such as ABS, represents a significant advancement in the circular management of plastic waste.

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P50.1

Sustainable approaches towards new furan-based polymers: new copolyesters based on 5,5′-oxybis(methylene)bis(furan-5,2-diyl)dimethanol (OBMF-H)

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INTRODUCTION

Due to their unique set of properties, polymers have quickly become an irreplaceable material and valuable resource to our society, with world polymer production reaching over 400 Mt in 2022.[1] The vast majority of these polymers (over 90%) are based on fossil resources, therefore, in a quest to develop more sustainable options, redesigning plastics and decoupling them from fuel-based resources is a priority already in place. This gave rise to the current surge for bio-based polymers. Among the countless polymers that fit this category, furan-based polyesters, such as poly(ethylene 2,5-furandicarboxylate) (PEF) are some of the most investigated.[2] However, despite their greener origin, the conventional synthesis of these polymers still involves harsh conditions such as high temperatures (180 - 220 ºC), the use of reduced pressure, and in the majority of the approaches making use of metal-based catalysts. So, another aspect of moving towards greener materials is to rethink their synthesis and develop more sustainable approaches.

EXPERIMENTAL

In this work, we studied alternative and greener methods for the synthesis of furan-based polyesters and copolyesters using 5,5′-oxybis(methylene)bis(furan-5,2-diyl)dimethanol (OBMF-H),[3] a derivative. Also, alternative pathways were explored, namely enzymatic catalysis for the synthesis of FDCA-based copolyesters.

RESULTS AND DISCUSSION

The copolyesters reached a maximum molecular weight of 17 800 g/mol, they were further characterized by FTIR, ^{1}H NMR, GPC, XRD, DSC and TGA.

CONCLUSIONS

This is OBMF-H's first application as a monomer, and it was successfully incorporated into novel copolyesters.

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P1.2

Development of poly(β-pinene) based tackifiers for use in hot melt adhesives

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INTRODUCTION

The interest in utilizing renewable biomass resources to replace petrochemical raw materials has significantly increased over the past decade due to the depletion of fossil oil reserves. Polyterpene resins, synthesized from terpenes such as α-pinene, β-pinene, and D-limonene, present a promising alternative. Polyterpene resins are typically produced through cationic polymerization, at temperatures below room temperature. Notably, polyterpenes exhibit a high glass transition temperature even at low molecular weights (approximately 2-3 kDa). This property makes them excellent candidates as tackifiers in adhesives, including hot melt and pressure-sensitive adhesives, where they can replace fossil-based hydrocarbon resins (C5-C8).

In this study, a set of poly(β-pinene) resins were synthesized by employing different reaction conditions (e.g., time, temperature, catalyst, catalyst/monomer ratio) and were then used as tackifiers in hot melt adhesives.

RESULTS AND DISCUSSION

The cationic polymerization of β-pinene was carried out under different conditions, and a solvent/catalyst pair was found that enabled the polymerization to occur at room temperature, producing poly(β-pinene) with suitable characteristics for use as a tackifier.

The use of the synthesized poly(β-pinene) in a hot melt formulation produced an adhesive capable of gluing cardboard. The elongation at break, one of the most important characteristics of a hot melt adhesive, was found to be similar to that of a formulation based on a fossil C5 resin.

CONCLUSIONS

The poly(β-pinene) resins, synthesized at room temperature, showed suitable properties to be used as tackifiers in hot melt adhesives formulations.

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P2.2

Improving thermo-sealing of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by blending with polycaprolactone

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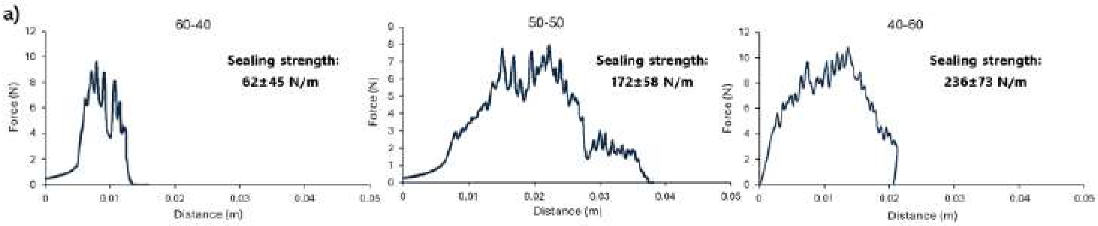
INTRODUCTION

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biodegradable, semi-crystalline polymer, synthesised by bacteria as a reservoir material and energy source, that could become a good alternative to current conventional plastics, which have caused a serious environmental problem, largely driven by food packaging. Nevertheless, its difficulty to heat-seal or thermoform makes its use difficult in the form of bags for food packaging [1]. Blending with other polymers, such as polycaprolactone (PCL), could be a good strategy to solve this problem. However, their blending could modify the barrier capacity of the films, affecting their effectiveness as a food packaging material. The aim of this study is to obtain and characterise blend films of PCL and PHBV, using a PHBV/PCL ratio of 60/40, 50/50 and 40/60, by melt blending and subsequent compression moulding, analysing the film microstructure and their mechanical and barrier properties to water vapour, oxygen and volatile compounds (limonene), as well as the thermal adhesion properties of the materials through measuring of sealing strength.

RESULTS AND DISCUSSION

The permeability to water vapour (WVP), oxygen (OP) and D-limonene (LP) increased with the concentration of PCL in the blend due to the lower barrier capacity of PCL and the polymer immiscibility observed in the film microstructure, which favours the preferential pathways for the molecular diffusion. The elastic modulus (EM) and resistance to fracture also decreased while extensibility (E%) rose at the highest PCL ratio. The sealing strength curves of the thermo-sealed films showed good thermal adhesion in every case, with strength values increasing when the PCL ratio increased in the film. Likewise, the peeling behaviours of thermo-sealed layers were different, the 60/40 samples mainly exhibiting layer separation (adhesive peel), which indicates lower resistance to layer separation than to layer beak during the mechanical test.



b)

Film	WVP·10^{12} (g/m·s·Pa)	LP·10^{14} (Kg·m/Pa·s·m^2)	OP·10^{13} (cm^3/m·s·Pa)	EM Mpa	TS (Mpa) (Mpa)	E (%)
PHBV	4.1±0.4	1.1±0.6	3.6±0.4	1350±110	33±5	2.7±0.9
60/40	5.9±0.8	6.7±1.8	1.7±0.1	1030±120	17±2	1.8±0.3
50/50	12.5±5.0	18.1±12	2.7±0.3	700±200	12±4	2.7±0.6
40/60	29.0±6.7	32.0±9.0	4.3±0.1	560±60	15±2	4.0±0.8

Figure 1. a) Typical force profile of the film separation in the seal strength tests of blends 60/40, 50/50 and 40/60, showing the mean values of seal strength (N/m). b) Mean values of water vapour (WVP), D-Limonene (LP), oxygen (OP) permeability, elastic modulus (EM) and tensile strength (TS) and elongation at break (E) of PHBV and the PHBV/PCL blends.

CONCLUSIONS

PCL improved the thermo-sealing ability of PHBV, making the bag formation easier for food packaging applications. Nevertheless, the barrier and tensile properties of the blend films were poorer than that of PHBV films. Therefore, the blend 50/50 could be the best option to ensure a good sealing of the bags for packaging, without so notable loss in the material performance.

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P3.2

Molar mass fractionation of wheat straw organosolv extracts: Structural characterization of lignin fractions

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INTRODUCTION

Thorough chemical and structural characterization of dissolved components of biorefinery process streams is essential for designing innovative bio-based products such as bio-based polymers in a future circular economy concept.

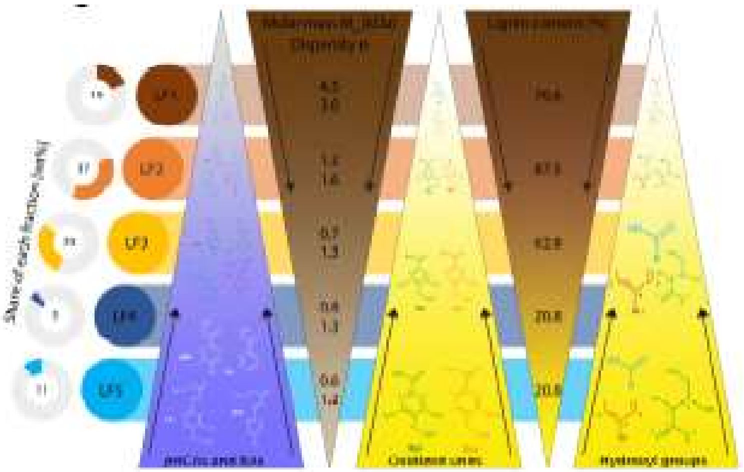
EXPERIMENTAL

In this work, an organosolv wheat straw lignin was fractionated using preparative gel permeation chromatography (GPC) with DMF as solvent. The resulting fractions were analyzed by size-exclusion chromatography (SEC), HSQC, and ^{31}P NMR spectroscopy. In addition, Klason lignin content and polysaccharides were addressed and monomeric compounds were identified by GCMS.

RESULTS AND DISCUSSION

Scheme 1 summarizes the main characteristics of the lignin fractions isolated from dried OSWE. One half of the isolated lignin (LF1 and LF2) consists of polymeric lignin with a Mw of >1000 Da, while the other half is characterized as lignin oligomers with strong contributions of pHCAs, indicated by HPSEC analysis and confirmed by 2D NMR spectroscopy. Further, with lower molar mass of the fractions, decoration of the lignin oligomers with pBA and BA esters increases and more lignin monomeric units carry α-oxidized structural motifs, which are assumed to derive from lignin depolymerization reactions during Organosolv extraction.

GPC fractionation of OSWSE yields lignin with lower dispersity of their molar mass than bulk WSL, and dispersity decreases the lower the molar mass of the fractions. Regarding functional groups, there is a trend to higher contents of free phenolic hydroxyl groups from LF1 to LF3, which is consistent with the decreasing molar mass of the fractions and the fact that the main interunit linkage of bulk WSL is of the β-O-4' type. Interestingly, phenolics are less abundant in LF4 and LF5, where instead the content of carboxylic hydroxyl groups is highest.



Scheme 1: Illustrative overview of the main characteristics of the isolated lignin fractions LF1- LF5, prepared from dried Organosolv wheat straw extract (OSWSE) via GPC fractionation.

P4.2

Isolated environmental microorganisms biodegrading polyurethane

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INTRODUCTION

Polyurethane (PU) is a versatile and widely used material, especially in the furniture, automotive and footwear sectors. However, **there are no sustainable solutions for waste management**, with landfill burial and incineration being the most common destination at the end of its useful life. Several studies were carried out to find novel solutions for its efficient degradation and recycling. Some strategies are based on the **isolation of new degradative microorganisms** from soil [1], plants [2] or various sources [1]. The objective of the present study was to **identify new PU-degradative microorganisms from environment, accessing waste accumulation areas** to isolate efficient strains in the PU foam recycling.

EXPERIMENTAL

Two waste accumulation areas were accessed, **taking soil samples and PU foam waste**. The samples were cultured in a **saline medium supplemented with an aqueous PU dispersion (MM-PU)** and incubated at 30ºC with shaking for 7 days. Next, serial dilutions of the cultures were inoculated in MM-PU agar plates and incubated until growth was observed. The colonies presenting a halo around them, **evidencing the degradation of the PU** present in the medium, were selected to **obtain pure cultures**. The PU degradation capacity of the isolates was evaluated using an **absorbance measuring method** at 600 nm.

RESULTS AND DISCUSSION

A total of **32 isolates** were obtained that showed a PU degradation halo. After the establishment of pure cultures, the isolates were categorized as bacteria or fungi and **morphologically and biochemically characterized**. **Eleven isolates stood out for their PU biodegradation capacity** when cultured in liquid MM-PU (**Figure 1**), being three filamentous fungi and seven bacteria.

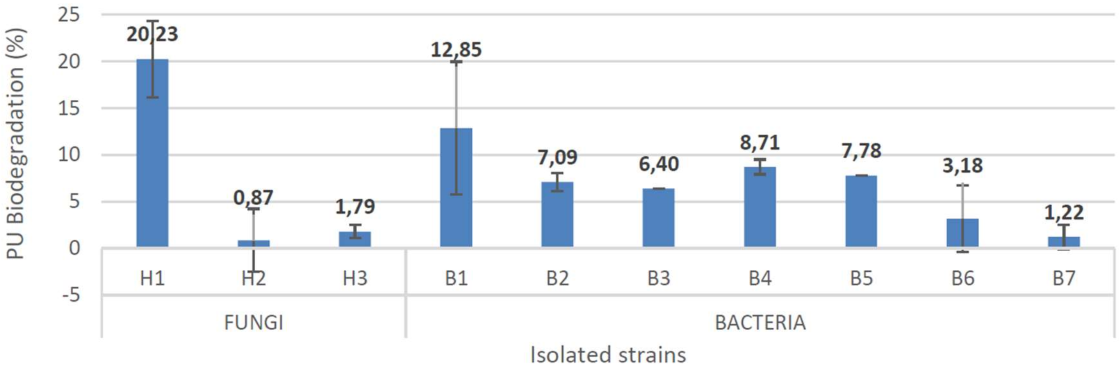

Figure 1. Biodegradation percentage of PU of isolates

CONCLUSIONS

32 isolates were obtained from **landfills** and polyurethane and plastics **waste accumulation areas**.

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P5.2

Water vapor transport properties of new bio-based food packaging

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INTRODUCTION

Recently, new bio-based and biodegradable materials have attracted interest, particularly in food packaging industry. Among the various choices of materials and architectures, a multilayer structure combining a hydrophilic layer of polylactide (PLA) with a high oxygen barrier layer of nanocelluloses, has shown very interesting properties[1]. However, if nanocelluloses layers provided high oxygen barrier properties, this advantageous is not preserved in presence of water vapor2. Consequently, to optimize the water and oxygen resistance of new bio-based food packaging, it is essential to deeply investigate the water transport phenomena in a multilayer architecture.

EXPERIMENTAL

This work studied multilayer films combining a PLA layer with coated layers of chitosan and nanocelluloses. Three types of nanocelluloses were deposited on PLA/chitosan (PLA/CS) films: cellulose nanocrystals (CNC), cellulose nanofibrils (CNF) and TEMPO-oxidized CNF. To understand the influence of each layer on the film water transport properties, complementary characterizations have been selected: water vapor permeability (cup method), dynamic vapor sorption (DVS) and adsorption-diffusion experiment3 (back-face relative humidity experiment).

RESULTS AND DISCUSSION

For the first time, the strong influence of nanometric polysaccharide coatings on water transport properties of multilayer films was demonstrated. The high water sensitivity of chitosan largely influenced the sample water vapor transport, and this behavior varied according to chitosan-nanocelluloses interactions. A chitosan coating of only 40 nm increased the sample moisture content by 12.8%, while in presence of nanocelluloses coatings, this value decreased down to 3.6%.

CONCLUSIONS

The combination of the well-employed cup method, with very precise DVS and back-face measurements highlighted the importance of understanding layer interactions to fully characterize a multilayer film. Chitosan and nanocelluloses layer synergy largely affected the sample water transport properties, despite representing less 1% of the sample mass.

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P6.2

Photoluminescent lignin nanoparticle synthesized from kraft lignin for bioimaging applications

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INTRODUCTION

Lignin is a high potential, carbon-rich biopolymer and gaining significant attention as precursor for various valuable products. It offers advantages like biocompatibility, sustainability, and potential for functionalization [1]. It is found in high abundance in the spent pulping liquor (black liquor (BL)) generated from paper industries and known as kraft lignin. This macromolecule is challenging to work with due to its complex structure and heterogeneity [2]. Therefore, the transformation of lignin into nanoscale particles (LNPs) with controlled size, and shape can expand its applicability in diverse sectors such as cosmetics, in targeted drug delivery and bioimaging due to their UV blocking capability, antioxidant and anti-inflammatory properties, as well as low cytotoxicity [3,4].

EXPERIMENTAL

First, the kraft lignin was precipitated from BL through acidification using an organic acid (acetic acid). The precipitate was separated by centrifugation followed by its washing to reduce impurities, drying and characterization. Subsequently, it was used for production of photoluminescent LNPs along with commercial alkaline lignin for comparative analysis. LNPs were prepared by a one-pot hydrothermal method using different molar ratios of citric acid and ethanediamine [4]. The prepared nanoparticles were characterized through SEM, FTIR, zetasizer and photoluminescence spectrophotometry.

RESULTS AND DISCUSSION

The precipitated lignin showed good purity with only ~1.5% inorganic content and comparable composition as that of commercial alkaline lignin. The hydrothermal process resulted into formation of well shape LNPs with photoluminescent properties. The characteristics of LNPs synthesized using precipitated lignin were comparable to LNP synthesized using commercial alkaline lignin.

CONCLUSIONS

The synthesis of photoluminescent LNPs from kraft lignin presents the opportunity to use a sustainable biopolymer for biomedical applications such as bioimaging.

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P7.2

Amino-yne click reaction of vegetable oils for biomedical applications

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Vegetable oils (VO) are produced on a large scale, making them a cheap and easily accessible raw material.[1] With sustainability issues in mind, it would be interesting to obtain a new material using these oils. The main goal of this work is to obtain a material derived from vegetable oils that can be used in biomedical applications. For this, it was necessary to modify the oils to obtain structures that would allow an amino-yne "click" reaction to take place. In this work, Acrylated Soybean Oil (AESO), was modified with two different amines, *viz.* putrescine and L-lysine, to obtain two distinct triglyceride structures with amine groups. To obtain the alkyne modified oil, Epoxidized Soybean Oil (ESO) was first subjected to an epoxide ring opening reaction, and then functionalized with propiolic acid. Castor Oil (CO) was also modified with propiolic acid.[2] It was already possible to carry out the "click" reaction which was successfully conducted allowing for the obtainment of a crosslinked structure.

EXPERIMENTAL

Synthesis of the VO amine: By a Michael addition reaction at 30 ºC for 15h, AESO was functionalized with Lysine using DMSO as a solvent. The modification with Putrescine occurred through a similar process. However, this functionalization only required 1h.[1] **Synthesis of the VO alkyne**: The synthesis of the alkyne derived from CO occurred through a esterification with propiolic acid, under reflux for 15h, using toluene as solvent.[2] The synthesis of the alkyne derived from ESO occurred through a similar process. Previously, the ESO epoxide rings were opened in a reaction with isopropanol, water and perchloric acid at a temperature of 50ºC for 2h. **Amino-yne 'click' reaction:** For this reaction, different ratios of amine:alkyne were mixed manually on a Teflon plate, at room temperature, for a few seconds until obtaining the crosslinked structure. **Formation of the films:** The processing of the obtained crosslinked structures was carried out using the press at around 170ºC and 25 bar.

RESULTS AND DISCUSSION

Both the amines and the alkynes synthesized were analyzed by Fourier Transform Infrared (FTIR) and Proton Nuclear Magnetic Resonance (1H NMR) spectroscopies. The functionalization of AESO was complete. It was also concluded that only 2 of the 3 hydroxyl groups of the Castor Oil were modified. Finally, it was observed that the replacement of the hydroxyl groups of ESO was not complete. Despite these results, it was decided to proceed with the crosslinking reaction between the amines and the synthesized alkynes. Different amine:alkyne ratios were tested and, after optimization, the films presented in Figure 1 were obtained. The films showed the ability of undergoing multiple processing cycles, suggesting that they could be able to be recycled.

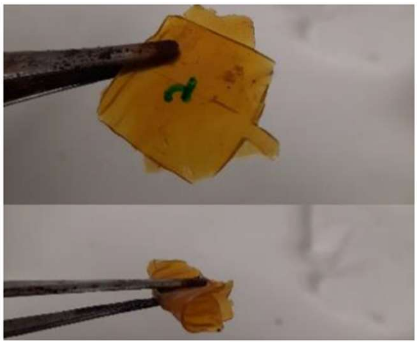

Figure 1. Materials obtained

CONCLUSIONS

Vegetable oils were modified with both amine and alkyne moieties, to allow their crosslinking using amino-yne "click" chemistry. The crosslinking reaction occurred at room temperature, without the need of solvents or catalysts, leading to the fast formation of polymeric networks with good mechanical properties. Moreover, due to the dynamic nature of the aminoacrylate bond formed, the materials also showed interesting recyclability properties. Therefore, we believe that this innovative material present relevant properties to be applied in the biomedical field.

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P8.2

Rosin-based aqueous dispersions for paper sizing

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INTRODUCTION

The natural source, low price, and abundance in nature along with its potential to chemical modification, makes rosin a valuable raw material for several applications [1,2]. Besides these advantages, the expected decrease of fossil fuel resources is directing both scientific community and industry to search for alternative renewable resources. Rosin, or colophony, is the common designation given to the non-volatile residue, mainly composed of resin acids (up to 95 wt.%), obtained after the distillation of the resin exuded by conifer trees as a slightly aromatic, semi-transparent brittle solid [1]. Chemical modification of rosin opens a wide range of possibilities for the exploitation of this raw material.

Given the intrinsic hydrophilic character of cellulose fibres, specific additives are introduced into most papers to reduce this tendency. This hydrophobization is known as paper sizing and can be achieved by bulk or surface treatment with adequate agents [3]. Alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD) dominate the actual industrial sizing, but these sizing agents have some drawbacks and are rather costly. The increasing use of water emulsion-based systems ensures a greater selection of raw materials that can be incorporated into applications, meeting economic and sustainability requirements. In this work, a rosin-based aqueous dispersion is developed as an alternative to ASA and AKD emulsions for paper sizing, by using a catastrophic phase inversion method and an anionic surfactant as interface stabilizer. The key for successfully developing these aqueous dispersions was a systematic tuning of the process parameters and conditions (controlled temperature, stirring speed, water flow rates and surfactant amount). They were characterized in terms of viscosity, pH, solid content, and particle size. The stability of the dispersions was also evaluated over time.

RESULTS AND DISCUSSION

By varying surfactant:rosin mass ratio (R), keeping constant the remaining process parameters, different particle size distributions are obtained (Figure 1). Increasing the amount of an anionic surfactant an unimodal distribution is obtained. This will affect the dispersion stability, as studied further.

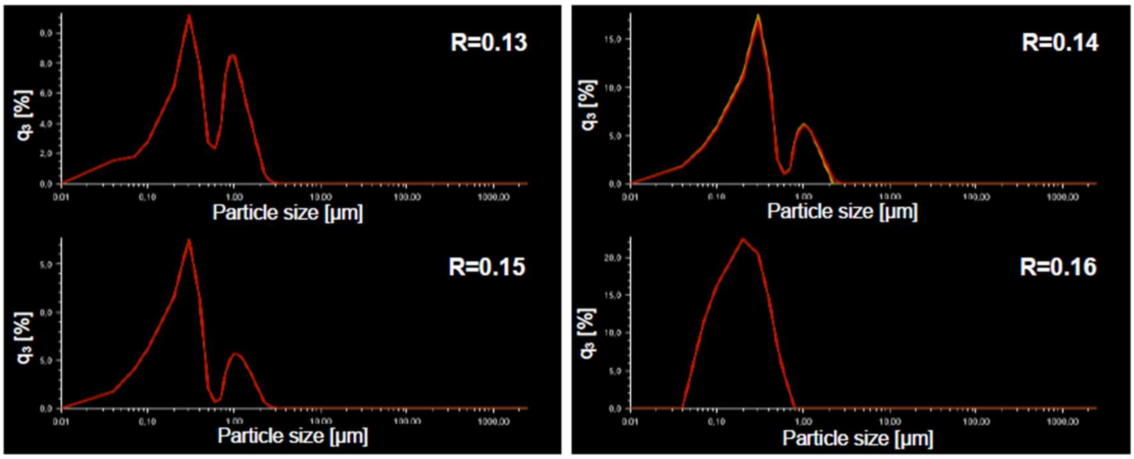

Figure 1. Influence of R on particle size distributions of rosin-based aqueous dispersions developed.

CONCLUSIONS

Rosin-based aqueous dispersions were developed to be used in paper sizing as an environmentally friendly alternative to the current ones. The minimization of the only costly component (surfactant) and the optimized process parameters allows envisaging a low-cost large-scale production.

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P9.2

Biodegradable TPS films with raw peach gum

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INTRODUCTION

Bioplastics, derived from biomass and prone to biodegradation, are particularly interesting when they come from natural sources and are biodegradable. Polysaccharides and proteins dominate this field, with polysaccharides, especially starch and cellulose, being the most significant. Thermoplastic starch (TPS) is essential in the development of biodegradable materials for food packaging and edible coatings, though it faces challenges such as low mechanical strength and susceptibility to recrystallization. Recent innovations include blending TPS with renewable polysaccharides such as agar and chitosan, improving its properties and expanding its potential applications [1, 2]. On the other hand, Peach Gum (PG) can inhibit bacterial growth and presents an antioxidant effect [3] that may be interesting for its use as an additive in thermoplastic starch formulations.

EXPERIMENTAL

TPS was developed using 65 wt% rice starch, 25 wt% glycerol, 10 wt% water and between 5-15 phr PG. Initially all compositions were mixed manually and subsequently extruded in an MC 15HT Xplore with a temperature profile of 120-125-130 ºC at 30 rpm for 3 min.

RESULTS AND DISCUSSION

It was found that TPS containing 5 phr exhibited mechanical properties similar to those of pure TPS. Increasing the amount of PG slightly reduced the mechanical properties, with the sample containing 15 phr of PG showing a decrease of about 20% in tensile strength and less than 15% in elongation at break. Nonetheless, adding 10 phr of PG was effective in slowing the retrogradation of starch, thereby delaying the stiffening of the TPS structure. Furthermore, the TPS-PG blends demonstrated enhanced solubility, with an increase of 24% observed in formulations containing 10 and 15 phr of PG compared to TPS. Additionally, PG improved the compostability of TPS, leading to quicker disintegration of the material.

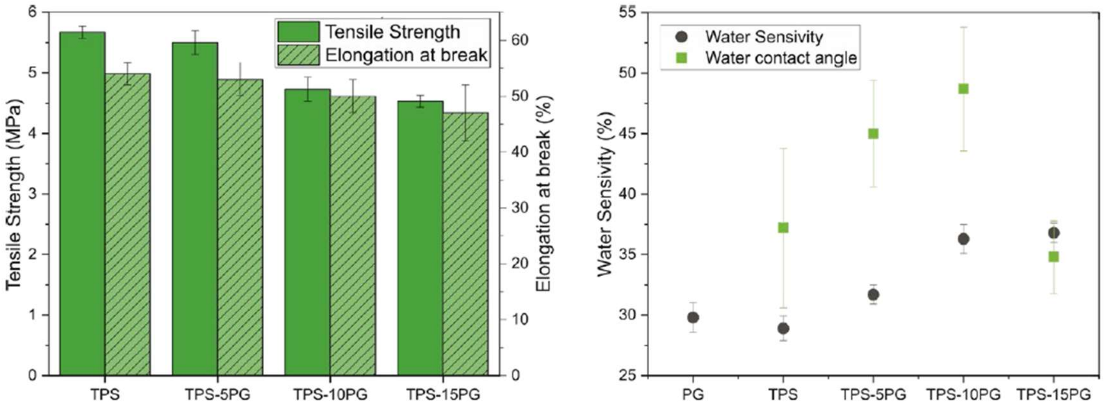

Figure 1. Example of an image inserted on the text.

CONCLUSIONS

It was found that incorporating PG at 10 phr as a sustainable additive can alter the biodegradation and water sensitivity of TPS with minimal impact its mechanical performance after processing, thereby extending its shelf life.

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P10.2

Fabrication of plasticized and unplasticized PLA-based nanofibers reinforced with ZnO NPs, and biodegradation study

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INTRODUCTION

Electrospinning is a versatile and low cost technique that permits the fabrication of polymeric fibers with diameters ranging from micro to nanometers [1]. Among various biopolymers, polylactic acid (PLA) has raised interest due to its biocompatibility and biodegradability. However, it presents poor toughness and a low degradation rate. The fabrication of nanocomposites is one of the main solutions to overcome these issues, through the addition of organic and inorganic nanoparticles (NPs). Among them, zinc oxide (ZnO) NPs are one of the most used for the development of these materials [2]. In this work, the fabrication of electrospun PLA-based fibers mats nanoreinforced with ZnO NPs at different concentrations, in particular 0.5, 1, 3, 5, 10 and 20 wt% with respect to PLA for unplasticized nanofibers and 0.5, 1, 3, 5 wt% for plasticized nanofibers is reported. The effect of the addition of both, lactic acid oligomer (OLA) as plasticizer and ZnO NPs, in the *in vitro* degradation is described as well.

RESULTS AND DISCUSSION

The addition of OLA not only changes their properties from the thermo-mechanical point of view but also in their hydrolytic degradation process, thus comparing plasticized and unplasticized electrospun mats. In both cases, the average diameter of PLA electrospun fibers is reduced by adding NPs. For the thermal behavior, in the case of PLA + ZnO NPs, the presence of NPs does not affect either the Tg or the Tm of the electrospun nanofibers mats. In the case of PLA:OLA + ZnO NPs, PLA:OLA shows a Tg of 32 °C due to the plasticizer effect of OLA. However, the presence of NPs leads to an increase of Tg from 32 °C until 40 °C, while Tm is not affected by OLA and NPs. In the formulation without OLA, all the materials show a very low degree of crystallinity (Xc), with the highest value for 3 wt% of NPs (10%). Nevertheless, in the formulation with OLA, PLA:OLA shows the highest Xc value (19%) that is reduced by the presence of NPs until 10% with 5wt% of ZnO. Electrospun nanofibers mats reinforced with ZnO NPs exhibit lower mechanical properties with respect to PLA electrospun nanofibers. Plasticized electrospun nanofibers mats show higher E and σ values with respect to electrospun nanofibers mats without OLA. However, reinforced electrospun nanofibers mats present lower values respect to PLA:OLA, except when 0.5 wt% of NPs is added. Moreover, it was observed an accelerating effect of NPs in the hydrolytic degradation of both formulations. Furthermore, the formulation with OLA showed faster degradation than unplasticized electrospun nanofibers mats.

CONCLUSIONS

With this work, it has been demonstrated that the presence of NPs affects the polymeric matrix from the morphological point of view but also in its thermo-mechanical properties, and the addition of OLA leads to a reduction in the Tg of electrospun nanofibers mats. Furthermore, plasticized electrospun nanofibers mats exhibit improved mechanical properties with respect to unplasticized ones. Additionally, the presence of ZnO accelerates the hydrolytic degradation process, which was further increased by the presence of OLA.

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P11.2

Antioxidant sodium alginate films with oil extracts from *Rugulopteryx okamurae* and polyphenols extracts from *Egeria densa*

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INTRODUCTION

Tons of plastic are launched into nature every year, increasing environmental impacts due to their long decomposition times [1]. In addition, problems associated with the spread of certain invasive seaweeds and aquatic plants have been increasing in the last decade [2]. The possibility to incorporate bioactive substances extracted from seaweeds and aquatic plants into biopolymers makes their valorization a potential strategy for food packaging applications. Antioxidant/antimicrobial properties of bioactives extracted from seaweeds and aquatic plants could beneficially affect food shelf-life and reduce food waste caused by spoilage [3]. This study aims to develop and characterize antioxidant sodium alginate films incorporated with oil extracts from brown algae *Rugulopteryx okamurae (RO)* and polyphenols extracted from aquatic plant *Egeria densa (ED)*, to evaluate their potential to extend food shelf-life.

EXPERIMENTAL

Sodium alginate films were prepared by casting. Eight formulations were tested: 20 wt% glycerol; 10 wt%, 20 wt%, 30 wt% *RO* oil; 10 wt%, 20 wt%, 30 wt%, *RO* oil + 5 wt% *ED* polyphenols extract; 20 wt% glycerol + 5 wt% *ED* polyphenols extract. The obtained films were characterized by evaluating thickness, mechanical properties, oxygen transmission rate (OTR), thermogravimetric analysis (TGA), transparency, color, and antioxidant activity (DPPH, ABTS, FRAP). Films with 20 wt% glycerol, 20 wt% *RO* oil, and 20 wt% *RO* oil + 5 wt% *ED* polyphenols extract were used in the study of shelf-life of strawberries and sardine fillets. The appearance, weight loss, color, vitamin C in strawberry and TBARS in sardine fillet was performed.

RESULTS AND DISCUSSION

The obtained sodium alginate films were flexible and homogeneous. The film blended with 20 wt% *RO* oil + 5 wt% *ED* polyphenols extract showed excellent mechanical and optical properties, oxygen transmission rate (OTR) and antioxidant activity. Their application in direct contact with strawberries and sardine fillets revealed good results after 6 days of storage to preserve the shelf life of food.

Figure 1. Developed films.

CONCLUSIONS

Sodium alginate films blended with RO oil and EG polyphenols extract were successfully developed showing great potential as active materials for food packaging. They can be considered sustainable and strong candidates to replace synthetic plastic materials for the preservation and monitoring of food freshness.

ACKNOWLEDGEMENTS

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P12.2

Grapefruit essential oil and curcumin-loaded co-axial electrospun poly (ethylene oxide) membranes. Application to smart packaging

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INTRODUCTION

The raising global interest in food safety and waste reduction has spurred the development of smart packaging solutions. Colourimetric pH sensors are valuable for real-time monitoring of food freshness and quality. The integration of electrospun membranes into food packaging materials enhances sensitivity and response to environmental changes, providing antimicrobial and antioxidant performance to extend food shelf life. Cyclodextrin (CD)-based metal-organic frameworks (MOFs) are able to effectively encapsulate and control the release of bioactive compounds through these membranes. This work focuses on developing and characterising co-axial electrospun membranes based on poly(ethylene oxide) (PEO) with grapefruit essential oil (GF-EO) and curcumin encapsulated in γ-CD-MOF.

EXPERIMENTAL

The γ-CD-MOF systems were synthesised by using microwaves technology. Curcumin, acting as a colourimetric and active sensor, was then encapsulated. Coaxial membranes were then fabricated using PEO as the polymer matrix, incorporating GF-EO at different concentrations in the bulk and the curcumin-γ-CD-MOF system on the outer layer. These electrospun membranes were characterised using FTIR, TGA, XRD, SEM, and DSC, as well as colour and pH sensing to evaluate their potential as smart food packaging materials.

RESULTS AND DISCUSSION

GF-EO and curcumin-γ-CD-MOF were successfully encapsulated within the membranes with encapsulation efficiency up to 40%. The incorporation of both additives to the coaxial electrospun membranes showed uniform morphology with controlled fiber diameter and thermal stability. These membranes also showed strong antioxidant performance, enhancing the food shelf life. Colourimetric studies suggested noticeable colour changes in response to pH variations in the packaged food.

CONCLUSIONS

Electrospun membranes based on PEO with the incorporation of GF-EO and curcumin-γ-CD-MOF showed high thermal stability, homogeneous network, noticeable colour change in contact to buffer solutions (pH 2 to 7), and high antioxidant activity. These results demonstrate the potential of this coaxial system for monitoring the shelf-life of perishable foods.

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P13.2

Effect of lignin-containing cellulose microfibrils on strength properties of packaging grade paper

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INTRODUCTION

Within the rapidly growing packaging industry, sustainability has risen to prominence, driven by increasing environmental concerns and enhanced consumer demand for eco-friendly products. In response, paper-based packaging has emerged as a promising alternative. However, its inherent lower strength properties require innovative solutions to overcome these challenges. In this regard, nanocelluloses have garnered attention, as they offer a combination of strength, versatility, and eco-friendliness, being a potential material for sustainable composite packaging solutions (Starkey et al. 2021; Jele et al. 2022).

EXPERIMENTAL

Laboratory handsheets were prepared using two types of pulp: regular unbleached eucalyptus kraft pulp and high yield kraft eucalyptus pulp. Lignin-containing microfibrillated celluloses (LMFCs), derived from these pulps, were incorporated into handsheets at different concentrations. The strength properties of these sheets were measured, and the results were compared.

RESULTS AND DISCUSSION

Tensile strength improved significantly with increasing the LMFCs concentration. This is in agreement with the literature (Aulin et al. 2010): an higher amount of LMFCs in the paper sheets increases the inter- and intra-hydrogen bonds and the relative bonded area (RBA) and thus improves the dry strength properties. The pulp with higher fine content exhibited superior strength properties attributed to the increased RBA.

CONCLUSIONS

Incorporating LMFCs in paper enhances its dry strength properties, with high yield kraft eucalyptus pulp exhibiting superior performance.

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ACKNOWLEDGEMENT

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P14.2

Development of edible films based on sheep's second cheese whey

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INTRODUCTION

When ovine whey cheeses are produced with ovine whey, a by-product is generated, which has proteins that are very useful in the elaboration of other products for the food industry. This by-product is named sheep´s second cheese whey (SCW) and one possible application for it is the manufacture of edible films. The objective of this work was to develop sheep's second cheese whey-based edible films, alone or combined with whey protein isolate (WPI) and compare their properties.

EXPERIMENTAL

SCW was ultrafiltrated/diafiltrated to increase its protein concentration. Afterwards, it was pasteurized and dried as indicated in [1]. The films were obtained with these SCW powders and/or WPIs using glycerol as plasticizer. WPI used was NatWPI90, supplied by InLeit Ingredients S.L.U. (Curtis, Spain). The composition of SCW powders and NatWPI are reported in [1].

WPI and SCW were weighed to obtain a final concentration of protein in the film solution of 8% (w/v). Then, five different films were obtained: WPI, films with whey protein isolate only; WS 2:1, films of WPI-SCW mixture in a protein proportion of 2:1; WS 1:1, films of WPI-SCW mixture in a protein proportion of 1:1; WS 1:2, films of WPI-SCW mixture in a protein proportion 1:2, SCW: films with sheep´s second cheese whey only. Water vapor permeability, thickness, dry matter content, solubility, density, color parameters and opacity, mechanical properties and antioxidant activity of the films were determined according to Cobos and Díaz [2].

RESULTS AND DISCUSSION

No remarkable effects of the substitution of WPI by SCW were found in the water vapor permeability, thickness and density of the films. However, dry matter content increases and the solubility of the films decreases with increasing concentration of SCW.

Important differences were also observed in the color and opacity and mechanical properties among the different films. The addition of SCW to the films decreased the values of L* and increased the values of a*, b* and opacity. The films with SCW only and with the highest proportion of SCW showed the lowest values of tensile and puncture strengths and elongation at break. No important differences in the antioxidant activity among films were observed.

CONCLUSIONS

The study demonstrated that SCW resulting from ovine whey cheese production, combined with WPI, may be used to prepare edible films, but they showed important differences in their properties depending on the proportion of each product.

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P15.2

Study of incorporation of different types of cellulose into a flexible polyurethane foam system

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INTRODUCTION

In recent years, concern has grown about the environmental impact of polyurethane foams, specifically in their flexible form. These foams are used in a wide range of applications ranging from furniture in sofas, chairs, in the rest sector to car seats, creating challenges due to their dependence on materials from non-renewable sources and the great generated by their wastes once their useful life ends. Currently, there is a growth in demand for more sustainable materials where research plays a crucial role in addressing part of the solution to these challenges. One promising avenue involves integrating bio-based materials, such as cellulose, into the foam matrix, which in the future will allow the adoption of green manufacturing processes to reduce the environmental footprint of flexible polyurethane foams.

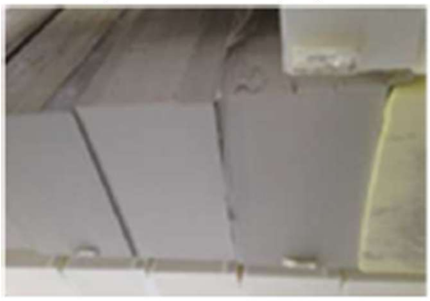

Figure 1: Flexible polyurethane foam.

EXPERIMENTAL

Four types of cellulose have been used at different concentrations: 1, 5 and 10 parts per hundred of polyol (pphp) incorporated in the formulation. The celluloses used were the following: raw cellulose Arbocel CW 630 PU Cellulose (ACW), synthetic carboxymethyl cellulose Finnfix Cellulose 10000 (FIN). microcrystalline Cellulose (CML) and thermoplastic cellulose acetate butyrate (CAB).

Cellulose and the rest of components of the formulation of flexible polyurethane foams, such as amine catalysts and blowing agents, were incorporated into the polyol component, and mechanically stirred at 2000 rpm for at least a minute and a half. Then the tin catalyst was added, and mechanical stirring was kept for about 30 more seconds. Finally, the TDI was added which is only stirred for about 7 seconds. The final mixture was poured into a container where the flexible polyurethane foam is obtained, which was subsequently analysed using infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) techniques. Mechanical properties of foamed materials such as apparent density (ISO 845), resilience (ISO 8307), remaining deformation (ISO 1856), tensile strength (ISO 1798) and compression resistance (ISO 3386) were determined. The results of this work were useful to understand the behaviour of foams obtained with cellulose.

RESULTS AND DISCUSSION

The incorporation of different celluloses at various concentrations (1, 5, and 10%) has allowed us to study their influence on the composition of the flexible polyurethane foam synthesized. The morphology of the cells has also been studied to determine if the cellulose is integrated into the structure of the cell or located outside it. Aggregates were only observed when cellulose acetate butyrate was used. Additionally, its influence on mechanical properties was studied where a behaviour similar to the reference flexible polyurethane foam was observed.

CONCLUSIONS

The main conclusion of this study on the incorporation of different types of cellulose in flexible polyurethane foams has revealed that although they do not improve the mechanical properties significantly of the foams, in most cases they do not worsen the mechanical properties, which allows obtaining a formulation with content in raw materials from renewable sources.

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P16.2

Additive Manufacturing of L-alanine Based Poly(ester amide)s for Biomedical Applications

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INTRODUCTION

Polyester materials, combining good biocompatibility, biodegradability and thermomechanical stability are extremely attractive for application in 3D printing and Tissue Engineering (TE). However, their low bioactivity, acidic degradation products and hydrophobic nature still hinder a more widespread use. α-Amino acids based poly(ester amide)s (AAA-PEAs), which combine the biocompatibility and biodegradability of polyesters with the superior mechanical properties of polyamides, have emerged as a promising alternative. The AAA-PEAs can be obtained with different structures, allowing fine-tuning of the physicochemical properties (e.g., stiffness, degradability). Cell-polymer interactions, cytocompatibility and biodegradability can be improved by the presence of α-amino acids. Despite these advantages, thermal processing of AAA-PEAs is still relatively unexplored.

In this work, novel AAA-PEAs based on L-alanine (PEA-ala), L-alanine/glycine (PEA-ala-gly(75:25)) and L-alanine/glycine/jeffamine (PEA-ala-gly-jeff (50:25:25)) are investigated as polymeric inks for extrusion-based 3D printing.

EXPERIMENTAL

The AAA-PEAs were prepared by solution polycondensation. The synthesized AAA-PEAs and PCL were then subjected to hot-pressing to obtain films. The films were characterized for their swelling capacity (SC), water contact angle (WCA) and *in vitro* degradation. The latter was conducted at 37 ºC in either PBS solution alone (hydrolytic) or in the presence of α-chymotrypsin (enzymatic). Hardness was also determined through nanoindentation tests. LIVE/DEADTM staining was used to study the *in vitro* cytotoxicity of the films seeded with human bone marrow derived mesenchymal stem cells (hBM-MSCs) over a period of 7 days. Finally, AAA-PEAs and PCL were processed into 3D scaffolds using an extrusion-based 3D printer (3D Discovery, regenHU) and their morphology assessed with scanning electron microscopy (SEM) and micro-computed tomography (μCT). Mechanical compression tests were performed on the different kinds of 3D printed scaffolds using block-shaped specimens (length—l0 of 4.0 mm, width—w0 of 4.0 mm, height—h0 of 4.0 mm). The specimens were immersed in physiological solution at 37 °C and tested at a rate of 1 mm/min up to a strain of 50%, using an INSTRON 5566 testing machine.

RESULTS AND DISCUSSION

The molecular weight of the synthesised AAA-PEAs ranged from 60kDa to 70kDa, with Đ≈1.50. The *T*g of the AAA-PEAs films was approx.15oC except for those with jeff (*T*g= -14 oC). WCA and SC values revealed a more hydrophilic nature of the AAA-PEAs films compared to PCL films, being those from PEA-ala-gly-jeff the most hydrophilic (WCA = 35.8º and SC=15%). The addition of jeff also led to an increase in mass loss of the AAA-PEAs films from 2% to almost 6%, over 4 weeks in PBS. This value increased to

15-17% in enzymatic degradation tests. All PEAs displayed lower hardness values compared to PCL. LIVE-DEADTM tests showed that hBM-MSCs remain viable over 7 days suggesting the absence of any significant cytotoxic effect induced by the films. SEM micrographs and µCT results revealed the production of 3D scaffolds with well-defined internal/external geometries and precise dimensions, confirming the good processability of AAA-PEAs.

CONCLUSIONS

Newly synthesized AAA-PEA show great potential as polymer inks for 3D printing of scaffolds in TE. This is confirmed by their easy processability and tailorable mechanical, thermal and biological properties compared to commonly used PCL.

P17.2

Chitosan-based mixed-matrix scaffolds for tissue engineering

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INTRODUCTION

The use of scaffolds, three-dimensional porous, biodegradable and biocompatible structures, that can be produced from natural polymers, synthetics, ceramics and metals is crucial in the tissue engineering field. Chitosan is a polysaccharide of natural origin, found in the exoskeleton of marine arthropods and in the cell wall of fungi, with enormous popularity in the production of three-dimensional materials for Tissue Engineering, in particular bone repair. This polymer has several advantages in the production of these structures in bone regeneration and repair: biodegradability, biocompatibility, non-toxicity and antimicrobial properties. This study aimed to prepare porous scaffolds, for bone repair of degenerative diseases in the spine with better performance and less secondary effects, based on chitosan and another biopolymer (sodium alginate) with the incorporation of calcium phosphates (hydroxyapatite and β-tricalcium phosphate), for tissue engineering application.

RESULTS AND DISCUSSION

The obtained scaffolds where prepared as briefly shown in Fig. 1, which were then object of a detailed characterization, namely with regard to their porosity through the ethanol method, degradation, positron annihilation spectroscopy (PAS), mechanical properties, scanning electronic microscope (SEM), thermal stability through thermogravimetric analysis (TGA), chemical composition through X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The results obtained showed that the different scaffolds presented pores able to support osteoid matrix growth. The crosslinking of scaffolds was also evaluated and resulted in pores with smaller dimensions and higher regularity in the chitosan-sodium alginate polymer without calcium phosphate scaffold. It was also possible to observe the effect of inorganics on mixed-matrix scaffolds, both morphologically and chemically. These scaffolds showed promising results in terms of mechanical and chemical properties, along with promising porosity for tissue regeneration applications.

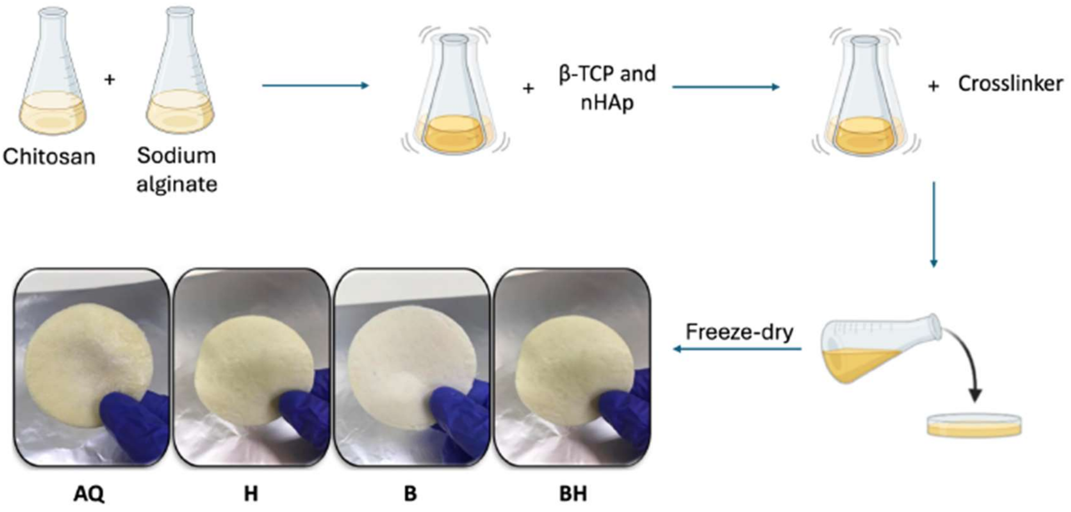

Figure 1. Schematic representation of the chitosan-based mixed-matrix scaffold preparation.

CONCLUSIONS

In general, all prepared membranes/scaffolds showed good potential for tissue regeneration applications in future studies.

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P18.2

Properties of composites of PLA and lignocellulosic fractions of *Posidonia oceanica*, as affected by cellulose purification degree

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INTRODUCTION

Numerous studies have focused on the extraction and application of natural fibres from plant materials to obtain polymer composites useful in developing materials with more sustainable characteristics due to their low cost, biodegradability and eco-friendliness [1]. *Posidonia oceanica* (PO) is an abundant aquatic plant in the Mediterranean Sea that produces a great accumulation of leaves on the coast, which are dumped in landfill sites when cleaning up beaches. This waste is a rich source of cellulose that can be used in the composite formulation. Nevertheless, cellulose purification represents a challenge because of the high amount of chemicals involved in the process. The aim of this study was to analyse the influence of the PO cellulose purification degree on the properties of biodegradable composite films based on PLA, in order to obtain low-cost food packaging materials. In this sense, a greener method to purify cellulose, based on subcritical water extraction (SWE), and subsequent bleaching treatments with hydrogen peroxide or sodium chloride, was applied.

EXPERIMENTAL

Composite films were prepared by melt blending and compression molding, using PLA and 5 % of powdered PO lignocellulosic residues (LR) with different purification degree of cellulose: PO powder, LR obtained after SWE at 150 oC (sample150) and 170 oC (sample 170), and the corresponding bleached samples with 4 % (samples 150 4% and 170 4%) or 8 % (samples 150 8% and 170 8%) of H2O2 at pH 12, and sodium chlorite (samples 150 oC and 170 oC). The obtained films were characterised as to their optical, barrier, tensile, and thermal properties.

RESULTS AND DISCUSSION

The whiteness index (WI) of the fibres markedly affected the internal transmittance and colour coordinates of composites, the higher the WI, the greater the film transparency and lightness and the lower the colour saturation. Every LR provoked a reduction of oxygen permeability in PLA films, the sample 170 being the least permeable. In contrast, all composites were more permeable to water vapour. The reinforcing effect (reflected in the increase of stiffness and decrease of stretchability) only occurred to a different extent for bleached LR, the main occurring for LR bleached with H2O2 at 8%. LR provoked a small decrease in glass transition and degradation temperature of PLA, with little difference between samples.

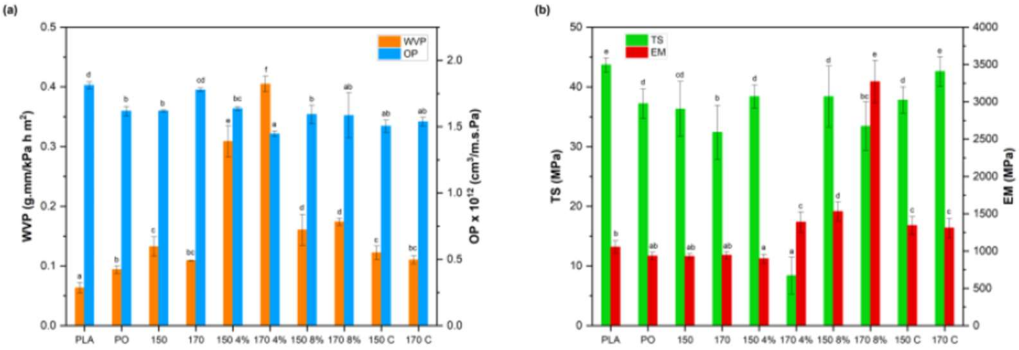

Figure 1. Effect of the different LR on the PLA properties: a) water vapour (WVP) and oxygen (OP) permeability, b) elastic modulus (EM) and tensile strength at break (TS).

CONCLUSIONS

The purification degree of PO cellulose affected the properties of PLA composite films, mainly optical properties and reinforcing effect. Nevertheless, modulated properties can be obtained for different applications, using PO waste submitted to different purification steps.

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P19.2

Polysaccharide Coatings for Enhanced Barrier Properties in Eucalyptus-Based Paper Packaging Materials

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INTRODUCTION

Enhanced paper-based packaging materials are currently at the forefront of promising substitutes for plastic-based packaging. However, their limited barrier properties hinder their widespread adoption in the industry [1]. Amidst current efforts to overcome these challenges, coating solutions comprising naturally occurring polymers, such as polysaccharides, have shown great potential in several studies [2].

This work explores the barrier-enhancing capacity, against water and oils/greases, of three polysaccharides (A, B, C) applied individually at different concentrations on Eucalyptus-based paper, in both single and double layers.

EXPERIMENTAL

Two aqueous solutions with varying concentrations were prepared for each selected compound. Subsequently, one and two layers of the solutions were individually applied on the paper substrate using a bar coating lab device. The final materials were then characterized by Cobb and Cobb-Unger tests, water contact angle measurement, Kit tests, and scanning electron microscopy.

RESULTS AND DISCUSSION

The application of the different biopolymers demonstrated a notable enhancement in barrier properties against oils and greases, as assessed through Cobb-Unger and Kit Tests.

The surface retention properties improved by 16 - 41% and 25 - 58% for single and double-layer prototypes, respectively, as determined by Kit Tests. In the Cobb-Unger tests, reductions of 70 - 90% and 80 - 90% were observed in oils and greases absorption for single and double-layer prototypes, respectively.

On the other hand, as expected the barrier against water did not perform as desired, due to the hygroscopic nature of the selected biopolymers.

CONCLUSIONS

The results underscore the potential of the selected compounds to establish an effective barrier, particularly against greases and oils, confirmed by a significant reduction of Cobb-Unger and Kit Test values. More research is needed to improve the barrier against water absorption.

ACKNOWLEDGEMENT

This work was carried out in the framework of the project agenda "From Fossil to Forest - FF2F", funded by the PRR - Recovery and Resilience Program, of the Portuguese Republic, and by the Next Generation European funds (Call N.º 02/C05-i01/2022, Component 5 – Capitalization and Business Innovation - Mobilizing Agendas for Business Innovation). Authors would like also to thank the CERES - Chemical Engineering and Renewable Resources for Sustainability Research Center, funded by Fundação para a Ciência e a Tecnologia (FCT), through the base (DOI: 10.54499/UIDB/00102/2020) and programmatic (DOI: 10.54499/UIDP/00102/2020) budgets.

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P20.2

Bioactive bacterial nanocellulose films loaded with *Paulownia elongata x fortunei* wood extract for food packaging applications

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INTRODUCTION

The growth of greenhouse gas emissions, global warming and the depletion of fossil resources has led to strategies to exploit natural renewable resources, such as the fast-growing tree *Paulownia elongata x fortunei*, towards a biobased economy [1,2]. This species has high biomass production and low growing necessities, and its hydrothermal extract was studied due to its high content in phenolics and oligosaccharides which may be potentially used as additives in functional films for food packaging [3].

EXPERIMENTAL

Hydrothermal extract of Paulownia wood (PW) (203 °C non-isothermal regime), with high content of xylooligosaccharides and phenolics [3], was characterized and tested for antibacterial activity against *S. aureus* and *E. coli*. The extract was incorporated into bacterial nanocellulose (BNC) films (produced by *Gluconacetobacter sacchari* in static growth for 15 days at 30 °C) at concentrations of 0-52.5 mg/mL/cm2, adding glycerol as plasticizer (25-30% w/w). The films were structurally (ATR-FTIR), morphologically (SEM), and thermally (TGA-DTG) characterized, and color parameters, antioxidant capacity, UV-vis spectra, tensile mechanical properties, and antibacterial activity were measured.

RESULTS AND DISCUSSION

Hydrothermal extract of PW comprised a high content in xylooligosaccharides and phenolics (45.3 and 6.3 g/100 g extract, respectively), with >87% DPPH inhibition at concentration ≥4.2 mg/mL, and inhibitory effect on bacterial growth at concentrations ≥26.25 mg/mL. When incorporated into BNC films, they exhibited high UV barrier properties (transmittance <0.5% at 200-400 nm) and DPPH inhibitions (≥84%). Additionally, films presented improved tensile properties (higher elongation to break and lower tensile strength and Young's modulus), thermogravimetric properties and antibacterial capacity (inhibitory effect on bacterial growth after 48 h) when compared to the unloaded BNC films.

CONCLUSIONS

Paulownia wood extract showed considerable antioxidant and antibacterial properties, that were explored to produce bioactive BNC films for application in active food packaging.

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P21.2

Encapsulation of lemongrass essential oil as an antimicrobial agent for food packaging applications

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INTRODUCTION

Essential oils (EOs) are complex mixtures of compounds, which are obtained from plants by extraction. These natural extracts are recognised by their health benefits, including wound healing, food preservation and disease prevention. However, their intrinsic hydrophobic nature poses a challenge in their potential uses since they tend to evaporate rapidly after extraction due to their high volatility and they are easily degraded under strict environmental conditions (1). Encapsulation of EOs has become an exciting area of research and development in the food sector, by offering several advantages, including protecting EOs from light, oxygen, and temperature changes, while improving stability and extending their shelf life. It also allows the precise control of the release of the active ingredients and the ability to mask the natural taste and odour of the EO (2). This study aims to explore the encapsulation of lemongrass EO using the spray drying technique, with optimization of the main processing parameters, such as concentration and type of host polymer.

EXPERIMENTAL

The encapsulated materials were produced by spray drying using four different polymers: maltodextrin (MD), α-, β-, and γ-cyclodextrin (α-, β-, and γ- CDx), at five different ratios of host polymer and EO (1:1, 2:1, 3:1, 4:1, and 5:1 *w/w* respectively). The encapsulation yield, efficiency, and loading capacity of the encapsulates were evaluated. Additionally, thermal, FTIR and SEM analyses, controlled release and antifungal and antioxidant activity tests were also conducted.

RESULTS AND DISCUSSION

Results showed that the encapsulation yield and efficiency were higher than 60% and 70%, respectively, for the combination with the four different host polymers (at 2:1, 3:1, 4:1 and 5:1 *w/w* ratios). The loading capacity of the encapsulates with α-CDx ranged from 20 to 31%, while from 42 to 60% with β- and γ-CDx, and from 38 to 60% with maltodextrin. The controlled release was found to be more stable over time in all materials encapsulated with γ-CDx at all concentrations, β-CDx:EO (2:1 *w/w*), and MD:EO (2:1, 3:1, and 4:1 *w/w*). Furthermore, the antioxidant activity was higher in the γ-CDx encapsulate (3:1 *w/w*), followed by β-CDx:EO (4:1 and 5:1 *w/w*) and MD:EO (2:1 *w/w*). Some samples showed antifungal activity after 12 days, and the best results were observed with the γ-CDx encapsulate (3:1 *w/w*) tested by the agar diffusion method at 1%, 3% and 5% *w/w* concentrations.

CONCLUSIONS

Twenty different encapsulates were efficiently synthesized. They showed good encapsulation yield and efficiency, as well as high loading capacity. Results for antioxidant and antifungal activities, as well as the controlled release, showed the potential of the γ-CDx:EO 3:1 *w/w* in food packaging materials. These results suggest that encapsulation with adequate host polymers could be used as a protective procedure for volatile EOs in active packaging systems.

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P22.2

Antimicrobial electrospun wound dressings based on poly(ester amide)s

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INTRODUCTION

Non-healing wounds (e.g. diabetic ulcers) are characterized by a delayed and incomplete healing process and are usually infected. The treatment of this type of wounds is associated with high costs for the healthcare system. In the search for new approaches to the treatment of these wounds, the use of bioactive dressings has been identified, which, in addition to the physical protection provided by traditional dressings, are also designed to have an antimicrobial effect. In this work, a new generation of wound dressings (WD) with antibacterial activity was prepared. For this purpose, cationic α-aminoacid based poly(ester amide)s (PEAs), whose structure was designed to resemble those of antimicrobial peptides, were synthesized and subjected to electrospinning, for the obtainment of the WD.

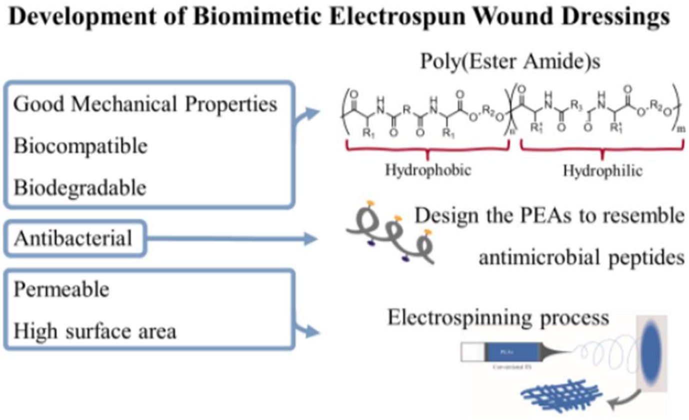

Figure 1 - Target characteristics for WD and how to achieve it.

EXPERIMENTAL

The PEAs were synthesized from the reaction of bis-α-(L-amino acid)-α, ω-alkylene diesters based on hydrophobic and cationic α-amino acids with an activated diester of sebacoyl chloride. The obtained PEAs were dissolved in a DMSO/CHCl3 solution with a concentration of 10% (m/v) and then, subjected to electrospinning, using the following parameters: distance tip-collector of 20cm, flux of 2mL/h, voltage of 21kV, humidity of 30%. The obtained electrospun mats were analyzed in terms of their chemical structure by proton nuclear magnetic resonance (1H NMR) spectroscopy. The thermal properties were evaluated by differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The morphology and the mechanical properties of the mats were evaluated by scanning electron microscopy (SEM) and by tensile tests, respectively. Water contact angle measurements were carried out to evaluate the hydrophilicity of the mats' surface. *In vitro* cytotoxicity tests were carried out using NIH3T3 fibroblast cells and the antimicrobial activity of the mats was tested against *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC2592.

RESULTS AND DISCUSSION

The mats obtained are free of residual solvents, as seen from the 1H NMR and TGA analysis. The mats have an amorphous nature, with a glass transition temperature of 40ºC, as determined by DSC. The SEM analysis showed that the mats are composed by well-defined and homogenous fibers. Contact angle and tensile tests results showed that the mats obtained have properties suitable for the application (WCA=120º; E=1,5 MPa). Moreover, the mats showed to have no cytotoxicity towards fibroblasts, whereas presenting high efficacy in killing bacteria from the *E. coli* and *S. aureus* strains.

CONCLUSIONS

PEAs with hydrophobic and cationic α-amino acids on their structure were successfully synthesized and were able to be electrospun. The obtained membranes showed individualized fibers, free of defects.

Also, the membranes presented good mechanical properties, did not show cytotoxicity towards fibroblasts and presented high efficacy against Gram-negative and Gram-positive bacteria.

P23.2

Aerogels of green rice straw cellulose. Effect of starch and crosslinker incorporation

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INTRODUCTION

Rice straw (RS) is one of the most produced agro-industrial residues worldwide, which is usually burned after the rice harvest, therefore contributing to environmental pollution. Due to its lignocellulosic-rich composition, typically 37 % cellulose, 20 % hemicellulose, and 21 % lignin, RS has a high potential for its valorisation in different industrial applications, including pharmaceuticals, animal fodder, fuels, reinforcing agents, or cellulose aerogels (CAs). CAs are ultralight, highly porous, non-toxic, biodegradable, low-cost materials that have been successfully used in different fields. Likewise, different polymers, such as starch, and cross-linking agents, such as polyamideamine-epichlorohydrin (PAE) resin, can be added to the cellulose dispersion to improve the functional properties of CAs. Recently, a sustainable and green extraction method, applying subcritical water extraction (SWE) and bleaching with hydrogen peroxide, has been used to isolate cellulose fibres (CFs) from RS [1]. In this study, CA were obtained from this "green cellulose" and characterized, by analysing the cross-linking effect of starch and PAE on the aerogel properties.

EXPERIMENTAL

CFs were obtained by applying SWE at 180 °C and bleaching with hydrogen peroxide [1]. Aerogels were prepared by frezze-drying of sonicated dispersion containing CFs at 0.5 % (sample C) or CF-potato starch blends, using 2:1 (sample S1-C) and 4:1 (sample S2-C) ratios, containing (P in sample code) or not PAE, at 8% with respect to the total solids. For comparison purposes, net starch aerogels (samples S1 and S2) using the same starch concentration in the aqueous phase were also obtained. The different aerogels were characterised as to their macro and microstructure, density, porosity, FTIR spectra, thermal stability, mechanical strength, and water (WAC) and oil (OAC) absorption capacity.

RESULTS AND DISCUSSION

The incorporation of starch into the cellulose dispersion gave rise to more cohesive aerogels, especially at the highest starch ratio (S2-C), with a porous network structure characterised by lamellae-like films surrounding the CFs. The mechanical resistance of CA increased with the starch ratio but with slightly reduced porosity, WAC, and OAC (Figure 1). The presence of PAE promoted the strength of the three-dimensional structure of the cellulose fibrils, enhancing mechanical resistance and OAC. Nevertheless, it was not so effective at a mechanical level in the aerogels containing starch, which were less thermally stable, and had lower WAC.

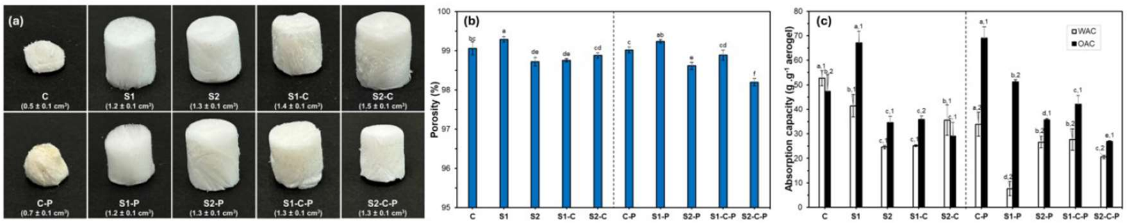

Figure 1. Visual appearance and volumes (cm3) (a), porosity (b), and water (WAC) and oil (OAC) absorption capacities (c) of the different aerogels with and without PAE (P).

CONCLUSIONS

The incorporation of starch, especially the higher starch:cellulose ratio (4:1), and PAE crosslinker is considered an interesting alternative for producing and modulating the properties of green cellulose aerogels from RS.

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P24.2

Intelligent packaging films based on betalains from beetroot wastes and starch/polyvinyl alcohol

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INTRODUCTION

Beetroot (Beta vulgaris) agro-wastes accumulation represent environmental and economic problems. However, peels and stems have a wide variety of active compounds in considerable quantities, especially polyphenols and betalains. These compounds are widely used as dyes in the food industry and they can be further subdivided into red/violet betacyanins and yellow/orange betaxanthins [1]. In recent years, these pigments have been applied to films of different polymers to improve their antioxidant and antimicrobial properties, while making them pH-sensitive and usable as smart packaging systems to control food freshness [2]. On this basis, eco-friendly, antioxidant and pH-sensitive films based on starch/polyvinyl alcohol (PVA) and loaded with extracts rich in betalains from beetroot peel (BPE) and stem (BSE) were prepared in order to evaluate their use as smart packaging.

EXPERIMENTAL

Microwave-assisted extraction (MAE) was performed to obtain active compounds from BPE and BSE. Response surface methodology (RSM) was used to maximize the total content of betalains and antioxidant capacity. The stability of the obtained extracts at different pH (2-12) and temperature (30-60 °C) values was also evaluated. Starch/PVA films containing 20 wt% of BPE and DPE were processed by casting. Subsequently, the developed films were characterized by thermogravimetric analysis (TGA), sensitivity to volatile NH3, colour and thickness. Moreover, the functional properties of films to monitor the freshness of shrimps were evaluated in terms of thiobarbituric acid reactive substances (TBARs), weight loss, pH and colour for two days at room temperature.

RESULTS AND DISCUSSION

The optimal MAE conditions predicted by a Box-Behnken design (BBD) provided a total content of betalains of 1385 ± 110 and 471 ± 14 mgBetalains 100 gdm^{-1} and DPPH values of 98 ± 2 and 40 ± 3 mgTrolox gdm^{-1} for BPE and BSE, respectively. The sensitivity of the obtained extracts to pH and temperature changes in the studied range was demonstrated, as well as to volatile NH3 2.5 M for 1 hour. Finally, the shrimp freshness study revealed significant color changes in films within two days at room temperature, as a consequence of the formation of volatile nitrogenous compounds during the decomposition process of these crustaceans.

CONCLUSIONS

Starch/PVA films loaded with betalain-rich extracts from beetroot waste have shown their potential to be used for intelligent packaging, showing significant color changes under alkaline conditions, while increasing also the added value of these natural residues within a circular economy approach.

Acknowledgements.
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P25.2

Synthesis and characterization of a fluorescent derivative of PMVEMA with pyrene

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INTRODUCTION

Poly(methyl vinyl ether-alt-maleic anhydride) (PMVEMA) is a versatile polymer known for its properties such as biodegradability and biocompatibility, making it suitable for biomedical applications. Furthermore, its use as a base polymer for the synthesis of nanofibers via electrospinning has already been described [1]. Its derivatization with fluorescent moieties, such as pyrenes, opens new fields of application [2]. In this work, a derivative of the PMVEMA polymer with pyrene (PMVEMA-Pyr) was synthesized.

EXPERIMENTAL

Pyrene 1-pyrenemethylamine was incorporated into the PMVEMA backbone via post-polymerization modification reaction through nucleophilic attack. The molar ratio of PMVEMA to pyrene in the reaction was 2:1. The chemical structure, thermal property, and photophysical performance were analyzed.

RESULTS AND DISCUSSION

The results of the chemical structure characterization by NMR and FTIR show signals corresponding to both starting materials, suggesting a successful post-polymerization. Additionally, the main absorption peaks of PMVEMA-Pyr at 267, 278, 330 y 346 nm correspond to the characteristic absorption bands of pyrene, confirming its presence (Figure 1A). Regarding the emission spectrum, two main peaks at 377 and 398 nm as monomer and a broad band around 480 nm are observed, consistent with low aggregation (Figure 1B). The thermogravimetric analysis shows main decomposition occurring above 400 ºC.

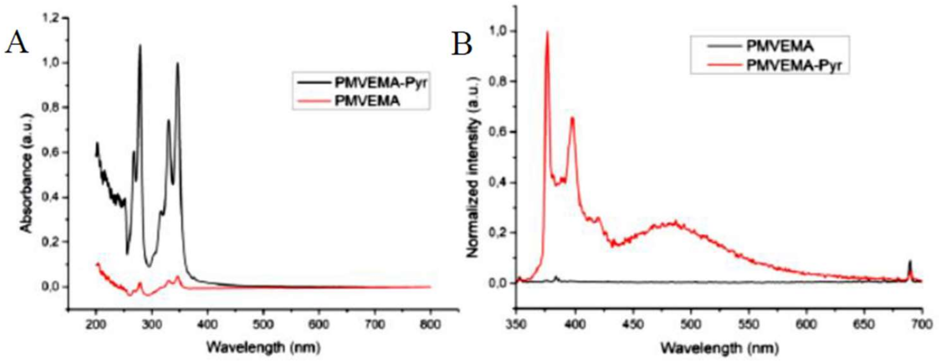

Figure 1. A. UV-vis absorption spectrum. B. Fluorescence emission spectrum of the PMVEMA-Pyr compound.

CONCLUSIONS

The results of the study demonstrate the successful synthesis of PMVEMA-Pyr. Future studies will involve biological investigations.

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P26.2

Smart biofilms based on blood orange peel: A new approach to valorize agricultural waste and improve food safety

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INTRODUCTION

The citrus industry currently produces a considerable amount of waste that generates a great environmental impact [1-2]. This waste can be used as raw material for the development of biomaterials based on pectins with the addition of bioactive compounds, such as anthocyanins that are sensitive to pH changes, resulting in a biofilm with potential to be used as smart packaging material. The main objective of this work is the formulation of a biomaterial for active and smart packaging to control food deterioration, based on pectins and anthocyanins extracted from blood orange residues by using sustainable extraction methodologies.

EXPERIMENTAL

A cascade microwave-assisted extraction (MAE) methodology was developed to obtain anthocyanins and pectins, using the blood orange peel as raw material. Biofilms were prepared by the casting method, using pectin and sodium alginate as polymer matrix and anthocyanins as active compounds. Moisture content, solubility, thickness, water vapor permeability, and FTIR, XRD, SEM, TGA and DSC tests were performed to get the full characterization of the obtained biofilms and to evaluate their potential to be used as a colorimetric indicator in food packaging systems.

RESULTS AND DISCUSSION

The pectin/alginate biofilms, with anthocyanins as bioactive compounds, have shown homogeneous structure and light colour, with no apparent cracks in their smooth surface. These alginate-pectin mixtures showed stability and their potential as smart biofilms was evaluated by monitoring their change in colour at different pH values. In addition, they showed good tolerance to water, making these biofilms resistant to high-moisture food.

CONCLUSIONS

The feasibility of alginate-pectin smart biofilms, with anthocyanins as active compounds, to allow controlling pH changes in food packaging systems was demonstrated. This will permit the valorization of blood orange residues by creating a smart packaging material. The cascade process based on MAE, proposed to extract compounds such as pectin and anthocyanins, has proved to enhance their valorization possibilities, while contributing to the circular economy approach.

ACKNOWLEDGEMENTS

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P27.2

Use of hydrothermal treatment for sequential extraction of high-value compounds from avocado peel residue and their use as active biomaterials

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INTRODUCTION

The peel and seed of the avocado fruit constitute more than 15% of the fruit weight, which leads to the generation of large amounts of waste by guacamole or avocado oil processing industries. Avocado residues contains a considerable amount of polyphenols [1], as well as, high amounts of polysaccharides [2] which can be extracted and used in the design of active packages and coatings for food preservation. Among different extraction methods, hydrothermal treatment is a technique increasingly used for the extraction of high value-added compounds and for the implementation of biorefineries to extract polyphenols, sugars and complex carbohydrates, as well as biofuels, oils, etc. This type of treatment, also referred to as autohydrolysis, is a treatment that employs high temperature and pressure, being an efficient alternative to the use of chemical treatments, using only water as the extraction solvent. The temperatures used in the hydrothermal treatment usually range from 140-200°C and can be used to produce oligomers of hemicellulose and pectins which are solubilised in the aqueous fraction.

The main objective of this work is to valorise avocado peel residue employing a mild hydrothermal treatment to obtain a polyphenol-rich extract with filmogenic capacity.

EXPERIMENTAL

Avocado peel residue was dried and milled to obtain a powder. The vegetal material was immersed in water and subjected at thermal treatment of 121 °C and 1.6 bar during 15 min. The mixture was filtered to obtain a liquor of extraction (HT7). The spend solid was immersed further in water with 2% (*w*/v) of NaOH and the same thermal treatment was carried out. After that, the mixture was filtered to obtain the liquor from this second extraction (HT13). The main extraction components (hemicelluloses, lignin and polyphenols) of the different extractions were quantified. In addition, films of HT7 and HT13 were performed and characterized, assessing their optical and thermal properties.

RESULTS AND DISCUSSION

The composition of the liquor from the first step (HT7) was rich in hemicelluloses, consisting mainly on xylan, arabinan, glucose and galacturonic acid. The second extraction step with 2% NaOH (HT13) gave rise to black liquor rich in lignin. Gel Permeation Chromatography (GPC) of alcohol insoluble solids (hemicelulloses-pectins) showed a molecular weight range from 1.3 to 20.8 KDa, exhibiting a great film-forming capacity. Moreover, both liquors presented a great antioxidant capacity due to the presence of polyphenols and lignin, respectively. Hemicelluloses extracted where converted into films, whereas lignin liquor from the second extraction was used to improve the functional properties of the films, providing them with antioxidant, UV-barrier, and antimicrobial properties.

CONCLUSIONS

Two extraction fractions with different chemical composition were obtained from avocado peel employing water and using a mild hydrothermal treatment. The fractions were valorized obtaining functional films that can be used as active coatings to preserve foods.

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P28.2

Synthesis and characterization of amine-rich cyclodextrin-based nanosponges for the removal of synthetic dyes

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INTRODUCTION

The discharge of contaminated effluents into natural watercourses represents one of the foremost environmental concerns of recent decades. Synthetic dyes, known for their recalcitrant and toxic properties, are one of the primary constituents of these effluents. Phenol Red (PhR) and Remazol Gold Yellow (AOR) are dyes extensively used as pH indicators and for the dyeing of textile fibers, respectively [1,2]. Currently, cyclodextrins (non-toxic, biodegradable oligosaccharides with amphiphilic properties) and nanosponges (crosslinked materials with high surface area and mesoporous structure) have been used as promising adsorbent materials for environmental remediation, mainly due to their capacity to form inclusion complexes [3]. In this work, amine-rich cyclodextrin-based nanosponges were synthesized, characterized, and applied for the removal of PhR and AOR from aqueous solutions.

EXPERIMENTAL

The amine-rich cyclodextrin-based nanosponges were obtained through a 4-step synthetic route (Figure 1), which includes 1) iodination, 2) amination with ethylenediamine, 3) crosslinking with terephthalaldehyde, and 4) reduction with sodium borohydride.

RESULTS AND DISCUSSION

The NMR analysis allowed to conclude about the success of the first two steps: for the iodination, the disappearance of the -OH protons at the C6 position suggested the complete substitution, while the presence of the NH2 and CH2 protons of ethylenediamine confirmed the occurrence of the amination step. Iodination and amination were also confirmed by FTIR, due to the presence of the C–I stretching and N–H stretching/bending bands, respectively. FTIR analysis also confirmed the crosslinking, by the presence of the C=N stretching bands, and the reduction, by the disappearance of the above-mentioned band. Adsorption studies, including solid-liquid ratio and pH effect, isotherms, and kinetics, demonstrated the excellent efficiency of the synthesized nanosponges for the removal of both dyes, with efficiencies up to 99%. Furthermore, thermogravimetric analysis revealed a decrease in the degradation temperature of the polymers after contaminant adsorption, possibly due to the decrease in the degree of compaction when dyes enter the nanosponge matrix.

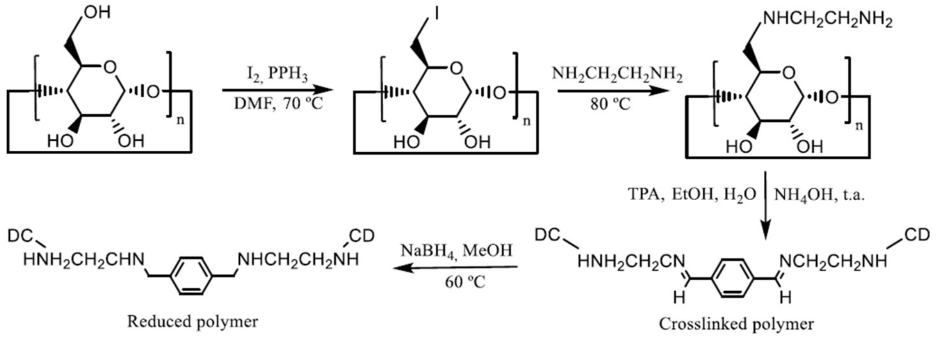

Figure 1. Synthetic route for preparation of amine-rich cyclodextrin-based nanosponges.

CONCLUSIONS

The results showed the successfulness of the synthesis of the amine-rich cyclodextrin-based nanosponges and their high potential for the remediation of dye-contaminated water effluents.

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P29.2

Extrusion blown films of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blends for flexible packaging

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INTRODUCTION

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biodegradable polymer with significant potential for use in food packaging. However, these polymers face certain challenges, including a narrow processing window, low thermal stability, high crystallinity, and brittleness. This brittleness arises from the glass transition temperature (*Tg*) being close to room temperature (0 - 5 °C), secondary crystallization of the amorphous phase at room temperature, and the presence of inter-spherulitic cracks. To overcome these obstacles, we developed blends consisting of 70 wt% PHBV and 30 wt% poly(butylene-co-succinate-co-adipate) (PBSA).

EXPERIMENTAL

For compatibilisation of PHBV and PBSA, organic peroxides such as dicumyl peroxide and 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane, were utilized as reactive compatibilizers to enhance the interfacial adhesion between the polymers. Additionally, acetyl tributyl citrate (ATBC) was employed as a plasticizer to improve processability and ductility. The scale up of the film blowing process was done with a single screw extrusion equipped with a 25 mm diameter screw having a length to diameter ratio of 20 L/D (SCAMEX Rheoscam, France) and a helicoidal blown film die of 50 mm in diameter with a gap of 0.8 mm.

RESULTS AND DISCUSSION

The film blowing of the formulation was successful. The inclusion of organic peroxides resulted in the formation of long-branched structures, as confirmed by the van-Gurp-Palmen plot. The melt flow index decreased from 30 to 9.8 g/10 min without ATBC and 15.5 g/10 min with ATBC. Successful production of blown PHBV/PBSA films was achieved on a pilot scale (bubble height 180 cm). These films exhibited heat-sealing capability and increased impact strength (7.7 kJ/m2). Moreover, the films maintained a maximum elongation at break of 4 % during a 3-month storage experiment with frozen food. Food safety was assessed through overall migration experiments, and the non-plasticized films received approval.

Figure 1. Hot sealed film of PHBV/PBSA/ATBC10/0.2Lp filled with 625 g of parfried frozen French fries

CONCLUSIONS

In conclusion, the compatibilized PHBV/PBSA blends demonstrate great potential as materials for manufacturing film-blown flexible packaging.

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P30.2

α-Amino Acid-based Poly(ester amide)s In Situ Forming Implant System for Drug Delivery Systems

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INTRODUCTION

In 2021, the industry trend for long-acting injectable drug delivery systems showed a shift towards technologies that enable easier development, manufacturing, and application, accounting for around 70 % of products in clinical development. *In situ* forming implants (ISFI) consist of low-viscosity polymer solutions containing the drug(s) of interest dispersed or dissolved, that solidify into a gel or solid depot after administration. Depot formation can occur by abrupt changes in polymer solubility, upon injection, due to solvent exchange. This type of ISFIs is commonly known as *in situ* phase separation systems. [1] Commercially available ISFI systems, such as Eligard® or Perseris® for cancer and schizophrenia treatment, respectively, use poly(lactic-*co*-glycolic acid) (PLGA) as the depot matrix. However, PLGA and other polyesters generate an acidic environment upon degradation under physiological conditions, leading to the acidification of surgical sites and causes inflammation. [2] α-Amino acid-based poly(ester amide)s (AAA-PEAs) are a promising alternative for the development of drug delivery systems. The careful choice of the monomers used in the synthesis of AAA-PEAs allows for the tune of their physico-chemical properties. Also, both acidic and basic by-products are released during the degradation of AAA-PEAs, which avoids an exacerbate inflammatory response. [3] For this reason, ISFI systems prepared by solvent exchange with AAA-PEAs have been envisioned as an attractive alternative for the preparation of drug delivery systems.

RESULTS AND DISCUSSION

AAA-PEAs with different hydrophobicities were prepared from the α-amino acids L-alanine and L-phenylalanine. It was found that the hydrophobicity of the AAA-PEAs as well as their molecular weight, influence an important parameter in depot formation, which is water tolerance. Similarly, the *in vitro* hydrolytic and enzymatic degradation under physiological conditions was dependent on the type of AAA-PEAs; the more hydrophobic the AAA-PEAs, the higher the mass loss.

CONCLUSIONS

AAA-PEAs are a promising biocompatible polymer family with very favorable water tolerance and biodegradability for its application as a long-acting injectable ISFI system by solvent exchange for the development of drug delivery systems.

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P31.2

PHBV production and agri-food valorization employing *Haloferax mediterranei* as cell factories

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INTRODUCTION

The sustainable management of conventional plastic waste has become a challenging problem for a global society. To solve this problem bio-based plastics are been studied to replace them. One of the most promising families of biopolymers are the polyhydroxyalkanoates (PHA), a class of aliphatic polyesters which are synthesised by many species of microorganisms as carbon and energy storage reservoirs usually under nutrient-limiting conditions. Specifically, the copolymer poly (3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV). PHBV is a biobased and biodegradable biopolymer produced by a few microorganisms without employing 3-hydroxyvalerate precursors, one of which is *Haloferax mediterranei*. *H. mediterranei* is an extreme halophile with a versatile metabolism, enabling PHBV synthesis from a broad range of substrates under environmental conditions that will restrict growth such as a nutritional limitation. PHBV shows higher flexibility and is less crystalline than other biopolymers such as the polyhydroxybutyrate (PHB). These properties enable the use of PHBV in applications such as biomedicine or packaging[1]. Nevertheless, despite an anticipated market potential of PHBV, the high production costs limit the industrial scale production and thus their commercial applications. However, the valorisation of agri-food industry waste, as proposed in the Agro2Circular and ViSS projects, can be a solution to reduce the production costs of PHBV. Agri-food waste is a potential feedstock for PHBV production, due to its high content of nutrients, which can replace commercially available sources of organic nutrients.
In this work, *H. mediterranei* is tested for the production of intracellular PHBV using different sources of agri-food waste as feedstock.

EXPERIMENTAL

Different kind of agro-food industrial, such as sugar-rich liquor residues from the food industry and skin, pulp and seeds from lemon and apple waste, by-products were tested as carbon sources to feed *H. mediterranei* and produce PHBV Furthermore, the PHBV was extracted and purified; then, the PHBV presence was confirmed with FTIR. After the extraction process, the PHBV properties were characterized; thermal properties with Differential Scanning Calorimetry (DSC) and chemical composition with Nuclear magnetic resonance (NMR).

RESULTS AND DISCUSSION

A successful method was developed to produce PHBV through a biotechnological process that valorise as raw materials different wastes from the agri-food industry. *H. mediterranei* can grow and produce the biopolymer. The obtained polymer was characterized by FTIR and RMN, confirming that the polymer is PHBV with a molar percentage of the monomer 3-HV between 8 and 14% without using any 3-hydroxyvalerate precursor. The best feedstock is lemon waste due to its high PHBV yields reached.

CONCLUSIONS

We demonstrated the production of the biodegradable biopolymer PHBV as high value products from the valorization of agri-food industry by-products. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 101036838 and Horizon Europe programme under grant agreement No. 101081931.

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P32.2

Polyhydroxybutyrate-co-hydroxyvalerate (PHBV) composites with grape stalk waste fillers for food packaging

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INTRODUCTION

PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) is a polymer belonging to the polyhydroxyalkanoate (PHA) family. Being biodegradable and obtained from renewable sources, PHBV is a sustainable alternative to conventional plastics for food packaging applications. The winemaking industry in Spain produces between 2 and 3 million tons of waste per year. Grape stalks constitute 12 % of the total by-products (1) and are rich in compounds such as polyphenols, cellulose, hemicellulose and lignin, which can be extracted for their revalorization. The objective of this study is to obtain and characterize PHBV composites incorporated with phenol-rich grape stalk powder (GS) and lignocellulosic fractions obtained from the GS subcritical water extraction at two different temperatures (170ºC and 180ºC), to modulate film properties while conferring antioxidant properties.

EXPERIMENTAL

The *Bobal* varietal grape stalks (Requena, Spain) were dried, milled, sieve and subjected to SWE, using a 10:1 water to solid mass ratio, at 170ºC or 180ºC, for 30 min to obtain the corresponding lignocellulosic fractions (R170 and R180). After sieving to 60 µm, GS, R170 and R180 powders were melt blended with PHBV at 1:9 mass ratio, and compression molded to obtain films that were characterized as to their mechanical, barrier and optical properties. Antioxidant properties of the fillers were also analyzed.

RESULTS AND DISCUSSION

The rigidity (elastic modulus) of the PHBV films (table 1) was significantly ($p<0.05$) reduced by the filler incorporation, without notable changes in stretchability and resistance to break. Colour was significantly affected by fillers, which caused a decrease in lightness and colour saturation, with a redder hue. These changes were enhanced in films with R170 and R180 due to the browner colour of these fillers because of the Maillard reactions occurred during SWE. The fillers decreased the oxygen permeability of the films, due to an increase in the tortuosity factor for mass transfer together with the potential oxygen scavenging effect of GS phenolic compounds.

Table 1. Mean values and standard deviation of the elastic modulus (EM), tensile strength (TS), elongation at break (E%), colour coordinates: lightness (L*), hue (hab*), and chroma (Cab*) and oxygen permeability (OP).

	PHBV	**GS**	**R170**	**R180**
EM (MPa)	2551 ± 180^{a}	1100 ± 120^{b}	1200 ± 200^{b}	1200 ± 120^{b}
TS (MPa)	33 ± 2^{a}	27 ± 3^{c}	32 ± 4^{ab}	30 ± 3^{bc}
E %	1.7 ± 0.2^{b}	1.8 ± 0.1^{b}	2.2 ± 0.1^{a}	1.9 ± 0.1^{ab}
L*	75.0 ± 0.1^{a}	37.1 ± 0.0^{b}	27.4 ± 0.0^{c}	27.7 ± 0.0^{d}
C_{ab}*	18.6 ± 0.2^{a}	13.4 ± 0.1^{b}	2.3 ± 0.1^{c}	2.5 ± 0.0^{d}
h_{ab}*	80.5 ± 0.0^{a}	51.1 ± 0.1^{b}	41.8 ± 0.1^{c}	41.7 ± 0.1^{c}
OP x10^{14} ($cm^3m^{-1}s^{-1}Pa^{-1}$)	39 ± 2^{a}	26.0 ± 2^{b}	26.3 ± 6^{b}	23.3 ± 5^{b}

CONCLUSIONS

The films tested in this study have potential application as food packaging materials with ability to extend the shelf-life of oxidation prone products, due to the antioxidant properties of compounds naturally occurring in the fillers. Further research in real food systems should be carried out to confirm the antioxidant effect.

ACKNOLEDGMENTS

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P33.2

Recycled and recyclable trilayer films based on rPLA/caseinate/rPLA reinforced with bacterial cellulose from Kombucha

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INTRODUCTION

The use of non-degradable plastics has increased waste accumulation, mainly in short-term applications such as food packaging. Therefore, the valorization of agro-food waste has garnered interest in the plastic processing industry to create more sustainable plastic formulations, aligning with the Circular Bioeconomy concept. In this study, three-layer films featuring a plasticized sodium caseinate (SC) film as an intermediate layer to enhance interlayer compatibility were developed, with two outer layers composed of poly(lactic acid) blended with mechanically recycled PLA and plasticized with acetyl tributyl citrate (PLA-rPLA-ATBC) and reinforced with kombucha bacterial cellulose (KC).

EXPERIMENTAL

SC was plasticized with 35 wt.% glycerol [1], the PLA-30%r-PLA-ATBC based inner layer was loaded with 1 wt.% of KC fermented in a sugared infusion of coffee waste [2].

RESULTS AND DISCUSSION

Transparent and homogeneous films based on PLA, r-PLA and SC, plasticized glycerol and ABTC were successfully obtained. SC tensile behavior is ductile while plasticized PLA/r-PLA shows a fragile fracture with low deformation and higher modulus than SC. The addition of the KC does not affect significantly and the tri-layer film, with the incorporation of the SC single film, shows a decrease in fragility. Although, the modulus and TS also are decreased. The improved performance of all these properties was attributed to the good adhesion between PLA and SC layers, ascribed to hydrogen bonding interactions.

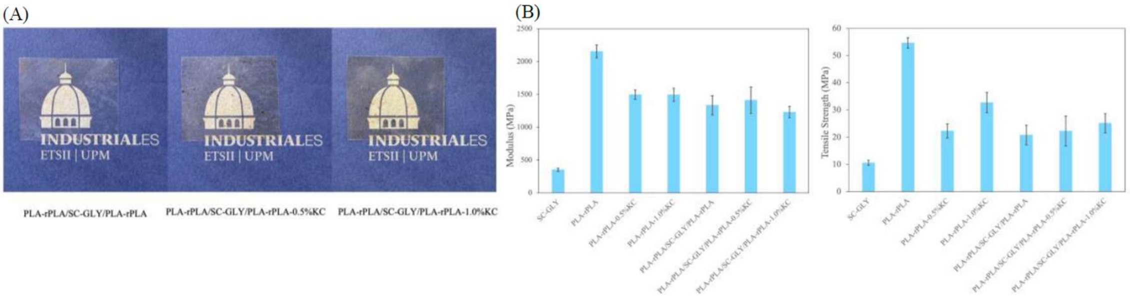

Figure 1. Results of (A) tri-layer obtained films and (B) mechanical properties.

CONCLUSIONS
The plasticized PLA-ATBC films reinforced with bacterial cellulose (KC) showed their potential for films for active food packaging applications.

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P34.2

Effect of renewable butylene succinate oligomers on the properties of poly(butylene succinate) films

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INTRODUCTION

Poly(butylene succinate) (PBS) is a biodegradable semi-crystalline aliphatic polyester of great interest for food packaging applications, which shows good processability and physical properties similar to polyethylene terephthalate (PET) [1]. PBS is synthesized by polycondensation reaction from succinic acid (SA) and 1,4-butanediol (BDO), with recent advancements enabling the sourcing of both monomers from biomass. Furthermore, the initial steps carried out during the synthesis process of PBS can also yield oligomers of butylene succinate (OBS) with varying molecular weights (MWs), which may serve as plasticizers, impact modifiers, and processing aids for PBS.

EXPERIMENTAL

Renewable SA was obtained from biomass, while BDO was prepared via high-pressure hydrogenation using a novel palladium-based catalyst (PID2021-128749OB-C33). Synthesis of low- and high-MW OBSs was carried out in two stages: melt esterification of SA and BDO to produce oligoesters, followed by time-controlled polycondensation through catalytic trans-esterification under high vacuum. The synthetized OBSs were studied using nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). Then, partially bio-based PBS was melt-blended with varying weight ratios (5 wt%, 10 wt%, and 15 wt%) of oligoesters in a mini-mixer. Films were prepared by thermocompression in a hydraulic press and characterized in terms of their morphologies, thermal properties, mechanical and thermomechanical performance, and global migration into food simulants.

RESULTS AND DISCUSSION

Low- and high-MW OBSs (OBS-LMW and OBS-HMW) were successfully obtained (Table I). The incorporation of different OBS contents reduced progressively the melt viscosity of PBS during mixing (Figure 1a). The presence of OBS also modified the physical performance of PBS films, opening up the development of materials with different mechanical and thermal responses (Figure 1b).

Table I. Chemical analysis (NMR and GPC) of bio-based PBS and OBS-LMW and OBS-HMW.

Sample	Mn (g/mol)	Mw (g/mol)	Đ
PBS	50,900	140,400	2.8
OBS-LMw	1,150	2,100	1.8
OBS-HMw	18,650	33,147	1.7

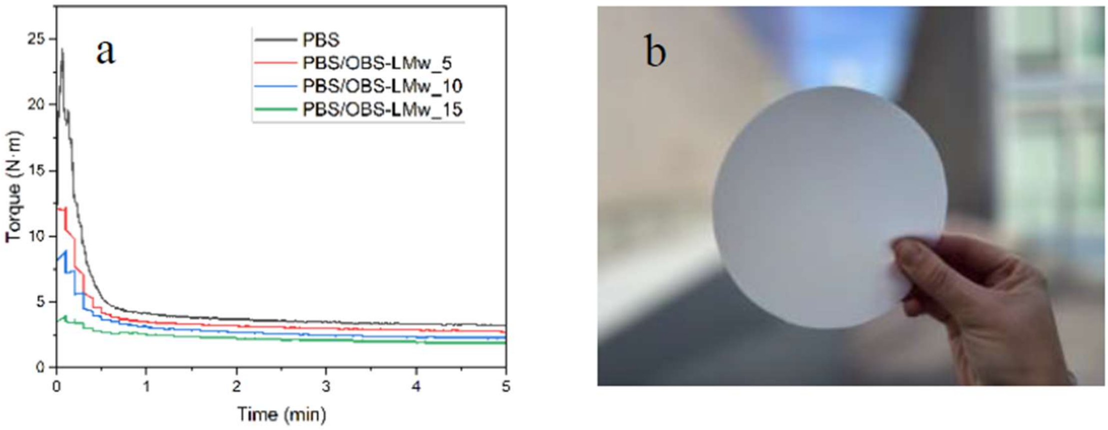

Figure 1. (a) Torque (N·m) vs time (min) during melt mixing of PBS and PBS/OBS-LMW. (b) PBS/OBS-LMW film.

CONCLUSIONS

Melt polycondensation of renewable SA and BDO can successfully yield OBS with MW values as low as 1,000 g/mol and with a polydispersity index (Đ) between 1.5 and 2. By incorporating these OBS at different ratios, the processability and physical properties of PBS films can be modified and adapted to suit the requirements of different food packaging applications.

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P35.2

Development of electrospun membranes based on poly(ester amide)s for the prevention of tendon adhesions

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INTRODUCTION

Tendon adhesions pose a significant challenge in orthopaedics, following tendon injury and surgery. Several studies have focused on addressing this issue, with the development of polymeric membranes showing promise as physical barriers. However, there remains a lack of suitable materials that meet all the needed requirements for this application, including degradation within an appropriate timeframe, cytocompatibility, and the lubricant properties. In this work, membranes were prepared using electrospinning (ES) and the polymers selected were poly(ester amide)s based on α-amino acids (AAA-PEAs). AAA-PEAs derived from L-alanine (ala) and L-phenylalanine (phe) were successfully synthetized and processed by electrospinning, yielding the envisaged membranes.

EXPERIMENTAL

The AAA-PEAs were synthetized by solution polycondensation between the di-p-toluenesulfonic acid salts of the bis-α-(L-amino acid)-α,ω-alkylene diesters based on ala or phe and activated esters of diacyl chlorides. The reaction took place at 75 ºC, for 5h, being then subjected to purification. Then, the AAA-PEAs were dissolved in 2,2,2 -trifluoroethanol (TFE) in a concentration between 20-30%w/v to be electrospun. A membrane from each AAA-PEA was successfully prepared, along with one from a solution containing 50%w/w of each AAA-PEA.

RESULTS AND DISCUSSION

Membranes with individualized fibers and free of defects were obtained (Figure 1). The membranes produced with PEA_ala exhibited fibers with a larger diameter, whereas the membrane with the blend of the two polymers demonstrated a broader diameter distribution. All the membranes presented pore sizes smaller than 8µm, being able to hinder the passage of fibroblast, which are key cells in adhesion formation. Also, they presented a water uptake above 100% which could facilitate the lubrication of the tendon, enabling and easiest tendon movement. Another important feature is the membranes's biodegradability, which obviates the need for surgical removal. However, they must maintain their integrity for at least 6 weeks, which is the time corresponding to the first stages of tendon healing. *In vitro* degradation studies conducted in both hydrolytic and enzymatic medium, for a 6-week period, degraded significantly, by a surface eroding mechanism.

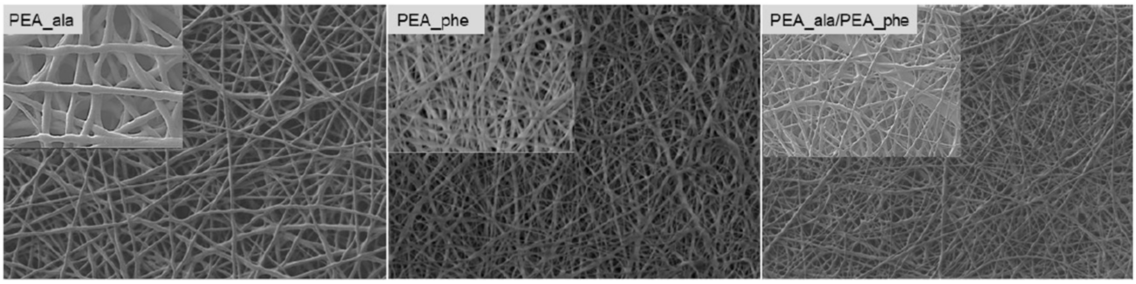

Figure 1. Scanning electron microscopy images of the prepared membranes at a magnification of x1000 and x2000 (insert).

CONCLUSIONS

This work showed the possibility of developing electrospun membranes from AAA-PEAs with characteristics that make them promising candidates for application in the prevention of tendon adhesions.

P36.2

Effect of accelerated UV weathering treatments on novel furan-based biopolymeric films

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INTRODUCTION

Environmental concerns have driven the development and implementation of biobased polymers in recent years. Among them, furan-based polymers are particularly attractive, since furan monomers could be obtained from a wide range of easily available renewable resources [1]. On the other hand, the chemical features associated with the heterocycle open the horizon to produce materials with promising characteristics and possible applications, including biomedical and electronic packaging, the automotive sector, and underwater devices [2]. In this context, this work aimed at developing furan-based films and assessing the effects of alternating cycles of UV light and moisture at controlled temperatures to simulate outdoor weathering on their properties.

EXPERIMENTAL

Poly (butylene 2,5-furanoate) (PBF) was prepared from 2,5-furandicarboxylic acid dimethyl ester (DMF) by a two-stage melt polycondensation synthesis using different atmosphere, temperature, and pressure conditions [3]. Furan-based films were produced by extrusion casting and subjected to cycles of drying (8h, lamps on) and condensation (4h, lamps off) under UVA irradiation ($\lambda = 340$ nm, $P = 0.76$ W/m2) according to ASTM D4329 for different times (0, 168, 326, 504 and 672 h).

RESULTS AND DISCUSSION

DSC was used to analyze the effect of UV treatment on the main thermal transitions for the furan-based films. Thermal stability and degradation processes were studied by TGA. Moreover, FTIR was used to evaluate the chemical and structural characteristics of the materials. As it is shown in Figure 1, UV irradiation treatment resulted in a decrease in the thermal stability of the materials, by reducing the initial decomposition temperature with the increase in the irradiation time. Similarly, infrared spectroscopy analysis indicated that peaks became weaker with longer UV irradiation time, which indicates that chemical structure of the materials could be negatively affected.

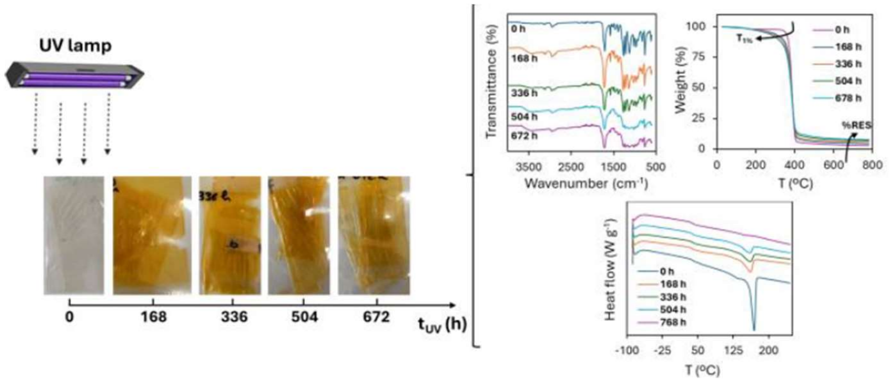

Figure 1: UV-irradiated PBF samples and their thermal and structural characteristics.

ACKNOWLEDGEMENTS

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P37.2

Fatty Acids Extracted from invasive *Rugulopteryx Okamurae*: A Promising Source for Phase Change Materials development

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INTRODUCTION

Rugulopteryx Okamurae (RO) is a brown macroalga native from the North-western Pacific Ocean that has, in recent years, colonized the South-western Europe coasts. Fatty acids are an important component of RO's composition, and they can be valorized for the production of bio-based phase change materials (PCM), which present some advantages, including a suitable melting temperature range, high heat capacity, and good chemical and thermal stability. [1] Based on the composition of the major saturated fatty acids extracted from RO, this study focuses on the development of new functional PCMs with different applications, such as energy storage or food packaging.

EXPERIMENTAL

The fatty acid profile of RO was analyzed by GC-MS. Based on this profile, different combinations of the major fatty acids and their methyl esters were prepared and characterized in their main structural and thermal properties by DSC, TGA, and FTIR.

RESULTS AND DISCUSSION

The GC-MS results indicated that the major saturated fatty acids present in RO are palmitic (C16:0), myristic (C14:0), and stearic (C18:0). Based on these results, different ternary eutectic mixtures were formulated. Figure 1A shows the DSC curves of a mixture of methyl palmitate, methyl myristate, and methyl stearate (19:4:1) fatty acid esters, while Figure 1B shows the DSC curves referred to fatty acids with no methylation. It can be observed that temperatures for phase changes were clearly lower for methyl esters, ranging around room temperature.

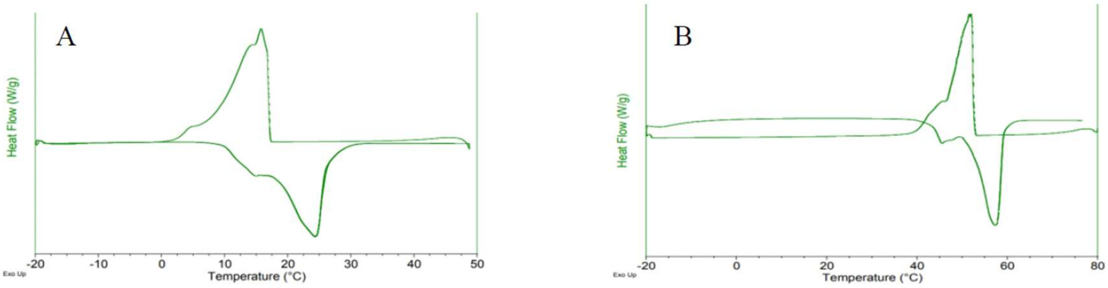

Figure 1. DSC curves obtained for the mixture of methyl palmitate, methyl myristate, and methyl stearate (19:4:1) fatty acids esters (A) and for the same mixture of fatty acids (B).

CONCLUSIONS

The obtained results revealed that fatty acids extracted from RO are a promising source for developing PCMs with possible applications in energy storage and food packaging.

ACKNOWLEDGEMENTS

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P38.2

Green composite hydrogels containing microcellulose from eucalyptus wastes to remove potentially toxic metals

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INTRODUCTION

Currently, the world faces difficulties related to the quantity of water due to industrial expansion, population growth, and urbanization intensification. Potentially toxic metals (PTMs) are widely used in various industrial activities (electroplating, metallurgy, leather, and textile), and are often found in wastewater [1]. The sorption process is considered an alternative technology with a high potential for the removal of these metals at low concentrations. The application of advanced materials such as starch/microcellulose hydrogels can be an alternative to increase the sorption capacity of these metals [2]. In this work, biodegradable composite hydrogels based on corn starch-containing cellulose microstructures (1 to 5% m/m) were developed and evaluated for the removal of PTMs (Cu^{2+}, Mn^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cr^{6+}) from aqueous media.

EXPERIMENTAL

The experimental conditions used for the synthesis of starch-based hydrogels containing microcellulose (MFC) are presented in Figure 1.

RESULTS AND DISCUSSION

SEM images showed that MFC extracted and isolated from eucalyptus sawdust residues had a fibrous character, with 7 µm of diameter and a length of 20 µm. After the incorporation of MFC, the starch hydrogels presented structures with irregular pores, which favored the increase in surface area (1.814 to 3.993 m^2/g), and apparent and real densities between (1.41 – 1.58) and (1.47 – 1.53) g/cm^3, respectively. The N_2 adsorption/desorption isotherms and pore size distribution showed that the hydrogels mainly presented a macroporous structure. The addition of MFC to the hydrogel reduced water absorption up to 24%, which indicates that the microfibers probably increased the rigidity conformation of the hydrogel. Additionally, the hydrogel samples had a high solubility in the aqueous medium without MFC (close to 30.1%). This result indicates that the hydrogel without MFC did not present satisfactory physical properties for application in sorption tests, while adding MFC to the starch hydrogel reduced the solubility in aqueous media up to 5%, increasing the potential for the adsorption experiments. Although MFC was efficient for the removal of the different PTMs, its incorporation in a reduced content (≤ 5%) in the final hydrogels resulted in a promising performance for Cu^{2+} adsorption, reaching efficiencies of about 52% and maximum adsorption capacities up to 0.258 mmol/g. Thus, starch-containing MFCs are efficient alternatives for treating contaminated waters.

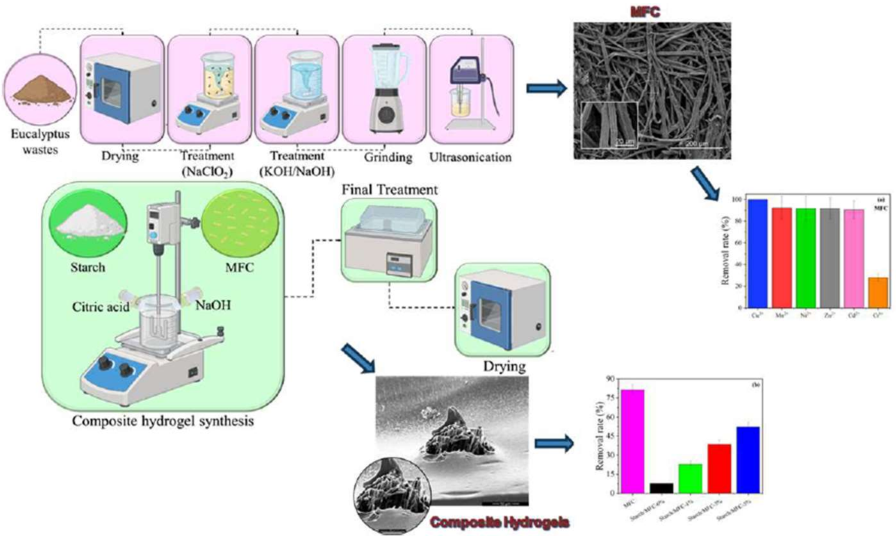

Figure 1. Schematic illustration of the synthesis of composite hydrogels containing MFC.

ACKNOWLEDGEMENTS

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P39.2

Development and characterization of a novel fully bio-based material composite of PHBV, PLA, and chitosan

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INTRODUCTION

Fossil-based plastics are widely manufactured and used by industries and their global consumption has been increasing over the years [1]. Even though they present properties such as being resilient, lightweight, and low price [1,2], conventional plastics' are associated with a series of disadvantages and environmental concerns (micro and macro pollution following ecosystem exposure and a series of known environmental impacts) [3,4]. A shift towards more sustainable solutions that follow the circular economy principles has been expanding [5]. In line with this, the work aimed to develop a new material composite fully bio-based and biodegradable containing cost-effective and available constituents. The developed formulations were evaluated in terms of their properties.

EXPERIMENTAL

PHBV, PLA chitosan, and bio-based additives were used in the developed formulations. Mechanical properties, Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), Melt Flow Index (MFI), and Water Contact Angle were used to evaluate the developed formulation properties.

RESULTS AND DISCUSSION

Table I. Mechanical properties of formulations. Average of 5 test specimens (AV ± SE).

Formulation	**Tensile Strength** (Mpa)	**Yield Strain** (mm)	**Young Modulus** (Mpa)	**Strain at Break** (mm)
PLA	51.9 ± 0.69	0.07 ± 0.00	804.9 ± 3.33	0.07 ± 0.00
PHBV	30.58 ± 0.92	0.04 ± 0.00	823.2 ± 5.79	0.05 ± 0.00
PHBV/PLA	32.17 ± 0.86	0.04 ± 0.00	804.23 ± 10.90	0.05 ± 0.00
PHBV/PLA/CS	25.40 ± 0.91	0.03 ± 0.00	871.23 ± 3.60	0.03 ± 0.00
PHBV/PLA/CS/OE/P/C	19.03 ± 0.92	0.04 ± 0.00	713.96 ± 30.20	0.04 ± 0.00

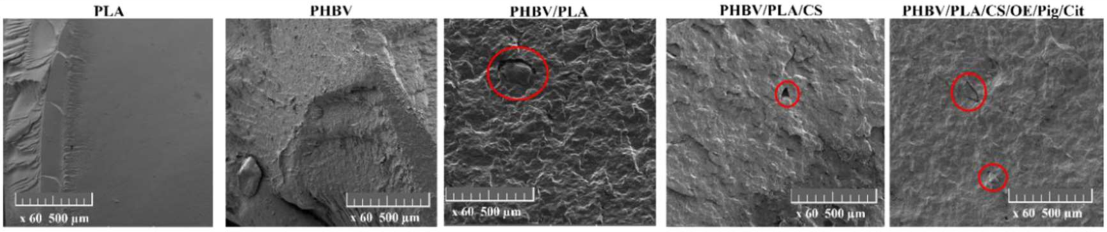

Fig. 1. SEM images of the developed material composites.

CONCLUSIONS

For the first time, a novel fully biobased biocomposite of PHBV, PLA, chitosan, and other bio-based additives (essential oil, citrate, and algae pigment) was developed and characterised showing promising applications in medical, packaging, and several other sectors.

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P40.2

Integrating Machine Learning and Molecular Simulations to Enhance Cell-Penetrating Peptide-Modified Nanoparticles

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INTRODUCTION

Chemotherapy for glioblastoma often fails due to the challenge of delivering drugs across the Blood-Brain Barrier (BBB). In this study, we explore the potential of cell-penetrating peptides (CPPs) to enhance the transport of nanoparticles across the BBB and target brain tumor cells. In this work, different active targeting molecules were evaluated for the usNLCs surface modification, including cell-penetrating peptides (CPPs), tumor-targeting peptides, receptor proteins, and cationic surfactants, in order to improve the transport of the drug across the BBB, and consequently target brain tumor cells. [1-2] We hypothesize that the surface functionalization of ultra-small nanostructured lipid carriers (usNLCs) with a novel class of cell-penetrating peptides (CPPs) could enhance their biological barrier crossability, increase their specific cellular uptake, and ultimately promote the delivery of the nanoparticles to target cells.

METHODS

The usNLCs were functionalized with distinct biomolecules adsorbed on the usNLCs surface and its ability as a targeting approach to BBB (HBMEC) and glioma cells (U87 cells) were evaluated in terms of physicochemical properties, cell uptake, permeability in the 2D-BBB model, and the tumor growth inhibitory ability. Formulations comprised several targeting strategies, including nanoparticles negatively and positively charged, which were further functionalized with CPPs differing in terms of amino acid composition, charge, and molecular weight, and also receptor-mediated molecules such as c[RGDfK], or transferrin. Machine learning methods[2] were used to predict those CPPs that are most likely to bind to and penetrate glioblastoma cells and those that are likely to have high efficacy in delivering nanoparticles to glioblastoma cells, based on known CPPs and their properties, such as charge, hydrophobicity, and secondary structure.

RESULTS AND DISCUSSION

Molecular Dynamics simulations allowed describing the interactions between CPPs and the model cell membrane, as well as between the peptides and the usNLCs. Monte Carlo simulations allowed describing the electrostatic-driven adsorption of the different CPPs to the usNLCs surface, by quantifying the adsorption degree of each model CPP chain, the coverage of the nanoparticle surface and the overall adsorption patterns of CPPs.

The best performance in terms of permeability in the 2D-BBB model was obtained with transferrin, followed by CPP4. However, the cellular internalization was higher for CPP4. BBB cells were more sensitive to the nanoparticles than glioblastoma cells. Functionalized-usNLCs were capable of the transportation of the celecoxib (CXB) into living cells and the cellular-uptake mechanism was activated on more than one route in an energy-dependent or -independent manner. The internalization was 2.5 times higher in glioblastoma cells than in the BBB cells, which could be favorable in the case of brain tumors.

CONCLUSIONS

This study provided valuable insights into the mechanisms of cellular uptake of nanoparticles and allowed optimizing the design of the nanoparticles to improve their binding and penetration efficiency towards a promising therapeutic strategy for the treatment of GB. The functionalized-usNLCs showed high affinity to BBB cells and tumor cells. The dual-targeting approach of usNLCs could significantly contribute to BBB transport and tumor growth inhibition.

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P41.2

Nanoblends of PLA/PVA re-dispersible in water for controlled drug liberation

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INTRODUCTION

Colloidal suspension of biodegradable polymer can be used for the liberation of active substances, such as drugs, in special of lipophilic substances dispersed in the non-water soluble biodegradable polymer. PLA nanoparticles have been used as support for drug release [1, 2], including lipophilic drugs [3, 4]. Here we describe a non-miscible blend composed of a dispersed phase of biodegradable poly (lactic acid) (PLA) in a water-soluble matrix of poly (vinyl alcohol) (PVA). The dispersed phase shows nanometric dimension and was used for the incorporation of lipophilic drugs such as vitamin D, for example. The blend can be used as device for drug liberation or can dispersed in water to give a stable colloidal suspension of PLA. If the PVA used is a low water-soluble grade it can be used for drug that need low liberation kinetics. The colloidal suspensions were characterized by DLS. The isolated beads from suspensions and the blends were characterized by SEM. All materials were characterized by thermal analysis (DSC, DMA and TG) and mechanical tensile tests.

RESULTS AND DISCUSSION

The blends are clear and slightly translucent and shows a very homogeneous dispersion of the dispersed phase of PLA beads with diameter ranging from 150 to 350 nm. The liberation of vitamin D shows a two mechanism process and lead 80 h for the release of 50% of vitamin D, which result in more than one weak for 90% of liberation. This condition was achieve using high soluble PVA which in contact with water or living fluids give rise to a colloidal suspension of PLA. Figure 1 shows the complete process of blend manufacture and the re-dispersion of PLA in water.

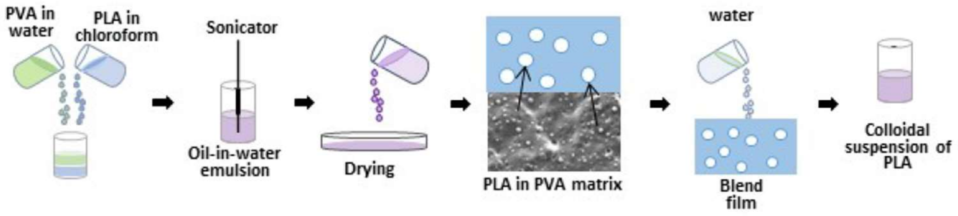

Figure 1. From a colloidal suspension to a nanoblend and again to a colloidal suspension by re-dispersion.

CONCLUSIONS

The O/W emulsion method using ultrasound for dispersion was efficient to obtain PVA/PLA nanoblend films, in compositions of 90/10, 75/25 and 50/50. The immiscible blends of a globular dispersed phase of PLA in PVA shows by SEM and DLS measurements that the PLA phase was very well dispersed, shows good compatibility with the matrix and with a diameters between 150 and 350 nm. Once in contact with water, the PVA matrix completely dissolves resulting in a stable PLA colloidal suspension. The material showed great potential for application in the medical field as a solid and/or liquid system to carry bioactive molecules due to its instantaneous dispersion in an aqueous medium. The authors acknowledge CAPES and CNPq.

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P42.2

Remove of tetracycline by chitosan-based polymers

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INTRODUCTION

The deterioration of water quality due to contamination with pollutants has significant impact on the health of all organisms that live in the aquatic environment. Water contamination is mainly caused by the release of various substances such as household, industrial, and agricultural wastes. Among these, antibiotics are emerging pollutants (also known as micropollutants[1]) that raise special concern due to the possibility of the development of antibiotic-resistance genes (ARGs) in bacterial pathogens. The conventional wastewater treatment does not completely eliminate antibiotics or their metabolites[2]. Among the several methods for the antibiotic removal, adsorption has proven to be the most economical, viable and highly effective. Several commercially available adsorbents are employed to remove antibiotics wastewater by adsorption, as carbon-based materials, zeolites, ion exchange resins, and clays. However, they have high costs and potential sustainability issues[3]. Chitosan is a polysaccharide with many free hydroxyl and amino groups, which makes it a good adsorbent[4]. Besides, chitosan has the advantage of being very abundant, non-toxic, inexpensive, and biodegradable. Taking these into consideration, we used naphthaldehyde and a naphthaldehyde derivative (2-hydroxy-1-naphthaldehyde) to functionalize chitosan in order to be used as adsorbent for tetracycline in aqueous media. To get molecular-level insight about interactions between tetracycline (TC) and chitosan-based derivatives, computational techniques such as density functional theory (DFT) and molecular dynamics were employed. Experimental tests of adsorption were also performed.

RESULTS AND DISCUSSION

The binding energy (BE) between chitosan and chitosan derivatives and TC calculated by DFT demonstrated the complex of high TC removal efficiency. Chitosan functionalized with 2-hydroxy-1-naphthaldehyde (CNF1) was the complex with lower BE, i.e., the most stable one. In agreement with DFT calculations, the experimental TC removal efficiency exhibited the same sequence. The best adsorption capacity was found at pH=6. The (CNF1) data were better fitted with the Langmuir isotherms and pseudo-second order kinetic (PSO) model.

CONCLUSIONS

The best performance for the removal of tetracycline is obtained with (CNF1) at pH=6. The study of isotherms indicated that the surface of the adsorbent is homogeneous, and adsorption occurs in a monolayer. The adsorption kinetics followed the PSO model, in agreement with the sorption isotherm mechanism. The theoretical calculations performed in this work indicate that electrostatic interactions, hydrogen bonding, and π -π electron donor–acceptor (EDA) contributions may be relevant for the adsorption of tetracycline onto chitosan derivatives.

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P43.2

Comparison between random and aligned PLA-Mg-NPs electrospun nanofibers mats

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INTRODUCTION

Biodegradable and biocompatible polymers are widely used in particular for the development of biodegradable implants. Polylactic acid is a cytocompatible and biodegradable polymer, however, it presents a slow degradation rate and lack of bioactivity [1]. It has been reported that the addition of Magnesium (Mg)-based nanoparticles (NPs) increases the bioactivity of polymeric scaffolds [2]. Furthermore, through the electrospinning technique, it is possible to obtain either random or aligned electrospun nanofibers mats that mimic the extracellular matrix [3]. In this work, the comparison between PLA-based random and aligned nanofibers mats reinforced with both magnesium oxide (MgO) and magnesium hydroxide ($Mg(OH)_2$) NPs at different concentrations, 0.5, 1, 3 wt% for aligned electrospun nanofibers mats and 1 wt% for random electrospun nanofibers mats, with respect to PLA, and their hydrolytic degradation in phosphate buffer saline (PBS) medium is reported.

RESULTS AND DISCUSSION

Random and aligned electrospun nanofibers mats show an average diameter in the range of 300 nm, however, oriented electrospun nanofibers mats present lower diameters. Aligned nanofibers are characterized by higher degree of crystallinity (Xc) due to the higher orientation achieved with the use of the rotating drum. It is important to point out that the orientation and the presence of NPs does not affect the Tg and the Tm of electrospun nanofibers mats. Mechanical analysis of random electrospun nanofibers mats reveals that both NPs at 1 wt% are able to increase E and σ of neat PLA, which present E and σ values of 41.2 ± 6.5 MPa and of 3.0 ± 0.6 MPa, respectively. In the case of aligned electrospun nanofibers mats, NPs decrease the mechanical properties of PLA electrospun nanofibers (E and σ values of 470.8 ± 83.6 MPa and 14.9 ± 5.1 MPa, respectively). However, aligned electrospun nanofibers mats exhibit very high values of E and σ with respect to random electrospun nanofibers mats, due to the higher orientation and crystallinity of the material. The *in vitro* degradation of both random and aligned electrospun nanofibers mats has been studied, however, degradation occurs faster in random nanofibers.

CONCLUSIONS

Electrospun fibers mats based on PLA reinforced with both MgO and $Mg(OH)_2$ NPs have been studied. The presence of NPs decreases the average diameter of electrospun nanofibers mats with respect to PLA electrospun nanofibers and the orientation leads to the formation of thinner electrospun nanofibers mats. Furthermore, aligned electrospun nanofibers mats presented a higher degree of crystallinity. Even if the orientation does not affect the thermal properties of nanofibers, it affects the mechanical ones, indeed the E value of aligned nanofibers is at least four times higher than that one calculated for random electrospun nanofibers mats. Additionally, both random and aligned electrospun nanofibers mats show fast degradation in PBS.

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P44.2

Magnetic Cellulose microbeads for the degradation of organic pollutants

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INTRODUCTION

Cellulose, the most abundant natural polymer, is being investigated to produce particles at the micro and nanoscales for a wide range of applications [1]. In this study, cellulose microbeads were prepared by dissolving wood pulp fibers in an organic electrolyte solution and by subsequent regeneration in water. Then, the microbeads were functionalized with iron oxide nanoparticles (Fe3O4NPs) to induce magnetic and oxidizing properties. The functional microbeads were fully characterized and their oxidizing power, towards the degradation of model organic pollutants via Fenton oxidation process, was assessed.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) data (Figure 1a,b) confirmed the sphere-like shape of the cellulose microbeads, with a notable change over the microbeads surface roughness after functionalization with the Fe3O4NPs. These microbeads were placed in a methylene blue (MB) and methyl orange (MO) solutions containing H2O2 at pH around 4 and 6. The generation of hydroxide radicals through the Fenton process, allowed the continuous degradation of MB at pH 6 and MO at pH 4, as displayed in Figure 1c. Additionally, the microbeads have magnetic properties (Figure 1d) and thus can be externally driven by magnetic fields. The movement of the microbeads will result in enhanced mass transfer for improved pollutant degradation/removal.

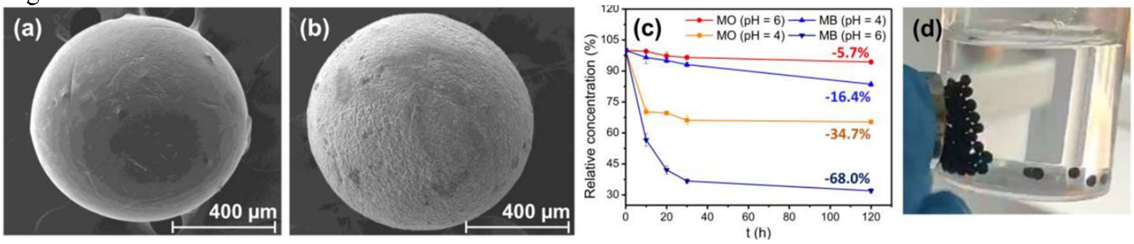

Figure 1. (a,b) SEM micrographs of the microbeads before (a) and after (b) functionalization with Fe3O4NPs; (c) evolution of concentration over time as a consequence of the oxidation of MB (665 nm) and MO (465 nm); and (d) visual evidence of the magnetic properties of the microbeads in the presence of a permanent magnet.

CONCLUSIONS

The production and functionalization of cellulose microbeads with Fe3O4NPs was successfully achieved. The resulting functional microbeads efficiently promoted the oxidative degradation of methylene blue and methyl orange in acceptable working pH interval through the Fenton reaction. These results enlighten the prospective application of these microbeads for the degradation of organic pollutants.

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P45.2

The BioUptake project: promoting the use of bioplastic composites to pave the way for the development of more sustainable products

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INTRODUCTION

The enduring worldwide plastic pollution has become of major environmental concern. With less than 10% of the produced plastic being recycled, tonnes of plastics end up in the environment each year, with ca 12 million tonnes finding its way to the several environmental compartments, with a pattern of continuous growth. Once in the environment, plastics may cause negative impacts on Human health, economy, biodiversity and climate. Following this scenario, the European Union (EU) adopted a strategy to promote a transition for a more sustainable, bio-based and circular economy, aiming to protect Human health and the environment. Specifically, the EU Plastic Strategy1 is a key element towards such a transition, by pursuing a reduction on greenhouse gas emissions and society's dependence on the use of fossil fuels. It also seeks to transform the way plastic products are used, developed, produced, and recycled in the EU. Within this context, the BioUptake project aims at developing flexible manufacturing processes to produce bio-based products for construction, medical, and packaging sectors.

Figure 1. Identification of the actions, defined in the EU Plastics Strategy, to which BioUptake contributes.

EXPERIMENTAL

In brief, the planned research component of the project, targeting to achieve the main goal, is structured in sequential work packages that involve (i) development of test protocols, develop pilot lines, and adapt assessment methods to effectively monitor the impact of biobased materials on environmental and Human health; (ii) design and develop new bio-composite intermediate formats based on thermoplastic and thermoset matrices; (iii) identify the main factors that influence the conventional manufacturing models by testing the newly developed bio-based formats in different manufacturing processes.

CONCLUSIONS

This comprehensive framework will allow the development of new bio-based products in three activity sectors (construction, medical, and packaging sectors), by using the concepts of safe-by-circular and safe-by design, promoting its higher sustainability and eco-friendliness. As well, BioUptake will accelerate innovation in the plastic industry and the market introduction of more sustainable products.

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P46.2

Barrier and mechanical properties of PLA and PHBV films incorporating almond skin extracts

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INTRODUCTION

Almond skin (AS), separated by blanching with hot water, is considered a waste product by the food industry. However, this skin contains significant amounts of phenolic acids with antioxidant and antimicrobial properties of interest for use in active packaging materials [1]. These phenolic compounds can be obtained by using subcritical water extraction, an innovative and effective technique that takes into account the principles of green chemistry, sustainable and without the use of organic solvents.

Poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) and polylactic acid (PLA) are biodegradable polymers with similar thermoplastic and mechanical characteristics than conventional plastics.

The present work analyzes the effect of the incorporation of active extracts, rich in phenolic compounds, obtained from AS by subcritical water extraction (SWE) at 160 and 180ºC, on the barrier and mechanical properties of biodegradable films based on PLA and PHBV.

RESULTS AND DISCUSSION

The results showed that the incorporation of the extracts into the polyester films resulted in colored films, with lower Ti in the visible spectrum. In general, they also become less resistant and stretchable, especially when incorporating the AS180 extract. This can be attributed to the presence of discontinuities in the polyester matrix caused by incorporating the extracts, as observed in the FESEM images of PLA films (Figure 1).

On the other hand, the effect of the extracts on the barrier properties depended on the temperature used to obtain the extracts (160 or 180ºC), which may be associated with the interactions developed between the polymer chains with the phenolic compounds in the extract [2].

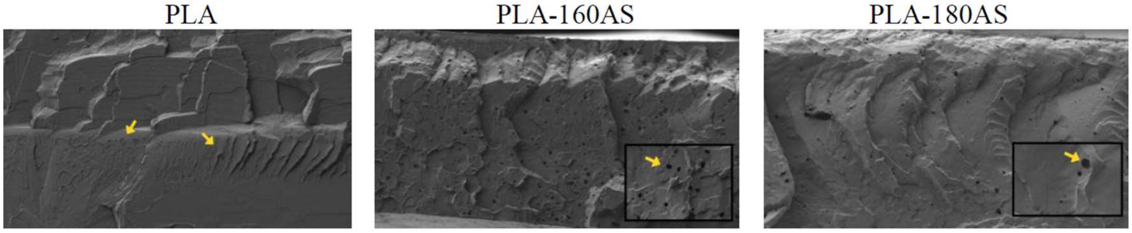

Figure 1. Micrographs obtained by FESEM of the cross section of the PLA films.

CONCLUSIONS

The incorporation of AS extracts with antioxidant and antimicrobial activity into biodegradable PLA/PHBV films has a high potential for the development of active materials for food packaging. This would achieve the revaluation of this agri-food by-product in the framework of a circular and sustainable economy.

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P47.2

High-barrier biobased multilayer packaging films with nanocellulose obtained from by-products from the agro-food industry

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INTRODUCTION

The agro-food industry generates a high amount of by-products (peels, shells, leaves…) [1], which are however still abundant in bioactive ingredients and lignocellulosic biomass and could be a sustainable source of active compounds and nanocelluloses [2]. Cellulose nanofibrils (CNF) for example have shown excellent gas barrier properties, which makes them of the highest interest for food packaging applications [3]. However, the nanocelluloses swelling, in presence of water vapor, thwarts their good gas barrier properties [4]. Our recent work on this subject has shown that a multilayer architecture starting with an hydrophobic layer of poly(lactide) (PLA) is a viable solution to protect nanocelluloses from humidity [5,6]. Here we exploit this architecture to valorize CNF extracted from agro-industrial wastes to make food packaging, aiming at a more circular economy.

Grape pomace is a high-quality residue left over from wine industry, accounting for about 20% (w/w) of the total grapes used [7]. It is constituted of pressed grape skins, seeds and stems, containing abundant bioactive components such as phenols, flavonoids and anthocyanins, as well as high amounts of lignocellulosic compounds. Active compounds from grape pomace are first extracted, then the remaining waste, mostly lignocellulosic biomass, retained after extraction is hydrolyzed to obtain cellulose nanofibrils (CNF). To make the bio-based multilayer films, polylactide (PLA) was used as a support substrate; the obtained CNF from grape pomace is coated on the surface of PLA using bar-coater method. Evaluation of structural and barrier properties of the multilayer films is made using microscopy (SEM and AFM) and permeation measurements.

CONCLUSIONS

This work presents the valorization of nanocelluloses obtained from agro-industrial by-products by the development of new bio-based materials. It shows potential applications for them, in accordance with the principles of the circular economy helping extending shelf life of food products, and ensuring their safety, freshness, and integrity.

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P48.2

Almond skin powder to obtain antioxidant biodegradable composite films

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INTRODUCTION

Almond skin (AS) is a by-product, produced in large amount during the industrial blanching of almonds, very rich in phenolic compounds with antioxidant, antimicrobial properties [1]. Its use in the production of composites with biodegradable polymers, such as polylactic acid (PLA) or polyvinyl alcohol (PVA), is a possible strategy for its valorisation, reducing the cost of the material for its use in food packaging applications. In this study, PLA and PVA composites with different ratios (5,10 and 15%) of defatted and ground almond skins (particle size less than 63 μm) have been obtained by melt mixing and compression moulding. The films have been characterized as to their water vapour and oxygen barrier capacity, optical properties and antioxidant capacity through their ability to prevent sunflower oil oxidation.

RESULTS AND DISCUSSION

Almond skin particles reduced the oxygen permeability of PVA and PLA, but only reduced the water vapour permeability of PVA films, as shown in Figure 1. AS also reduced the films transparency while modified colour coordinates of the films, making them darker and brown, depending on the AS ratio. This represents an advantage to prevent light induced reactions in packaged food. To evaluate the antioxidant capacity of the composite films, single-dose bags of the different materials were obtained by heat-sealing, in which sunflower oil was packed. These were submitted to an accelerated oxidation test, at 40ºC under fluorescent light, analysing the formation of peroxides and the diene and triene content at different storage times (between 0-45 days). Compared to an unpackaged control samples, composite films notably reduced the sunflower oil oxidation.

	PLA	PLA + 5% AS	PLA + 10% AS	PLA + 15% AS	PVA	PVA + 5% AS	PVA + 10% AS	PVA +15% AS
								
WPV x 10^{11} (g/m.s.Pa)	8 ± 0,8	16,3 ± 2,3	34 ± 5,6	38 ± 4,7	218,9 ± 5,2	187,3 ± 16,8	184,5 ± 10,9	190,6 ± 20,5
OP x 10^{14} (cm^3/m.s.Pa)	190,1 ± 6,2	193,6 ± 10,2	181,2 ± 1,8	149,1 ± 1,9	11,5 ± 0,8	8,1 ± 1,6	6,7 ± 0,7	9,5 ± 0,1

Figure 1. Oxygen and water vapour permeability of PVA and PLA films.

CONCLUSIONS

Composite films from almond skin and polar and non-polar biodegradables polymers can be obtained with improved barrier capacity and antioxidant properties, while almond skin waste is valorised.

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P49.2

Unveiling the uncommon crystallization features of 3,4-PEF, a thermal and *ab initio* study

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INTRODUCTION

The development of furandicarboxylic acid (FDCA) based polyesters polymers and materials is an ever blooming research topic in both academia and industrial scene due to the need to replace fossil-based polymers, such as poly(ethylene terephthalate) (PET), by more sustainable counterparts [1]. The most well-known FDCA-derived polymer is poly(ethylene 2,5-furanoate) (2,5-PEF) [2]. Nevertheless, there are many other biobased polymers, such as poly(ethylene 3,4-furanoate) (3,4-PEF), synthetized from the 3,4-FDCA isomer, whose detailed characterization is still lacking and, thus, their potential underexploited. In this work, the structural preferences of 3,4-PEF polyester in the crystalline domains have been studied using vibrational spectroscopy and ab initio calculations. Additionally, the literature gap on 3,4-PEF thermal characterization was herein also fulfilled.

RESULTS AND DISCUSSION

Results suggested that in the crystalline domains, the ethylene glycol (EG) moiety in 3,4-PEF chains adopt preferentially the *trans* conformation, while the FDCA fragment assume the *syn* conformation. Differential scanning calorimetry (DSC) analysis revealed that 3,4-PEF has a glass transition temperature (T_g) and a melting temperature (T_m) of 39 °C and 155 °C, respectively. The lower T_m value (compared with 2,5-PEF) is in accordance with a much lesser contribution from the hydrogen bonds interactions to the 3,4-PEF crystallization. According to kinetic studies, the fastest crystallization rate for 3,4-PEF occurs at 110 °C, with a half crystallization time of 12 min. Interestingly, at comparable molecular weights, this is faster than the half crystallization time of 2,5-PEF at its optimal crystallization temperature (170 °C), but still lower than that of PET.

CONCLUSIONS

The 3,4-PEF presents itself as a promising fast crystallization renewable polymer. It was stated with this work that the chain conformation for 3,4-PEF in the crystalline domains is (EG)-trans (FDCA)-syn. Additionally, it was also proved that 3,4-PEF presented a faster crystallization in comparison with 2,5-PEF.

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Scientific Employment Stimulus to AFS (CEECIND/02322/2020) (DOI 10.54499/2020.02322.CEECIND/CP1589/CT0008) and for the research contracts for doctorate grants to SVP (2023.01628.BD) and BA (2020.04495.BD). This publication is based upon work from COST Action FUR4Sustain, CA18220, supported by COST (European Cooperation in Science and Technology).

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P50.2

Towards plastics sustainability: a holistic study on aliphatic polyesters enzymatic polymerization

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INTRODUCTION

Biocatalysis is a valuable tool for synthesizing polymers sustainably. While most aliphatic polyesters (PEs) require chemical catalysts and high temperatures to be synthesized conventionally, enzymatic polymerization is an alternative approach, where non-toxic enzymes are used as catalysts. Additionally, side reactions that may occur during conventional polyester synthesis are avoided thanks to the low reaction temperatures and the enzymes' high selectivity [1]. In the first part of the study, the enzymatic polymerization of aliphatic polyesters is investigated by evaluating critical process conditions (monomers nature, by-product removal rate, solvent). In the second part, the scalability of enzymatic polymerization is thoroughly investigated, aiming to fill the relevant gap in the literature.

RESULTS AND DISCUSSION

The effect of diacid monomer length (6, 12 and 14 C atoms) on polymerization rate was firstly investigated; 1,8 octanediol-based PEs were enzymatically synthesized via solution technique in toluene [2]. The longer-chain diacids presented higher affinity with the biocatalyst (N435) due to their increased hydrophobicity, favouring diffusion into biocatalyst hydrophobic active sites. Even though molecular sieves were used to remove the polycondensation by-product (water), the obtained polyesters presented low intrinsic viscosity (IV) values (up to 0.189 dL/g), indicating the need to increase water diffusion rates. Thus, diphenylether was used as a high-boiling point solvent in the next step, permitting vacuum application. The obtained octanediol-based PEs presented higher IV of up to 0.346 dL/g [3]. However, the relevant family of polyesters presented low Tm (58–75°C); thus, PBS, with Tm 114°C, was examined as an alternative bio-based and biodegradable PE. The enzymatically synthesized PBS in diphenylether presented low IV (0.180 dL/g, $\bar{\bar{M_n}}$ 3700 g/mol) due to its short-chain monomers and/or higher diol volatility, which resulted in deviation from the end groups' stoichiometric balance. On that basis, a two-step process was conducted to prevent the 1,4-BDO loss, with a slightly positive effect on the final $\bar{\bar{M_n}}$ (3900 g/mol). Solventless systems were also examined to facilitate the scaling-up of PBS enzymatic polymerization [1, 4]. The most critical parameters of the bulk, two-stage process were investigated, and thanks to its simplicity, it was scaled up (based on the optimized conditions), resulting in 20 g of enzymatically synthesized PBS for the first time, thus filling the relevant gap in the open literature. The scaled-up PBS grade presented slightly lower MW compared to the small-scale products (1g) due to mass transfer limitations that are more intense on large scales. In the context of a case study, the scaled-up prepolymer was examined as a carrier in an encapsulation system for the first time.

CONCLUSIONS

A holistic study to delve into aliphatic polyesters' enzymatic polymerization was conducted. The key parameters of enzymatic polymerization were thoroughly investigated, establishing a simple and scalable process to produce aliphatic polyesters.

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