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Abstract book

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CIRMAT Symposium. Abstract book

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Fecha de edición: 2022

URI: http://hdl.handle.net/10016/35645

Preface

“ This book collects some of the most prominent advances in terms of circular technologies and materials exhibited at the CIRMAT symposium. The editors want to thank the contributions of all the participants who wanted to join us, and especially all the collaborators for all their work and support.

El reto de CIRMAT fue claro desde el principio, tomar uno de los principios de la economia circular y ponerlo a disposición de todos, tal y como reza el objetivo de desarrollo sostenible 11: “Reducción de las desigualdades”. Hemos trabajado con ayuda de muchas personas para llevar a cabo un evento transversal donde se han podido encontrar estudiantes, profesores, investigadores y profesionales de multitud de sectores en un mismo plano. La idea era clara, debatir y encontrar soluciones para afrontar el reto del presente, y planificar un futuro que debe ser prometedor.

Alberto García-Peñas
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POLYMERS, BIOPOLYMERS AND COMPOSITES

Compostable polymeric materials for active food packaging

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One of the main challenges in food industry is to substitute petroleum-based non-biodegradable polymers such as polyethylene (PE) used in packaging by bio-degradable polymers such as polylactic acid (PLA), or Ecovio (PLA-polybutylene adipate (PBAT) blends) to solve plastic waste problem [1][2]. Another challenge in food industry is to improve food safety, preserve the quality of the packaged food and extend its shelf life. Active packaging with additional properties like antioxidant or antimicrobial activity offers a unique approach to addressing these demands. In this work, we develop compostable active systems based on biodegradable PLA and Ecovio films with acetyl tributyl citrate (ATBC) as plasticizer, and phosphate microparticles (AS020P) as antimicrobial additive. Different polymer/ATBC/particles composite blends (Figure 1A) were obtained by melt mixing with a co-rotation twin-screw miniextruder. Then, films were prepared by compression molding and characterized by conventional techniques such as differential scanning calorimetry and thermogravimetric analy-

sis. The mechanical properties as well as the antimicrobial behavior of the films were also studied. Figure 1B displays the antimicrobial properties of the films against S. aureus, which demonstrated a high efficiency. The degradation of the materials was determined following the UNE-EN ISO 20200 [3] standard under compost conditions and Raman Confocal Microscopy was used to analyse the evolution and degradation. The degradation rate of the samples under compost conditions is represented in Figure 1C. It is clearly that the PLA based samples (PCA and PSA) degrade faster than the Ecovio blends [4].

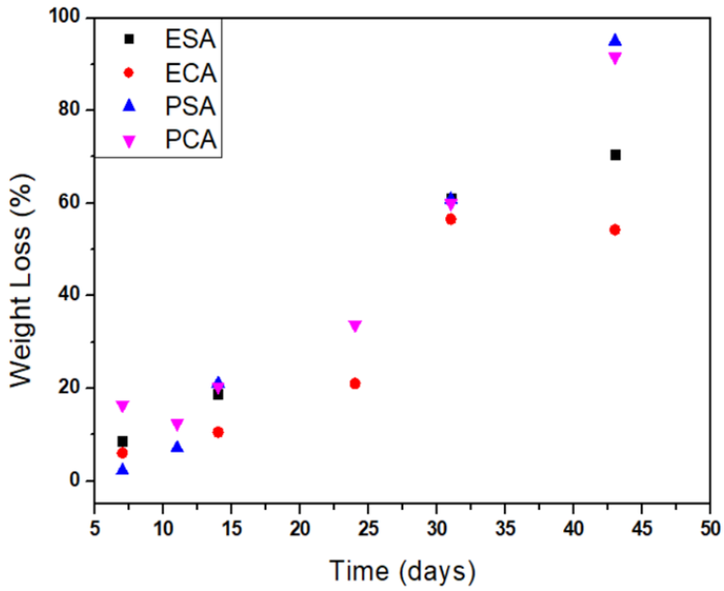
A

Sample	Polymer	% Polymer	%ATBC	%AS020P
PSA	PLA	85	15	-
PCA	PLA	84	15	1
ESA	Ecovio	85	15	-
ECA	Ecovio	84	15	1

B

Sample	Bacterial reduction (%)
PCA	72.5± 0.0
ECA	99± 0.5

C



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Recovery and reuse of microplastic

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The excellent properties of plastics, their ease of moulding, high mechanical and chemical resistance and low cost, have promoted their widespread use. Since the development of the first synthetic polymers in 1950, their production has been steadily increasing and is expected to double in the next 20 years [1]. Although its usefulness is undeniable, the generation and mismanagement of plastic waste represents a major environmental problem. Its degradation leads to the appearance of plastic particles in the order of micrometres (microplastics, MPs). These MPs have a big stability and they accumulate in water environments or in crops, resulting in their ingestion by aquatic organisms or plants into the food chain. Moreover, the interaction of these solids with a variety of chemicals, antibiotics, heavy metals, pesticides and aromatic fuel derivatives, among others, is expected to play an important role in their potential risk, as they can act as carriers of contaminants. The proposal of this work is to recover and reuse plastics by means of different novel technologies and nanomaterials. Thus, for the recovery of microplastics it is proposed to use two types of materials, magnetic nanoparticles that can capture microplastics through adsorption mediated by a hydrophobic surfactant and subsequent collection by magnet and a second proposal using micromotors that propel and move the microplastics to the sur-

face to be collected [2]. Two options are also proposed for their reuse. The first is adsorb pollutants on the surface of microplastics and recover them by one of the previous methodologies. The second option is to use them together with magnetic nanoparticles to build robust catalysts that can later be used for the degradation of small amounts of pollutants, both organic pollutants and metal ions. These proposals have initially been tested with very good results using magnetite nanoparticles and polylactic acid microplastics [3]. The synthesis and subsequent use of manganese oxide micromotors with hydrogen peroxide has also been tested.

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Feasibility of using recycled PP & PE in the manufacture of protective pipes in agriculture

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With the development of this project, the aim is to look for new applications for residual plastics, specifically polypropylene and polyethylene materials in the field of agriculture, in the manufacture of plant protective pipes, which must meet the requirements of protecting the plant against animal attacks, for which impact resistance is required, and avoiding possible damages made by atmospheric agents, therefore, with good resistance against aging, and also against the effect of UV radiation, since it is a product exposed to the elements. In addition, the plant protective pipes must have enough light transmission characteristics in order to not harm the development of the plant. This project fulfills Circular Economy criteria by meeting the objective of using recycled plastics in new applica-

tions, with the consequent savings in raw materials.

The development of the research carried out in the Polymer Technology laboratory of the ETSIDI UPM, has consisted of: selection and preparation of two groups of mixtures of polypropylene (PP) and polyethylene (PE) virgin and recycled; manufacture of plates for the characterization of the properties of the mixtures; simulation of environmental conditions of use of the product; and systemic and systematic comparison of its properties: rheological, thermal, mechanical and optical. For the simulation of the behavior under environmental conditions, all the plates will be subjected to an accelerated aging process in a climatic chamber, combining humidity, radiation and heat cycling conditions. In this work we present the results of optical transmission and induction time to oxidation (TIO) before and after climatic chamber, properties and variation of them that give a good idea of the quality and functionality of the final product.

VIRGIN MATERIALS
PP4060 TOLSA (ρ=0,905 g/cm³; IF=3 g/10 min)
HDPE TR 135 (ρ=0,938 g/cm³; IF=0,12 g/10 min)

RECICLED MATERIALS
PP CORDOPLAS (IF=0,60 g/10 min)
HDPE LA RED (ρ=0,956 g/cm³; IF=0,02 g/10 min)

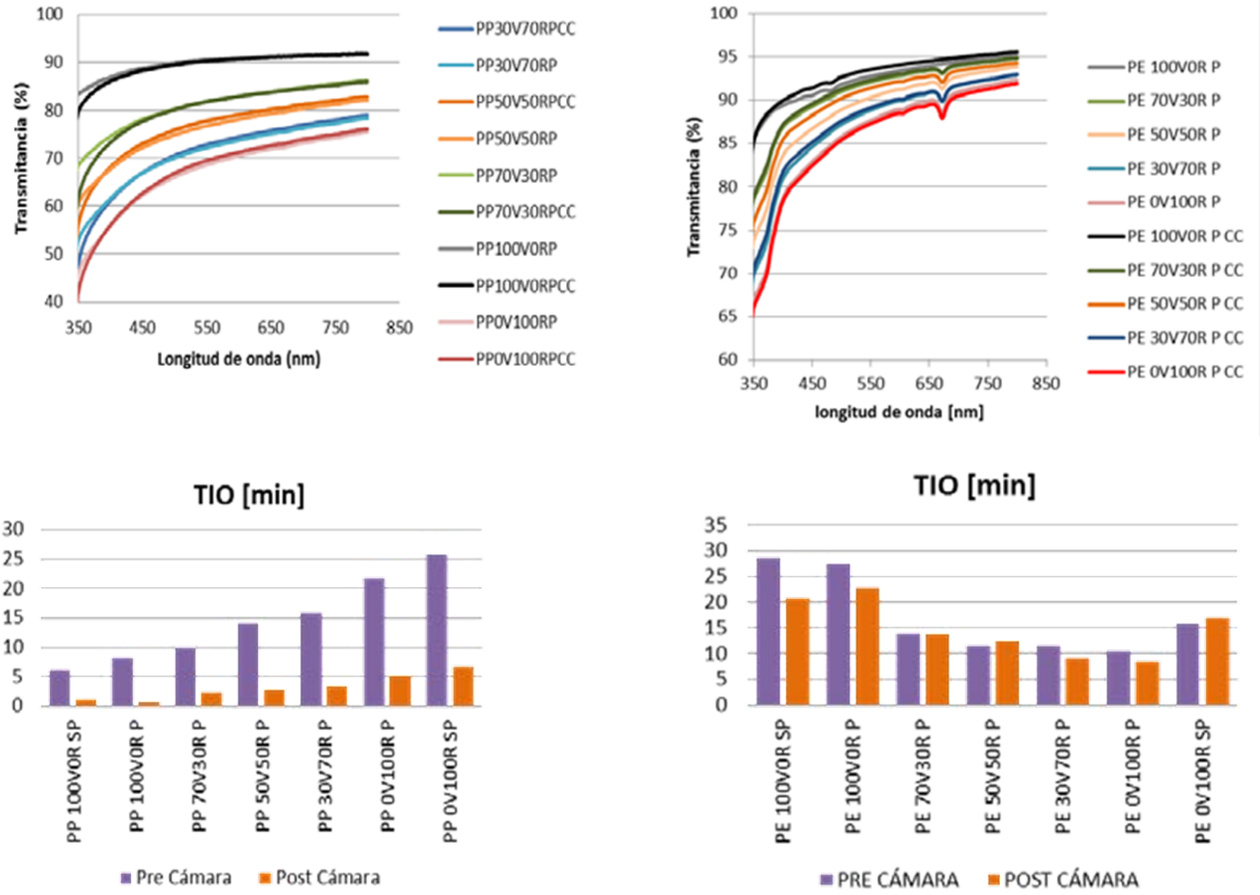

Figure 1. Transmittance of PP and PE blends, before and after of climatic chamber

Figure 2: Oxidation induction time for PP and PE blends, before and after climatic chamber

Synthesis of polyurethanes by chemical upcycling of PET through a circular economy model

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According to the Sustainable Development Goals, a green treatment and management of plastic waste must be developed, moving from a linear production procedure to a circular economy model [1]. Poly (ethylene terephthalate) (PET) is the fourth polymer most produced in the world, but only 19% of PET is properly recycled, with a recovery rate of 31% for bottles.

Related to this, chemical recycling of PET presents versatile procedures and the possibility of obtaining high-added value products, such as polyurethanes (PUs), whereas the mechanical approach has a limited number of cycles in which properties decrease significantly after the second cycle compared to pristine PET [2]. Currently, chemical recycling methods require drastic reaction conditions

(high temperatures, pressures, etc.) that increases the final price of the product, leading to its exclusion from the recycling cycle and loss of valuable product.

The aim of this proposal is the chemical upcycling of PET under milder reaction conditions (moderate temperatures and atmospheric pressures) using different basic catalysts, cheap and sustainable reagents (ethylene carbonate, EC), and PET waste (grinded PET or bis(2-hydroxyethyl) terephthalate (BHET)). As a result, oligomeric polyols characterized by two "OH" terminal groups are obtained, in which three different units can be distinguished (Figure 1). The final chemical composition and molecular weight are determined by ^{1}H-NMR,[3] showing high versatility depending on the catalyst used. Subsequently, these polyols are employed in the synthesis of polyurethanes (Figure 1), as a high-added value products with potential applications in gas membranes, lithium batteries and hydroponic foams.

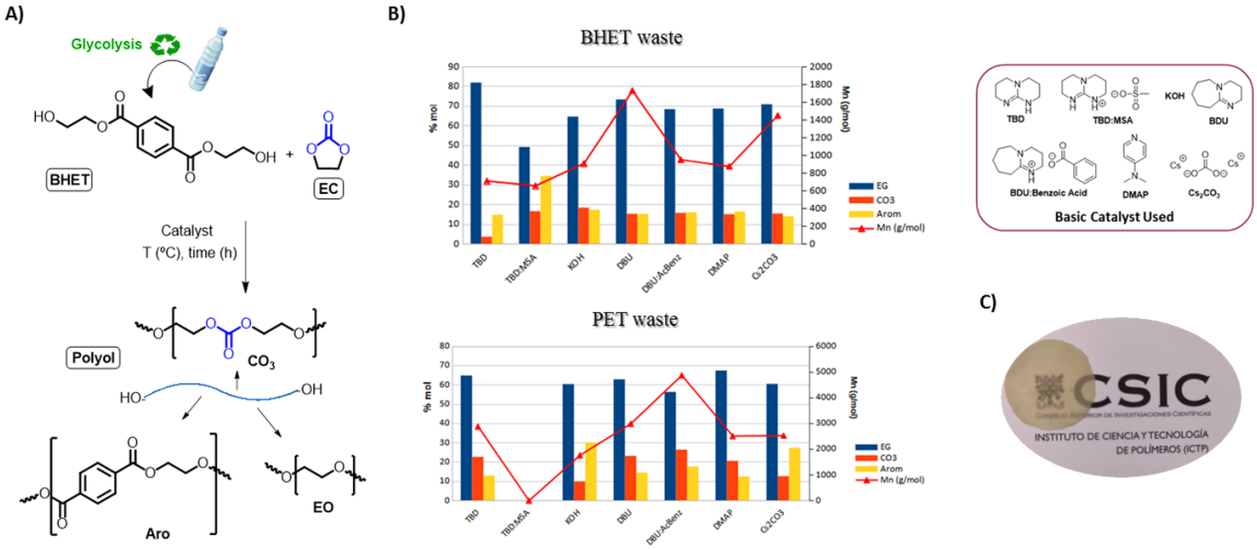

Figure 1. A) Synthetic scheme of the polyols from PET waste; B) Chemical composition and molecular weight of the polyol using different basic catalysts; C) Polyurethane obtained from versatile polyols.

Acknowledgments:

Financial support provided by Spanish National Research Council JAEINT_20_00798 and Ministry of Science and Innovation RTI2018-096636-J-100, RTC2019-007287-2 and PID2020-119047RB-I00.

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New biodegradable polymers derived from itaconic acid with antimicrobial activity

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In the last years, antimicrobial peptides have inspired the synthesis of novel antimicrobial polymers with potent efficiency for the treatment of microbial infections. These polymers are typically amphiphilic cationic structures able to attach to negatively charged bacterial membranes and, then, insert into them through the hydrophobic parts disrupting the cytoplasmic membrane. This action is rapid and makes relatively difficult for the bacteria to develop resistance.[1] However, the cationic polymers are most based on non-degradable backbones, which limit their application in clinical uses as they can be accumulated in the body and exert long term toxicity. Biodegradability is also an important and desired property for many biomedical applications. On this basis, itaconic acid (IA) is a very

promising biobased building block to prepare biodegradable polymers.

Here, we proposed a new versatile method to modify IA by incorporating pendant alkyne groups leading to clickable IA derivative that can be polymerized. This new approach can be used to further functionalize the IA-biobased polymers by copper-catalyzed azide-alkyne cycloaddition (CuAAC) click chemistry. The facile and efficient reaction will allow the incorporation of bioactive groups such as azoles moieties. The antimicrobial activity was subsequently provided via N-alkylation of these azole groups using methyl iodide or butyl iodide which led to the corresponding cationic polymers with pendant azolium groups, PTTI-Me and PTTI-Bu, respectively (See Figure 1).[2]

Then, the antimicrobial properties of the polymers were tested against different Gram positive (S. epidermidis, S. aureus and resistant strains, Methicillin-resistant S. aureus) and Gram negative (E. coli and P. aeruginosa) bacteria. The antimicrobial activity of these polymers is clearly more effective against Gram positive bacteria probably because of the additional outer membrane of Gram negative bacteria that provides a tough barrier to be overcome.

At last, biodegradation test was performed following a standard method for determining aerobic biodegradation of polymeric materials in soil, by measuring the carbon dioxide evolved by the microorganisms as a function of time. The biobased polymers were able to degrade rapidly in soil, in less than 60 days.

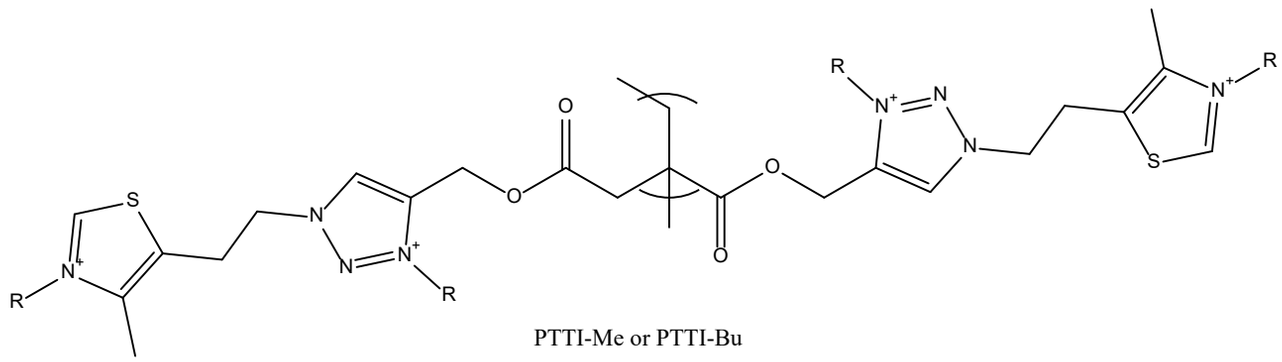

Figure 1. Structure of antibacterial biodegradable polymer (PTTI-Me and PTTI-Bu).

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Bioplastics that grow on trees

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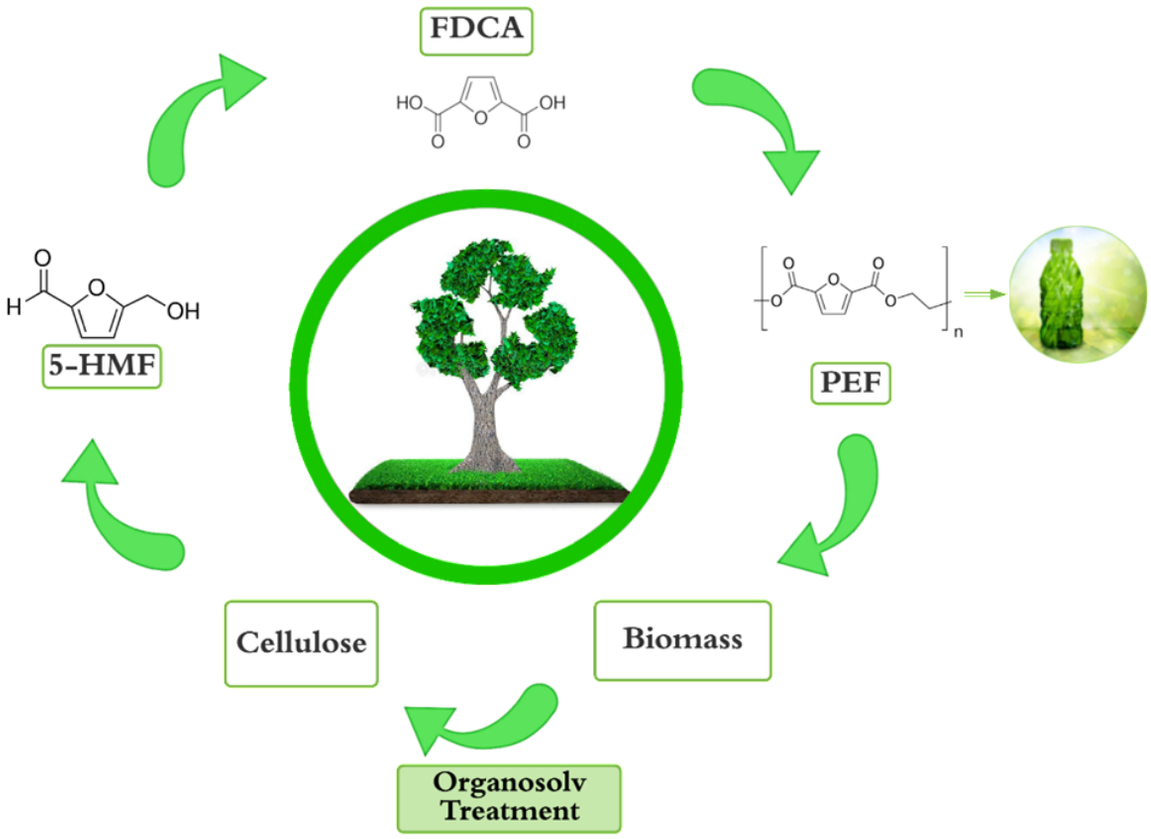
Currently, we find ourselves in a world economy turning towards sustainability, and with plastic in the crosshairs of environmental campaigns. Thus, bioplastics are the sustainable solution of the future. The search for new energy sources as substitutes for fossil fuels is necessary because these are finite resource. A new alternative is the use of lignocellulosic biomass because it offers a high potential for the production of value-added compounds in the framework of a circular economy. In addition, lignocellulosic biomass represents an important source of raw materials without compromising the food supply.

In this work, we will focus on the fractionation of biomass by catalyzed bi-phasic organosolv process [1] because it has a highly compacted structure made up of cellulose, hemicellulose and lignin. The next step after pretreatment is carbohydrate hydrolysis to generate a sugar-rich stream that is used as a platform for the production of a large array of bioproducts.



In Figure 1 we can distinguish 5-Hydroxymethylfurfural (5-HMF), a platform chemical product that is produced by dehydrating sugars, which in turn is obtained from the conversion of cellulose [2]. The importance of obtaining 5-HMF lies in the fact that this compound can be oxidized to FDCA, which is a precursor of PEF, a polymer that is the current alternative to plastics obtained from PET.

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Devulcanization methods and advanced characterization of recycled rubber from end-of-life tires

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Tires are complex products that reach high technical requirements in terms of security, durability and many other factors. Devulcanization is a proven and efficient method to enhance circularity in the useful life cycle of tires. It consists in the breakage of the polymeric chains to recover a new material that can be used for other applications. There are two big groups of devulcanization methods: those that produce random scission and those that produce only the sulfidic-bond scission (selective devulcanization).

In this work many of these methods are studied: selective devulcanization using thiol-amine treatment, thermo-mechan-

ical devulcanization and microwave heating devulcanization. The final compounds are characterized, obtaining the spatial distribution of crosslinks after each treatment (see Figure 1).

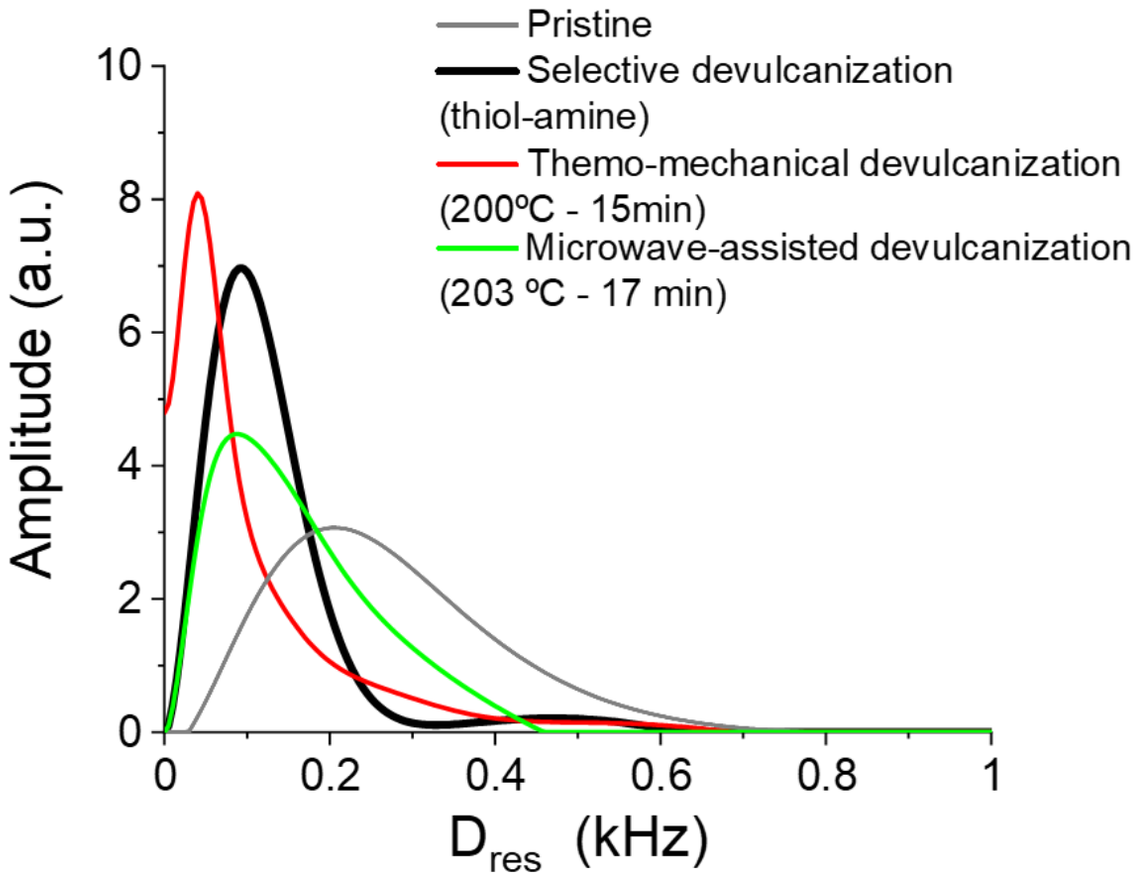

Figure 1. Variation of dipolar coupling distribution of pristine sample with different devulcanization treatments.

This characterization was carried out on all the specimens by experiments of double quantum nuclear magnetic resonance (^{1}H DQ-NMR), from this technique quantitative advanced characterization of the elastomeric network was obtained, as well as the amount of network defects, entanglements, and crosslink densities [1]. Thus, it was possible to determine the effect of the devulcanization treatment on the samples studied. The samples of end-of-life tire powder (ELTp) devulcanized show a lower average value of residual dipolar coupling due to the breakage of crosslinks (selective treatments) and the polymeric chains (random scission treatments).

[1] J. L. Valentín, R. Pérez-Aparicio, A. Fernández-Torres, P. Posadas, R. Herrero, F. M. Salamanca, R. Navarro, L. Saiz-Rodríguez. "Advanced characterization of recycled rubber from end-of-life tires" Rubber Chemistry and Technology, vol. 93, pp. 683–703. 2020.

Making circular the life cycle of polyurethane foams

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Polyurethane (PU) occupies the sixth position of the most used plastics in the world [1]. PUs find a wide range of applications and can be classified mainly in foams (flexible used in mattresses, comfort, or rigid applied in building and refrigeration insulation) and in the so-called CASEs (coatings, adhesives, sealants and elastomers).

Due to the multitude of applications, an increasing amount of nonbiodegradable PU wastes are generated worldwide. Traditionally, PU wastes have found their end-of-life destination in landfills, but the increase of waste generation, the rise in PU raw materials prices, the space restrictions in the landfills, the new environmental regulations and the pressure of public opinion are forcing to find a greener destiny for PU wastes [2]. Therefore, get a solution for this environmental issue is an urgent task, converting the PU production and application into a circular economy activity.

The chemical recycling of PU waste would help to solve this problem. The glycolysis was selected as process for recovering the raw materials from polyurethane. Besides, the use of an excess of glycol, immiscible with the polyols used in flex-

ible foams, allows to obtain a biphasic product, in which the upper phase (UP) is mostly composed by the recovered polyol, while the bottom phase (BP) contains excess of glycolysis agent and reaction by-products. Thus, the recovered polyol has higher quality than the product from a single-phase process.

The glycolysis is carried out at high temperatures and vigorous agitation ensuring complete homogenization, for a maximum time of 3 hours allowing the complete degradation of the polyurethane into polyol and aromatic amines [3]. Different glycols have been proven, employing a ratio with respect to the polyurethane foam greater than 1, to obtain a split phase product. The product obtained is separated by decantation, obtaining the UP and the BP, both are characterized by GPC, NMR and FTIR. Besides, the UP was purified by different washes with water or other solvents to improve the purity of the recovered polyol, achieving a recovered polyol with a purity of up to 98%, which was employed in the synthesis of new PU foams. Finally, the mechanical, structural, and thermal characterization of the synthesized foams is carried out and compared with the characteristics of commercial ones.

Figure 1 summarizes the process described, which allows creating a circular economy of PU foams.

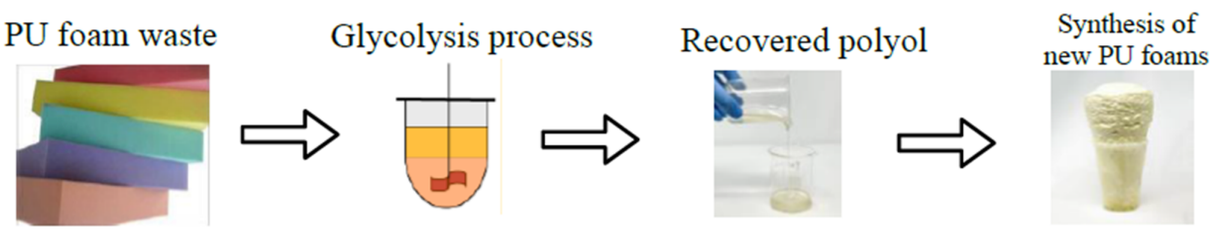

Figure 1. Summary of the recycling of PU foams to convert the process into a circular economy.

- [1] D. Hicks, A. Austin. "A Review of the Global PU Industry in 2016 and Outlook for 2017" Pu Magazine, vol. 14. 2017
- [2] W. Yang, Q. Dong, S. Liu, H. Xie, L. Liu, J. Li. "Recycling and Disposal Methods for Polyurethane Foam Wastes" Procedia Environmental Sciences, vol 16, pp. 167–175. 2012.
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Synthesis and characterization of cellulose derivatives for biomedical applications

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INTRODUCTION

Cellulose is the most abundant biopolymer on Earth. In the need of environmentally friendly materials, cellulose has generated keen interest over the years, being used in applications found in different fields. In this work, a novel antimicrobial structure is proposed, obtained by the functionalization of cellulose with 1-methylimidazole. This innovative structure could have potential applications in the biomedical field, like a wound-healing product.

METHODS

A two-step reaction is performed, producing firstly, a substitution of cellulose with thionyl chloride (CLC) to make cellulose accessible to the incorporation of the methylimidazole, secondly, via N-alkylation (CelMIm) (Figure 1). The resulting samples were characterized by different techniques.

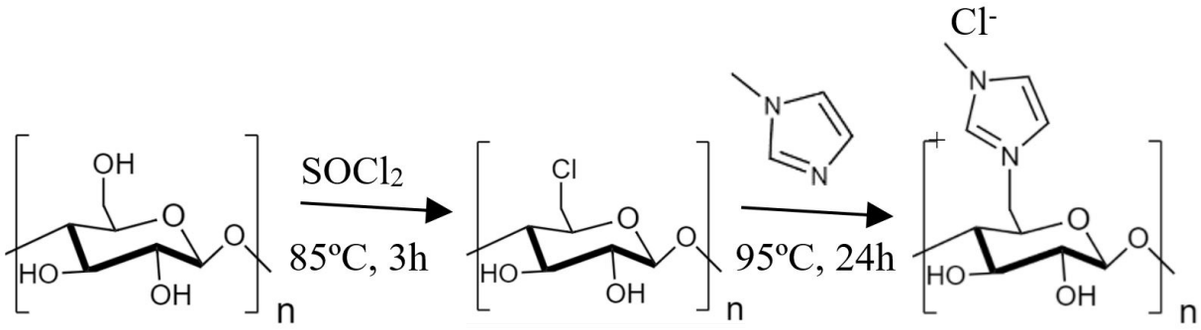

Figure 1. Cellulose modifications into chlorodeoxycellulose (CLC) and cellulose substituted with 1-methylimidazole (CelMIm).

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FTIR) showed the incorporation of the chloride ion in CLC with the vibration Cl-C and its following disappearance and further appearance of stretching and bending vibrations typical from methylimidazole in the spectrum of CelMIm. X- ray diffraction measurements proved that a higher modification of the structure would result in a decreased crystallinity, whereas the Z-potential gave negative values in case of CLC (-48.4 mV) and positive ones in the case of CelMIm (+14.2 mV), agreeing with the composition of each structure and being the positive values a key factor for the antimicrobial properties. Thermogravimetric analysis also showed the success of the chemical modification. A bulk oxidation of CLC due to the formation of hydrochloric acid is observed while in the final product, CelMIm, the break of hydrogen bonds and intermolecular forces is appreciated. Finally, scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) proved that not only the modifications had been produced but also, they were homogeneous in the structure.

CONCLUSIONS

We have developed an easy-accessible approach to synthetize cellulose derivatives with potential antimicrobial applications. The different techniques used in the characterization corroborate these modifications, allowing us to go to the next step, which would be antimicrobial susceptibility.

Direct 3D printing of zero valent iron@ polylactic acid catalyst for tetracycline degradation

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Due in part to extensive production and use, antibiotics are becoming emerging pollutants. Among others, Tetracycline (TC) antibiotic is commonly used for veterinary and human treatments in Europe, representing, around 20% of the total antibiotic consumption.

Several techniques have been studied to remove antibiotics from wastewater, including coagulation, membrane separation, adsorption, and biodegradation. Among the abovementioned water treatments, advanced oxidation processes (AOPs), have received increasing attention because of their high oxidation capacity and rapid reaction rates. However, conventional homogeneous Fenton oxidation has several drawbacks, like the

recovery, regeneration, and reuse of the catalyst. To overcome such disadvantages, alternative heterogeneous catalysts for replacing Fe^{2+} are commonly used, such as magnetite, goethite, ferrites and zero-valent iron (ZVI). Specifically, ZVI catalysts can react with persulfate ions, $S_2O_8^{2-}$ (PS) or oxidize with oxygen and water to form Fe^{2+}. Moreover, the PS reaction with the generated Fe^{2+} leads to the formation of sulphate radicals ($SO_4^{-}\cdot$), (E° = 2.5-3.1 V).

The development of highly active and stable structured catalysts represents a challenge for the treatment of large water flows. Commonly, the most studied catalytic supports for iron oxide doping are pillar clays, activated carbon, alumina, zirconium oxide and zeolites. However, the poor anchorage of iron oxide particles jeopardises their reusability through iron leaching. In this context, the manufacturing and design of 3D-printed objects has started to take on special interest for the development of robust and durable catalysts for pollutant remediation, with any desired morphology.

Herein, we report an alternative method based on 3D printing technology to obtain zero-valent iron polylactic acid prototypes (ZVI@ PLA) in a single step and without post etching treatment. ZVI@ PLA was used to activate persulfate (PS) for the removal of Tetracycline (TC) in recirculating mode under two different heating methodologies, thermal bath and contactless heating promoted by magnetic induction (MIH) [1].

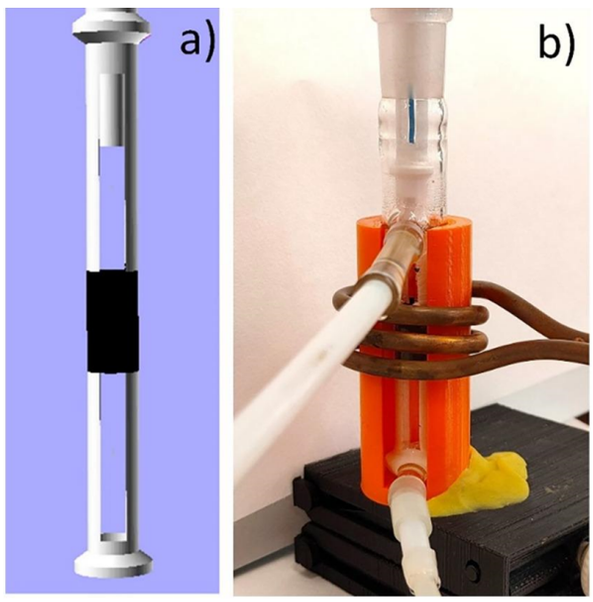

Figure 1. a) Digital prototype images of the ZVI@PLA prototype. b) Experimental setup for the MIH test, where ZVI@PLA is placed in the centre of the solenoid.

[1] S. Fernández-Velayos, J. Sánchez-Marcos, A. Munoz-Bonilla, P. Herrasti, N. Menéndez, E. Mazarío. "Direct 3D printing of zero valent iron@polylactic acid catalyst for tetracycline degradation with magnetically inducing active persulfate" Science of The Total Environment, vol. 806, pp. 150917. 2021.

The role of iron oxide nanoparticles in the recovery of microplastic wastes

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The concern towards emergent contaminants (ECs) from daily used household products has increased in recent years due to their human and ecological adverse effects. These ECs can be found in products like pesticides, pharmaceuticals, personal care products and industrial chemicals [1]. Within cosmetics, there are some facial scrubs that include polyethylene microplastics (MPs) in their formula, which in turn and after use end up in aqueous effluents as ECs. On this regard, it is important to find alternatives to recover and/or eliminate these MPs from water, returning them to the manufacturing process to help the establishment of a circular economy considering the recycling of these materials.

In this work, multicore iron oxide nanoparticles (IONPs) with high magnetic moment per particle have been synthesized by an optimized scaled up polyol procedure [2]. These IONPs were attached to the surface of MPs extracted from a commercial facial scrub and removed from aqueous suspensions using a magnet (Figure 1). The polyol molecules at IONPs surface are promoting the attachment of the particles to the MPs, leading to 100 % removal yields. Optimum parameters for the magnetic harvesting are MPs/IONPs ratio >1, pH 7, 30 min of contact time and a magnet with a field at the surface of 0.4 kA/m. In this way, it is possible to purify the MPs for reuse, as well as the IONPs that can achieve several removal cycles with 100 % efficiencies. Furthermore, we have also tested the possibility to eliminate these MPs by a two step-procedure: 1) Hydrolysis of the MPs at 150 ºC and, 2) Mineralization of organic carbon by a Fenton-like reaction using the IONPs to generate reactive oxygen species. Preliminary results exhibited great efficiencies with 100 and 65 % yields for the first and second step of the degradation processes. In general, these IONPs seem a great alternative to recover and/or eliminate MPs from water, as it has been shown for other remediation processes [3].

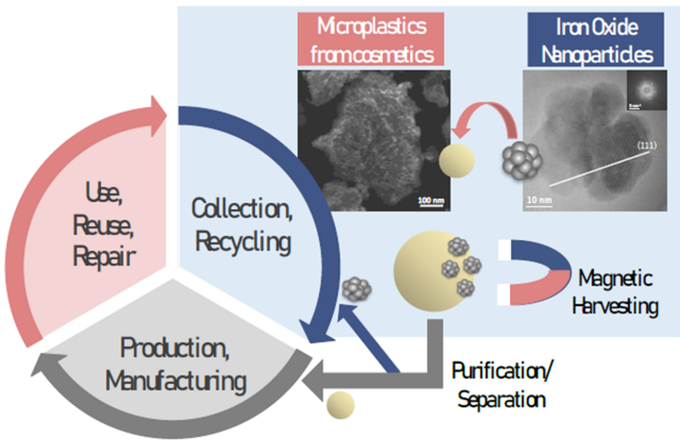

Figure 1. Multicore iron oxide nanoparticles (TEM image on the right) for the magnetic harvesting of microplastics (SEM image on the left) from commercial cosmetics.

- [1] S.D. Richardson, S.Y. Kimura. "Water Analysis: Emerging Contaminants and Current Issues" Analytical Chemistry, vol. 92, pp. 473-505. 2019.
- [2] A. Gallo-Cordova, J. G. Ovejero, A. M. Pablo-Sainz-Ezquerra, J. Cuya, B. Jeyadevan, S. Veintemillas-Verdaguer, P. Tartaj, M. del Puerto Morales. "Unravelling an amine-regulated crystallization crossover to prove single/multicore effects on the biomedical and environmental catalytic activity of magnetic iron oxide colloids" Journal of Colloid and Interface Science, vol. 608, pp. 1585-1597. 2022.
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Recovery and re-use of carbon fibers from recycled end-of-life epoxy based composites

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Carbon fiber composites stand out for their high specific stiffness and excellent strength-to-weight ratio. However, the exponential growth in carbon fiber composites use, with an annual increase rate of 10-12% per year, accelerates the need to develop recycling routes and implement strategies to re-use these fibers in other applications. Within this context, this work has achieved three major goals: Firstly, the optimization of the pyrolysis process to be applied for fiber recovery to cured carbon fiber reinforced epoxy matrix composites was conducted. The elastic modulus and fracture toughness of the recovered fibers were maintained. A 94% retention of tensile strength with respect to virgin carbon fibers was achieved

from this self-sustainable methodology. Furthermore, the use of recycled fibers reduces by half the price of composites and contributes to decreasing pollutant emissions.

Secondly, the implementation of manufacturing technologies to the re-use of the recovered carbon fibers to produce non-critical structural composite components was adapted:

Continuous fibers were introduced in thermoset matrix by a modified resin film infusion technique, ensuring the proper control of the reinforcement alignment and volume fraction. The tensile properties of the composites made with recycled fibers were identical to the same type of composites reinforced with virgin fibers.

Long fibers were used to reinforce thermoplastic resins through injection moulding. The enhancement in tensile and bending properties, with respect to the unreinforced materials, was superior to that found in literature.

Short fibers were evaluated as potential reinforcement of thermoplastic polymers in additive manufacturing processes.

Thirdly, the use of the recycled fibers for electrode fabrication in Li-S batteries was studied as a novel application. The fibers proved to constitute exceptional cathode materials due to their high cycling stability, superior to other carbon-based materials.

This work shows that the use of recycled fibers to produce new composite materials offers an environmentally friendly and performance-competitive alternative to current structural materials. Besides, it opens the opportunity to manufacture more economical composite components without compromising their mechanical properties, fulfilling the life cycle of lightweight carbon fiber reinforced polymer structures and reducing their carbon footprint, in agreement with the circular economy principles.

Novel sustainable materials for food preservation: starch-polyester bilayer films with phenolic acids for meat preservation

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The use of biodegradable, sustainable and active materials for the development of active food packaging is necessary in order to reduce the environmental impact of plastics.

In this study, sustainable and biodegradable bilayer materials were developed, based on starch and polyesters that allow the increasing generation of plastic waste and food waste to be addressed from the scientific field. For this, a natural biodegradable bioplastic such as starch and

a blend of two biodegradable polyesters known as PLA and PHBV obtained from natural resources were used. The PLA-PHBV polyester blend, the one that comes into contact with the food matrix, incorporated antioxidant and antimicrobial compounds of natural origin (ferulic, p-coumaric and protocatechuic acids) that slow down the physicochemical and microbiological phenomena that lead to degradation of the food. These phenolic acids were chosen because they are antioxidant and antibacterial components present in extracts obtained from agri-food residues and thus their use in active packaging follows the principles of circular economy. These active bilayers were characterized as to their mechanical and barrier properties and as to their performance as packaging materials for pork meat slices. The results showed that the incorporation of phenolic acids promoted the water vapour and oxygen barrier capacity of bilayers while reducing their stiffness and resistance to break, mainly in the case of protocatechuic acid. Phenolic acids significantly improved the antioxidant capacity of the bilayer films, reducing the lipid oxidation of packaged meat during storage. Phenolic acid loaded bilayers also reduced the microbial counts of meat, mainly for lactic acid bacteria. These effects positively affected the development of the sample pH and colour parameters throughout storage. Sustainable and biodegradable active starch-polyester bilayer films exhibited great potential as a means of extending the shelf-life and improving the quality preservation of pork meat.

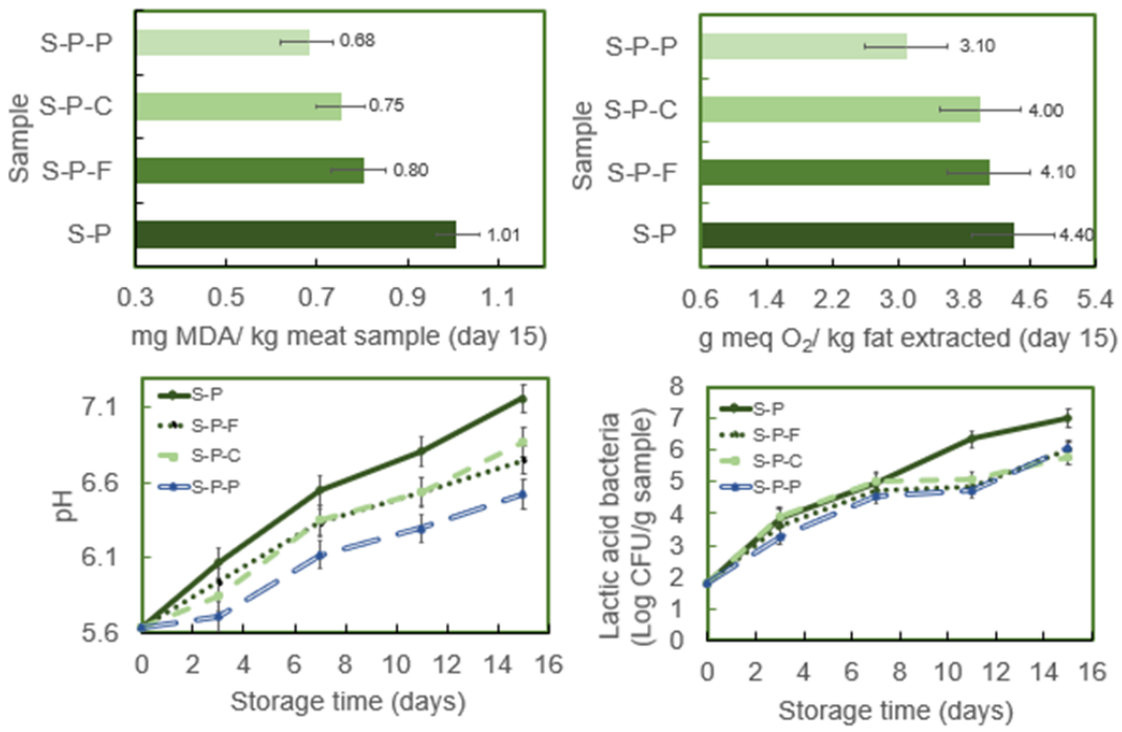

Figure 1. a) TBARs, b) Peroxide Index, c) Development of the pH and d) Microbial counts (lactic acid bacteria) of fresh samples (t = 0) and of those stored during 15 days at 5 ºC, packaged in bilayer films without phenolic acids (S-P), with ferulic acid (S-P-F), p-coumaric acid (S-P-C) and protocatechuic acid (S-P-P).

Circular economy in carbon fiber and glass fiber reinforced polymers recycling: recycled carbon fibers and glass fibers as reinforcement in composite materials

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The rapid growth in the application of carbon fiber reinforced polymer matrix composites (CFRPs) raises a challenge to waste recycling. CFRPs are being used in a variety of industries, from sports equipment to aerospace or pressure vessels. The need of recycling these materials is aligned with the objectives of a circular economy, in order to make manufacturing and recycling processes more efficient while minimizing the waste of CFRP composites at their end-of-life.

To this end, the present study covers the current technologies applied in recycling processes, as well as an analysis of the use of recycled fibers and recycled composite materials as reinforcement in CFRP, paying special attention to the adhesion between the recycled fibers and composite materials and the matrices containing them, since this adhesion is responsible for many of the mechanical properties of the composite. In addition, the compatibility of recycled fibers and composites with thermoplastic matrices, which result in carbon/glass fiber reinforced thermoplastic composites (CFRTP/GFRTP), is considered. For this purpose, the difference between using short, long, and continuous fibers, the matrix-fiber adhesion, the thermal behavior, and mechanical resistance, as well as the durability in aggressive environments of the thermoplastic composites are studied.

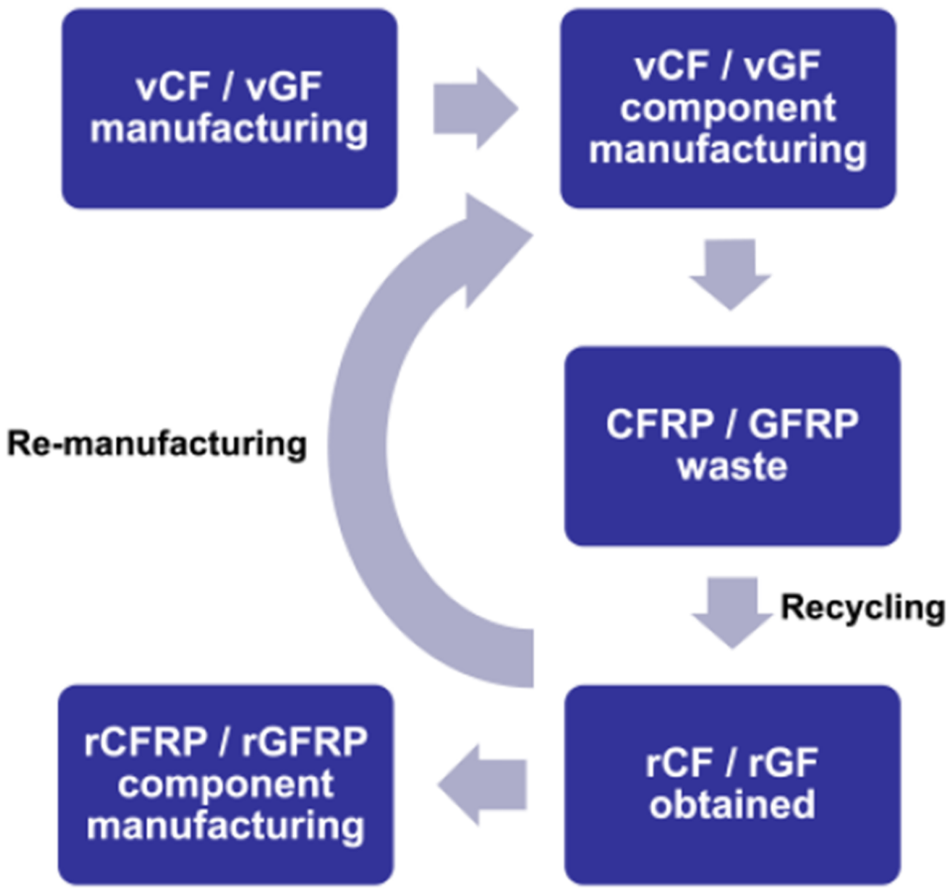

Figure 1. Circular economy in CFRP/GFRP recycling, where recycled carbon fiber and recycled glass fiber reinforced polymers (rCFRP/rGFRP) components are manufactured from recycled carbon and glass fibers

[1] J.A Butenegro, M. Bahrami, J. Abenojar, M.A. Martínez, "Recent Progress in Carbon Fiber Reinforced Polymers Recycling: A Review of Recycling Methods and Reuse of Carbon Fibers". Materials, vol. 14, pp. 6401. 2021.

IoT microbial electrochemical sensor: real time analysis of water quality

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Water reuse is a real and feasible solution for the problem of water scarcity in the framework of Circular Economy. Real time analytical tools are required to develop highly efficient and optimized wastewater treatments. Microbial sensors based on Electroactive Biofilms (EAB) [1] have been shown as one of the most promising applications for Microbial Electrochemical Technologies (MET). Recorded electric current is a direct measurement of metabolic activity of microorganisms, being sensitive to changes in organic matter content, temperature, and presence of toxic compounds.

Metabolic extracellular electron transfer activity [2] is proportional to the concentration of biodegradable organic matter (electron donor). There exists a good correlation between the electric current re-

corded as function of the organic matter content in wastewater streams (Fig.1B). This feature can be used in other applications such as: detection of acetate concentration in biotechnological processes; or as vigilance of water quality in natural water bodies.

Temperature variations affect the value of the electric current recorded through bioelectrochemical reactions taking place in bacterial metabolism. Regarding this relationship, any toxic compound that affects metabolic activity will be detected by the microbial sensor and identified as a sudden and deep decrease in the value of the electric current (Fig.1C). This is a unique and singular feature not available in any other kind of sensors used nowadays.

IoT Microbial Electrochemical Sensors have a high potential for their application in the field of wastewater treatments. They provide real time information about significant parameters like BOD, crucial for assessing the performance of wastewater treatments. Furthermore, these sensors are the only devices nowadays that can provide information about toxicity. This parameter will become key in the future reuse of treated wastewater.

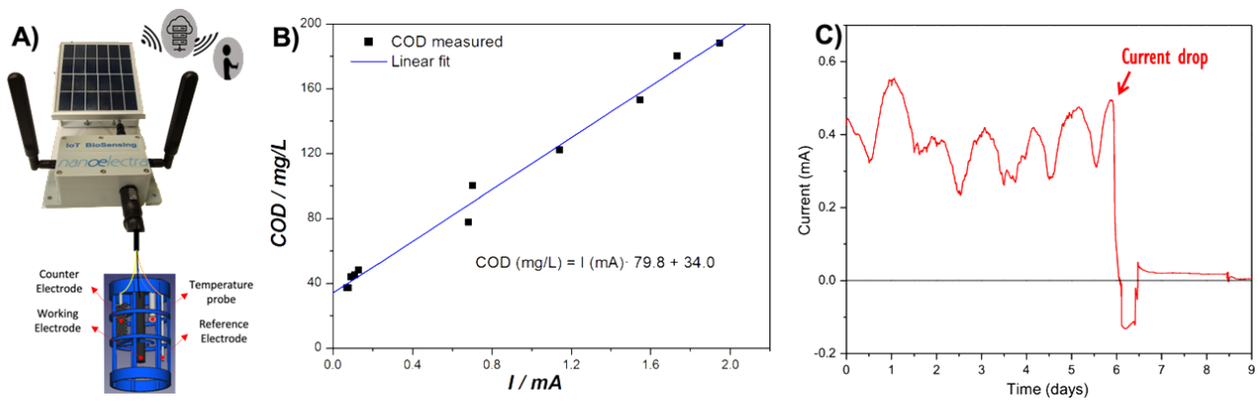

Figure 1. A) IoT Microbial Electrochemical Sensor. B) COD vs. electrical current plot. C) Effect of toxic compound presence over the IoT Microbial Electrochemical Sensor response.

- [1] O. Modin, F. Aulenta, "Three promising applications of microbial electrochemistry for the water sector" Environmental Science: Water Research & Technology, vol. 3:3, pp. 391-402. 2017.
- [2] D. R. Bond, D. R. Lovely. "Electricity production by Geobacter sulfurreducens attached to electrodes" Applied and Environmental Microbiology, vol. 69:3, pp. 1548-55. 2003

MANDALA strategy towards a circular model for multilayer packaging films

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Recycling multilayer plastic packaging is a major technological challenge. These materials constitute a substantial volume of packaging plastics, only 14% being recycled, with over 70% simply not recovered at all. Furthermore, despite their inherent value, virtually all packaging plastics (> 95%) are lost after one single use. Clearly, if Europe's ambition for a circular economy is to become a reality, this scenario must change dramatically. The European Commission's has defined the 'European Strategy for Plastics in a Circular Economy' to address this. However, implementation faces several sticky issues. A major challenge is that to improve performance, packaging materials are increasingly more complex, often incorporating mixed multilayer materials that are strongly bonded and almost im-

possible to recycle.

Possible solutions to this are: Firstly, create mono-material packaging that offers the same benefits as current multi-material films. Secondly, develop technologies to make separation and sorting of multi-material packaging easier. The MANDALA project [1] aims to deliver an innovative adhesive for multilayer products that enables sustainable solutions incorporating eco-design, dual functionality and end-of-life, and develop bio-based multilayer mono-material films to compete with existing packaging.

In the ICTP-CSIC we have developed a dual-functionality polyurethane resin (PUR)-based laminating adhesive that incorporates thermoreversible (TR) bonds that can be broken and reformed on the application of heat, Figure 1. This will facilitate recycling as an alternative to downscaling, landfill or incineration for multilayer multi-material films. Since PURs are by far the most employed laminating adhesives, this strategy aims to provide a drop-in solution to film providers with immediate applications in current packaging films based on petroleum-derived polymers, as well as for future bio-based polymer laminates. Furthermore, incorporation of radiation-absorbing nanoparticles into the adhesive provides remote triggering of bond breaking for easy implantation into dynamic recycling processes.

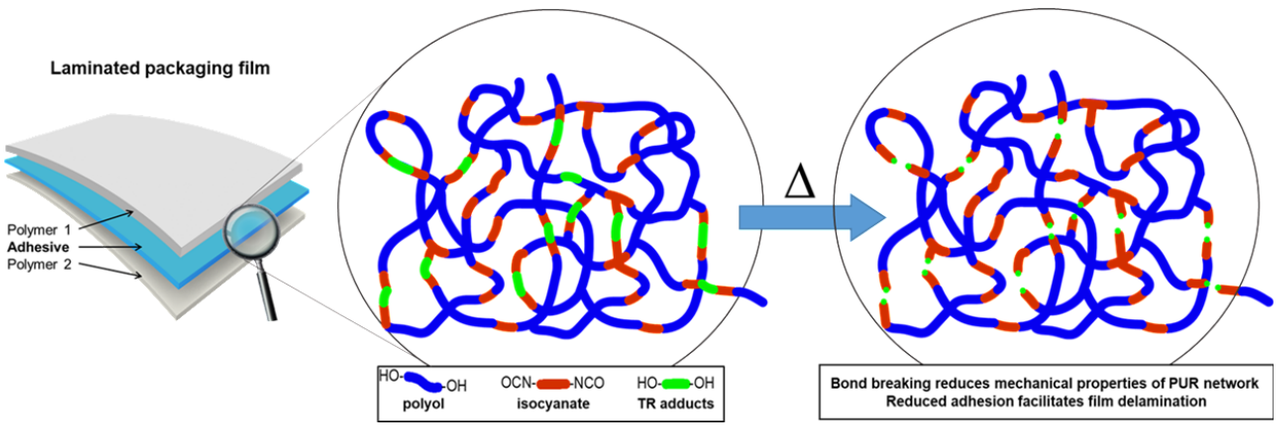

Figure 1. The MANDALA adhesive strategy

Acknowledgments:

Funding for MANDALA in the EU Horizon 2020 Research and Innovation Programme in the Bio-Based Industries Joint Undertaking (BBI-JU), Grant Agreement no. 837715.

[1] Mandalaproject.eu. "MANDALA a sustainable future for multilayer packaging." Available: https://mandalaproject.eu/

Hybridization of carbon fibers reinforced biopolymers with natural flax fibers: an opportunity for the circular economy

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Nowadays, global environmental safety, ecological concerns, recyclability, eco-efficiency, and economic factors are fundamental driving forces to increase the employment of bio-based materials [1]. Biocomposites are reinforced polymeric materials in which one of the matrix and reinforcement components or both are from bio-based origins. Recycling and utilizing these bio-based constituents are recognized as critical factors in circular economy (CE) development.

This study highlights the potential of hybrid biocomposite carbon/flax reinforced biodegradable thermoplastic polymer as an environmental-friendly alternative for similar carbon fiber reinforced polymer (CFRP) composites. Incorporating flax fibers in CFRPs would not only enhance the biodegradability of the entire composite system but also improve some of the mechanical properties [2]. In this regard, hybrid biocomposite materials made of Poly-Butyl-Succinate (PBS), flax and carbon fibers are fabricated by hot-press technique. The mechanical properties of the manufactured composites are compared with the un-hybrid ones. Results indicate that replacing one CF layer with FF layers leads to a hybrid composite with superior tensile and flexural properties. Accordingly, the manufactured hybrid biocomposites, which have recycling and reusing potential due to their biodegradable matrix and incorporated natural fibers, are able to enhance productivity and sustainability in the CE and robust the effectiveness of this concept.

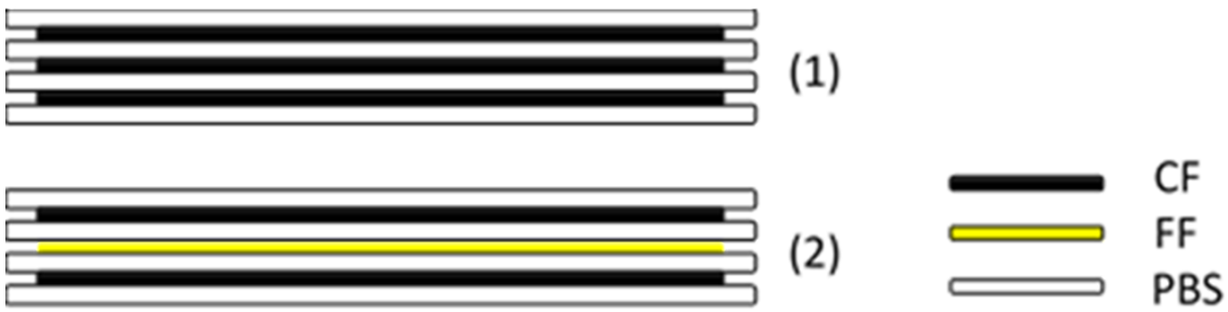

Figure 1: Manufactured composites configurations: (1) PBS-3CF, (2) PBS-2CF/FF

- [1] V. Shanmugam, R. Afriyie Mensah, M.Försth, G. Sas, A. Restás, C. Addy, Q. Xu, L. Jiang, R. Esmaeely Neisiany, S. Singha, G. George, Tomlal Jose E, F. Berto, M. S. Hedenqvist, O. Das, S. Ramakrishna. "Circular economy in biocomposite development: State-of-the-art, challenges and emerging trends," Composites Part C: Open Access, vol. 5, pp. 100138. 2021.
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Development and production of wires by powder metallurgical techniques for additive manufacturing

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Additive manufacturing (AM) allows the production of structural parts with very complex geometries. Wire Arc Additive Manufacturing (WAAM) is a type of direct process in AM that uses metal welding wire as the feedstock and an arc as the heat source. This technology, which is especially interesting for light alloys, is limited by the commercialisation of wires with specific compositions [1]. Nowadays its development continues to grow. The design of wires with new chemical compositions, characteristics and properties is necessary.

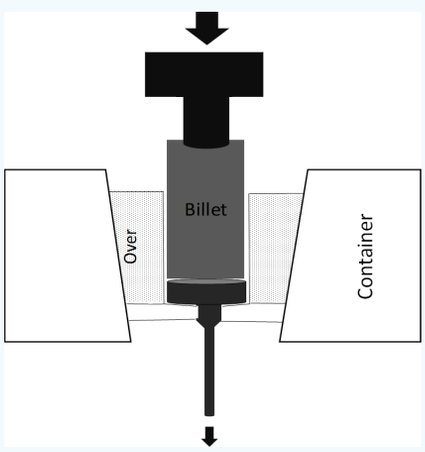


Figure 1. Direct extrusion process

In this work, Al-Cu-Li alloy wires belonging have been produced by a powder metallurgy route combined with extrusion (Figure 1): powder pressing and extrusion to obtain a bar. Al-Li alloys are used in the aerospace sector for their lightness, good specific resistance, ductility, and competitive cost [2]. Lithium is the only alloying element that increases strength and modulus while reducing density in aluminum alloys. Reducing weight means reducing fuel costs.

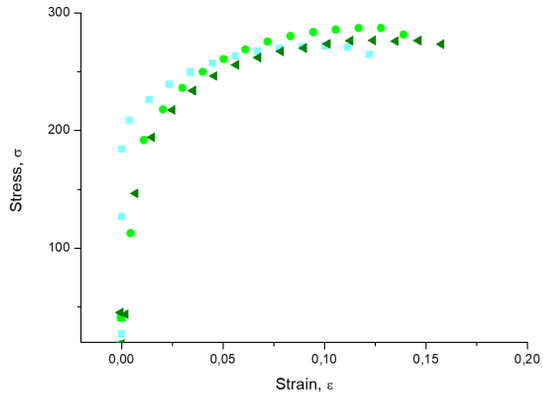


Figure 2. Tensile test on three samples obtained under the same conditions

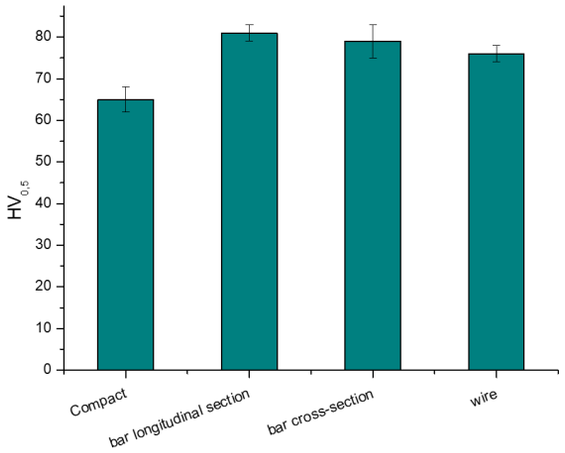
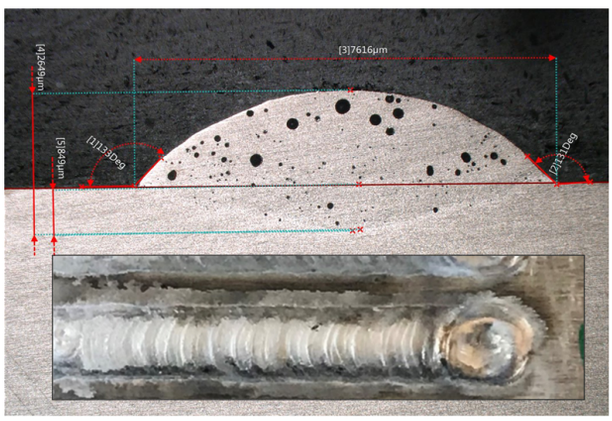


Figure 3. Vickers Hardness test 0.5 (500 g/f).



The tensile yield stress values are between 200-210 MPa and the ultimate tensile strength are between 270-290 MPa (Figure 2). The elongation values are important for obtaining the final wire by further steps of rolling and drawing. The ductility of the bars is (14±0.08) %.

As expected, all extruded products significantly increase hardness compared to that from the compact (Figure 3) due to all the phenomena involved in extrusion forming as the increase in strain hardening, orientation of grains, diffusion of the alloying elements and formation of new phases among others.

The wire was obtained from the bars by drawing and rolling process in collaboration with the company of Sintef Raufoss. The final tests were carried out by WAAM. Equipment parameters were optimized. The photograph of the beam and the microstructure are shown in Figure 4.

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Metal ions: from pollutants to applicable materials

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Heavy metals are a serious problem when dissolved in wastewater and their removal has been the subject of research for decades. The concentration of the metals can be very large depending on where we are. To reduce the toxicity associated with such metals, it is desirable to treat industrial effluents to decrease their concentrations and them to within permissible limits before being discharged into water bodies. One of the methods used is the precipitation of ferrites of the metals [1]. The procedure is simple and based on the addition of a Fe^{3+} salt and basic medium to water contaminated with metal ions, allowing the formation of metal ferrite. A similar process can be produced using an electrochemical methodology. The method consists of the oxidation of an iron sheet producing

Fe^{3+} ions in the medium and a cathode of iron where the generation of OH^- was produced by water reduction. With this methodology, it is possible to eliminate smaller amounts of ions from the medium, and it is possible to generate ferrites with tunable properties. Ferrites find applications in many fields, they are used in biomedicine in magnetic resonance imaging, drug delivery, hyperthermia, or sensors. However, their applications can be extended to the wastewater treatment [2]. A scheme of the electrochemical flow reactor is showed in Figure 1 [3]. In this work 100 ppm of metal ions and 40 mM NaCl were used as simulated pollutant solutions. Direct current of 0.7 A was supplied and the solution flowed by means of a peristaltic pump operating at 30 mL/min. The magnetically collected sample at the end of the experiments was washed several times and finally the product was characterized by different techniques (X-ray diffraction, Transmission electron microscopy, VSM).

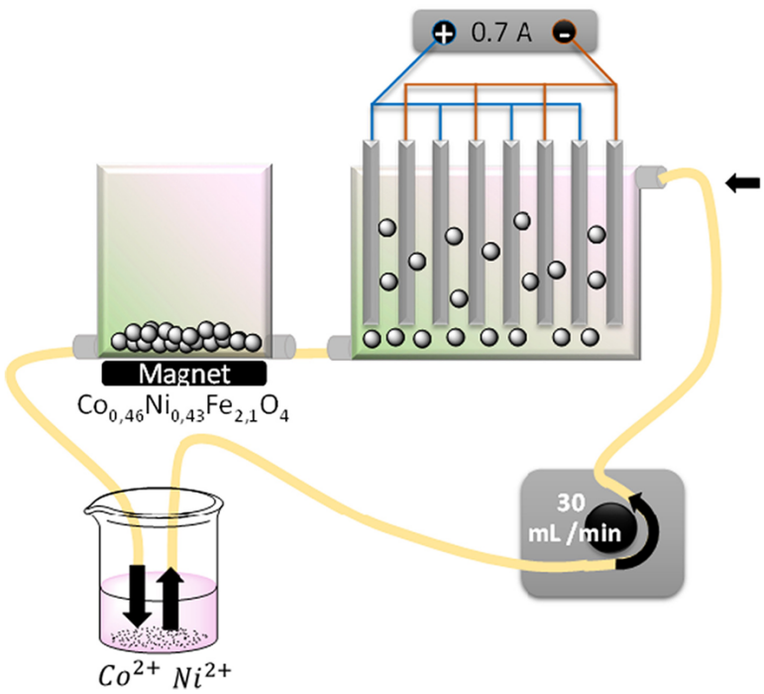

Figure 1. Scheme of the electrosynthesis of ferrites from water contaminated by metal ions

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The HMF, the key to green chemistry through the circular economy

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The circular economy is essential for the sustainability of our planet and is strongly linked to green chemistry and its principles, where not only the fact of using waste is important, but also the possibility of working at low or moderate temperatures, using green solvents and catalysts or working with systems capable of obtaining products with a high-added value in the most efficient and safe way possible.

In this work, two main objectives are studied: firstly, the use of lignocellulosic biomass residues to obtain its main components separately (cellulose, hemicellulose and lignin) after treatment with a green solvent. Secondly, use cellulose to obtain a very important product in the petrochemical industry, 5-Hydroxymethylfurfural (HMF), which is a precursor platform molecule for many high-added value compounds such as biofuels, solvents, resins, adhesives, coatings, additives and even bioplastics...

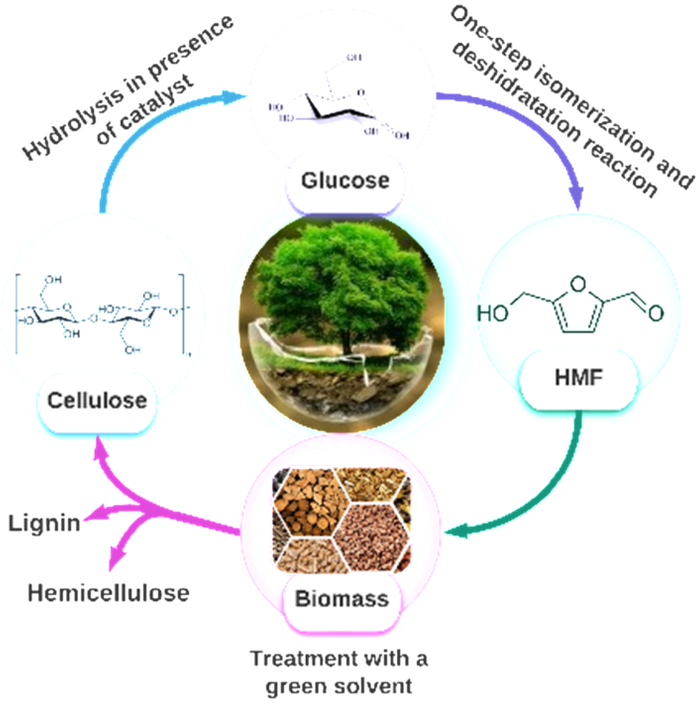

Figure 1. Scheme with the main objectives of the work applying principles of green chemistry.

As shown in the following scheme, from lignocellulosic biomass, a treatment will be carried out with green solvents that can be reused (ionic liquids [1] or inorganic salt hydrates [2]). After that, cellulose is recovered and will be used in acid hydrolysis to obtain glucose [3], then this sugar will convert to HMF in one-step in a second step. This transformation is catalyzed by a bifunctionalized heterogeneous catalyst with Lewis acid sites (LAS) centers based on Metal Organic Frameworks combined with Polyoxometalates like Brønsted acid (BAS). LAS catalyzes the glucose isomerization to fructose and BAS the dehydration of fructose to HMF [4]. This catalyst shows a high reusability.

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Tests on several sorbents for Neodymium recovery

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Rare earth elements (REEs) are valuable elements with applications in several technological fields: chemical engineering, metallurgy, nuclear energy, etc. [1], [2]. Not all of them can be considered rare in terms of abundance, but, rather, because of their accessibility, their separation and purification processes may be difficult and expensive [2]. Due to their characteristics and the increasing demand, the European Commission defined them as "critical elements". REEs include 14 lanthanides, among which there is the Neodymium (Nd). This element is currently used for permanent magnets, catalysts, lasers, etc. Given the economic value of REEs on a global scale, finding secondary sources becomes an urgent task: Red Mud (RM) is an abundant residue from Bayer process, and it may be

used for this aim, since it contains a high quantity of metals and REEs, including Nd [1], [3]. Green processes can be applied to extract metals and REEs from RM, followed by their recovery. Several studies have been conducted to recover REEs from the liquid phase: chemical precipitation, ion exchange, solvent extraction. Nowadays, biosorption has been recognized as a green alternative to recover elements from water since metals interact with the active sites present on the sorbents [4], [5]. This study aims to test several sorbents in recovering Nd from a synthetic aqueous solution. The sorbents tested were alginate, alginate with Fucus vesiculosus, gellan gum (all three as gel balls), powdered almond shells, sugar beet pulp and Fucus vesiculosus. Best results in terms of metal ion uptake (q (mg/g)) and metal adsorbed percentage (M %) were achieved with sugar beet pulp and alginate gel. A kinetic study was conducted on these two sorbents with two different concentrations of Nd, 20 and 100 ppm in 100 ml Erlenmeyer. With the highest concentration, a M up to 97% was reached for both the sorbents and a q of respectively 14 and 15 mg/g. The evolution of q over time was modelled with pseudo-first, pseudo-second order curves and Elovich model. The experimental values from sugar beet pulp tests fits linearly with pseudo-second order curve, alginate ones with pseudo-first order. All the sorbents were tested at 100 ppm in two different set-ups, in a thermoblock-shaker with 15 ml falcons and in 50 ml: the former showed worse results indicating that for such set-up the contact between the liquid phase and the sorbent is kinetically unfavorable.

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ENERGY APPLICATIONS AND MOBILITY

Sustainable synthesis of triphylite $NaFePO_4$ as positive electrodes for sodium-ion batteries: from materials to recycling

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$NaFePO_4$ with a triphylite structure is one of the most attractive materials for sodium ion batteries (NIBs) due to its high theoretical capacity, 154 mAh g^{-1}, with an average voltage of 2.95 V vs. Na^+/Na, which allows to design batteries with a high theoretical energy density (450 Wh kg^{-1}). $NaFePO_4$ is analogous to $LiFePO_4$[1], a commercial material for low-cost lithium ion batteries (LIBs), with safe voltage and excellent capacity and performance [2,3].

In spite of being a material based on abundant and low-cost materials, the main drawback of $NaFePO_4$ is that it cannot be synthesized as triphylite phase by a direct method, being *maricite* [4] the thermodynamic stable phase, which was known to be poorly active electrochemically (although recently its electrochemical activity has been reported, but always with worse performance than *triphylite*) [5]. Therefore, the only way to obtain *triphylite* $NaFePO_4$ is from the extraction, whether chemical or electrochemical, of lithium from $LiFePO_4$, obtaining $FePO_4$ followed by the insertion of sodium. Up to this date, the process has been performed using expensive and/or toxic reagents, which were difficult to handle ($NOBF_4$ and NaI), being required the use of an inert atmosphere [2,3] or alternative indirect methods of low industrial applicability [6,7]. In order to make this material suitable for commercial development as cathode for NIBs, it is required to lower costs using economic and eco-friendly reagents, along with simple and scalable synthesis methods, as shown in this work. Moreover, the possibility to recycle $LiFePO_4$ batteries and reuse its positive electrodes is presented, detailing how to decrease the costs of LFP recycling [8] while also reducing the environmental impact and encouraging sustainability.

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Novel biphasic multiblock copolymers for fuel cells: A new strategy to prepare proton exchange membranes for clean energy generation

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The climate change is a serious problem worldwide. Many governments are trying to solve this issue by creating, among others, new regulations to eliminate the CO_2 emissions from fossil fuels [1]. Hydrogen fuel cells are promising devices to obtain clean energy because the final product is water [2]. The electrolyte in polymeric membrane fuel cells is a polymeric membrane which has two main goals, it is a separator between anode/cathode and is also responsible of

the proton transport [3]. In this work, a series of proton exchange membranes based on multiblock copolymers with three polysulfone and polyphenylsulfone (PSU/PPSU) ratios (5/5, 6/4 and 7.5/2.5) has been synthesized and characterized. To prepare conductive materials, sulfonated copolymers were prepared. For that, a polymer:sulfonating agent ratio of 1:9 has been used. A selective sulfonation of the PSU blocks was observed by means of ^{1}H-NMR analysis and ion-exchange capacity values. Thus, in the copolymers with a higher proportion of PSU (6/4 and 7.5/2.5) the PSU unit has the highest percentage of sulfonic groups and achieving a separation of hydrophilic and hydrophobic domains which is observed by SEM. The water uptake capacity was higher in these materials (WU% values at 60 ˚C are 31.2 and 57.3% for SPES 5/5 and SPES 7.5/2.5, respectively) while the tensile strength (56 and 40.6 MPa for SPES 5/5 and SPES 7.5/2.5, respectively) report high values. The behavior of the novel material in the membrane electrode assemblies (MEA) improves with increasing the proportion of PSU in the copolymer. Ionic conductivity of SPES 7.5/2.5 membrane measured in situ ranges from 28 (at 30 °C) to 31 mS cm^{-1} (at 80 °C). The maximum power density of this membrane is 621 mW·cm^{-2} at 80 °C and 100% RH. This value is the same order of magnitude than that observed for the commercial membrane Nafion 112 was 922 mW cm^{-2} and clearly higher than those betterment for SPES 5/5 (400 mW cm^{-2} a 70 ˚C y 100%) (Figure 1). So, an improvement of this material in terms of performances in fuel cells is obtained.

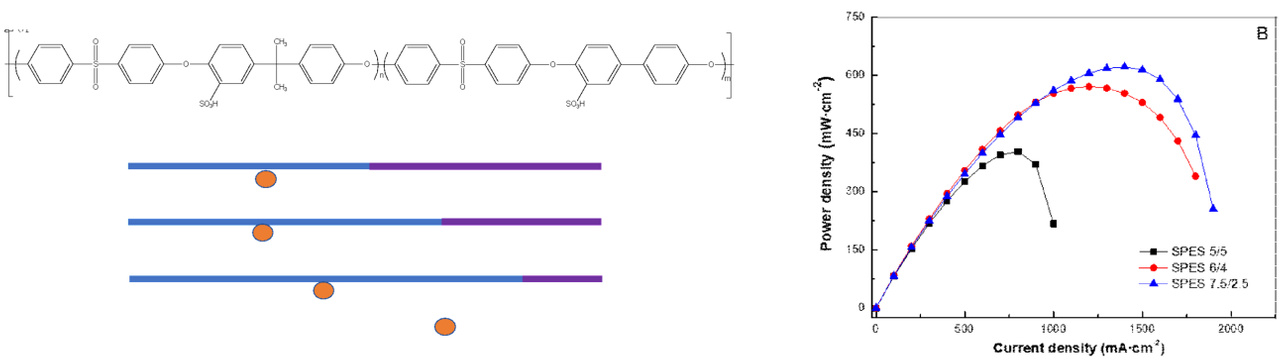

Figure 1. Copolymer proportions and power density results.

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Towards the search for solutions to achieve sustainable development goals 7, 11 and 13: New eco- efficient materials for solar thermal energy storage

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This work focuses on the search for new solutions to improve the mitigation of climate change as well as the commitment to renewable energies. Therefore, the research is in line with three of the objectives of Sustainable Development (**SDG 7, SDG 11 and SDG 13**). The construction sector should be rethought, as cement production implies not only high CO_2 emissions (5-7% of the total), but also for the high water consumption and high fossil fuel use, which represents

about 12-15% of the total energy consumed in the industry [1,2]. This work proposes to develop new eco-friendly materials (alkali-activated and hybrid materials) composed by **industrial by-products** (blast furnace slag, fly ash) that strongly reduce the use of Portland cement (PC). Besides, because of abiotic depletion, eutrophication, acidification [3] or CO_2 emissions [4], fine aggregates (sand) should be replaced, and this work proposes the use of **common wastes**, such us **recycled glass, mattresses and steel, textile, and rubber from tires**. Waste recovery will help to avoid waste accumulation in landfills or its incineration promoting the circular economy. Early life cycle assessment (LCA) studies of the alternatives indicate a carbon footprint improvement of more than 100% comparing to PC systems (Figure 1 (a)) [1]. Moreover, they are suitable for use as a thermal energy storage (TES) medium, in concentrated solar power (CSP) technology. The simulation results show that the new systems present a higher heat transfer rate compared to the conventional PC system (Figure 1 (b)).

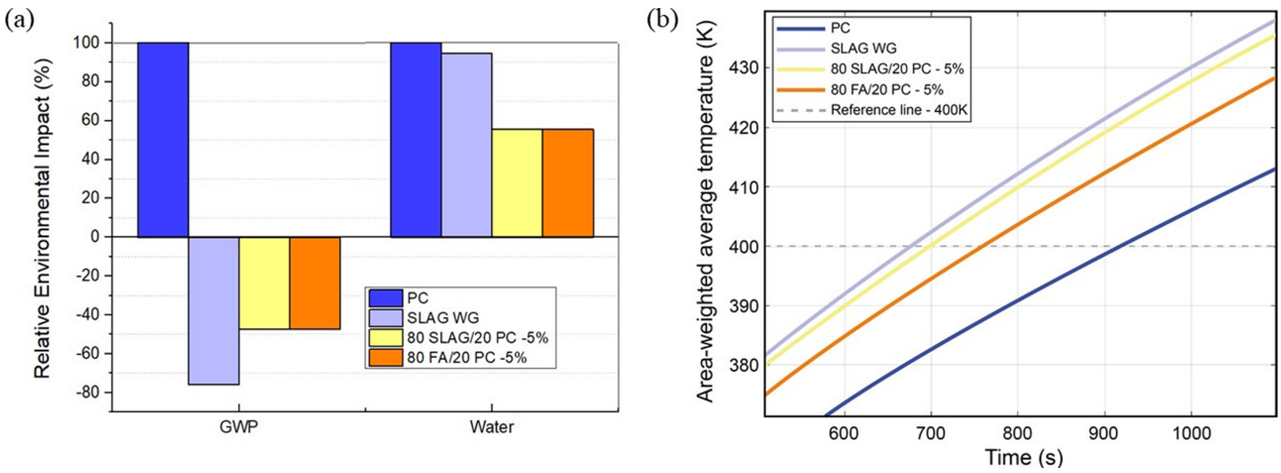

Figure 1. (a) Relative environmental profile (%) of the case studies. (b) Comparison of time among mortars to reach a certain temperature (for example, 400 K).

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Metal phosphide nanoparticles for the hydrotreatment of methyl laurate to produce green liquid fuels

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The production of green diesel by catalytic deoxygenation (hydrotreating) of waste vegetable oils could have a great impact on the transition to a circular economy, less dependent on fossil fuels and less polluting. One of the most promising active phases for hydrotreatment processes are transition metal phosphide nanoparticles (NPs). This work aims to test the activity of catalysts based on phosphide NPs supported on silica in the hydrodeoxygenation of methyl laurate (model compound for waste oils).

Ni and Ni-Mo phosphide NPs ($Ni_{1.6}Mo_{0.4}P$ and Ni_1Mo_1P) have been synthesized by a facile molecular precursor route[1]. Prepared NPs were characterized by chemical analysis, TEM and XRD. TEM anal-

ysis indicates the formation of spherical NPs with a narrow distribution. XRD results showed that the peaks of the Ni^2P phase were shifted to a lower Bragg angle, indicating an expansion of the crystal structure due to the insertion of Mo in the structure. These results suggest the formation of bimetallic metal phosphides NPs. The NPs were incorporated into silica support by incipient wetness impregnation of NPs solution. A reference MoP/SiO_2 catalyst was prepared by wet impregnation on silica using Mo and P precursors dissolved in water followed by in situ reduction to form the phosphide[2]. The prepared catalysts were tested in the hydrodeoxygenation (HDO) of methyl laurate to hydrocarbons at two different reactant flows and temperatures (Figure 1). Ni^2P and $Ni^{1.6}Mo^{0.4}P$ catalysts showed low catalytic activity at both temperatures and flows whereas MoP and Ni^1Mo^1P were very active catalysts. The comparison of activity between Ni phosphide monometallic catalyst and Ni-Mo bimetallic catalysts prepared by the molecular precursor route points out a synergy for bimetallic catalyst with a certain Ni-Mo ratio. With increasing the temperature from 300 up to 350ºC the activity of all the catalysts increased but showed a clear deactivation with reaction time. With decreasing the space velocity from WHSV= 5.22 h^{-1} (LHSV= 6 mL/g/h) to WHSV= 2.61 h^{-1} (LHSV= 3 mL/g/h), the activity of all the catalysts also increased but less than with the increase of the temperature.

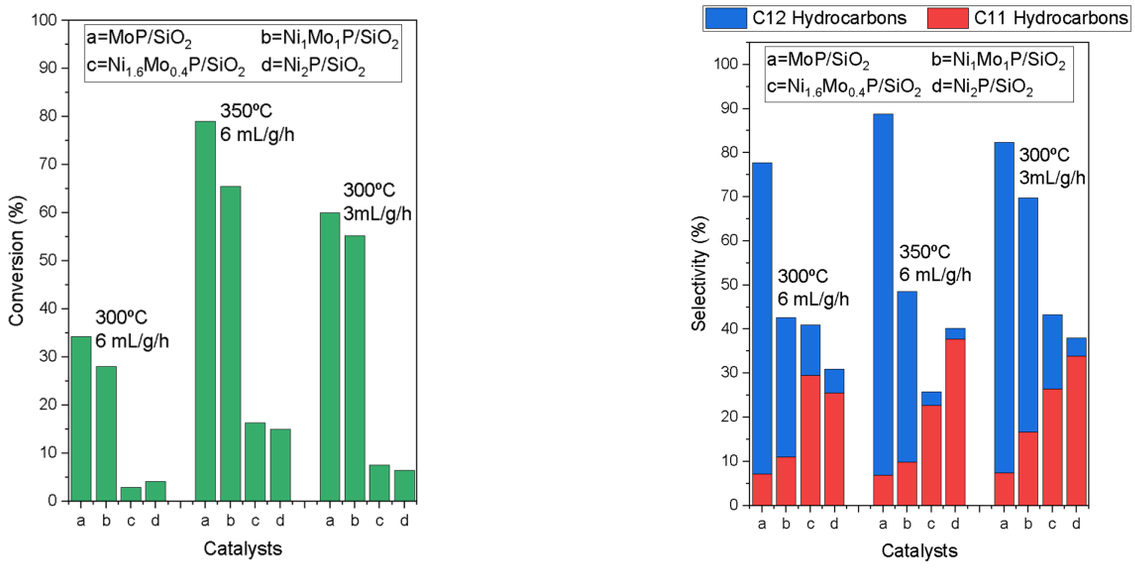

Figure 1. Average conversions and selectivities for HDO of methyl laurate.

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Biomass derived mesoporous carbons for their application as electrodes in supercapacitors

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Supercapacitors (SC) are an increasingly popular technology due to their advantages of high power density, stability, and short charge-discharge times compared to other energy storage devices. The main problem lies with electrode production involving the use of silica templates and toxic chemicals for their removal. As an alternative, sustainable mesoporous carbons (MCs) can be produced from polysaccharides directly as monoliths or powders. Herein we present on the synthesis of a starch-based MC, Starbon® produced via gelation, retrogradation and pyrolysis for use as a SC electrode.

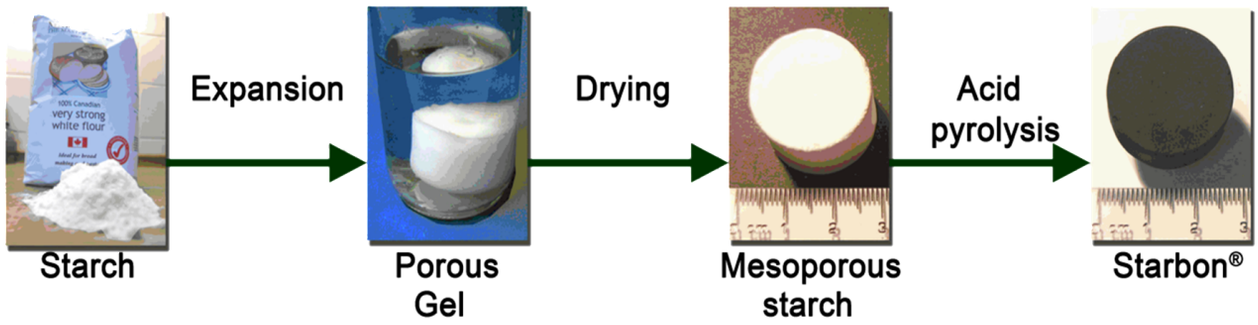

Figure 1. Starbon® fabrication process

Aqueous solutions of starch and graphite oxide (GO) were agitated and heated in a microwave to form a gel. This was then poured into moulds, retrograded and pyrolysed at 800ºC, to form Starbon® monoliths. Porosimetry, microanalysis, TGA, SEM, conductivity, Raman spectroscopy and electrochemical (EC) testing were performed.

Table1. Textural properties of Starbon® at different GO %.

GO (w/w)	0%	0.5%	3%	5%
BET surface area (m^2/g)	202	264	215	160
Micropore volume (cm^3/g)	0.083	0.110	0.090	0.060
Mesopore volume (cm^3/g)	0.287	0.333	0.310	0.279
Pore diameter (nm)	0.748	0.760	0.860	0.870

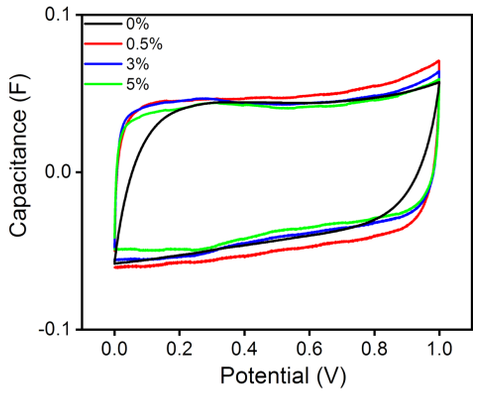

Figure 2. CV results.

A two-electrode EC cell containing H_2SO_4 2M as the electrolyte was subjected to cyclic voltammetry (CV), galvanostatic charge/discharge cycles and impedance spectroscopy tests. GO addition results in increased conductivity that combined with the mesoporous character of the samples, led to a capacitance of 198 F/g. Good energy (27 W·h/kg) and power density values (3067 W/kg) proved them to be sustainable and cost effective alternative energy storage materials.

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Application of Tape-Casting and Hot-Pressing for obtaining Solid State Electrolytes: Towards Sustainable Sodium Batteries

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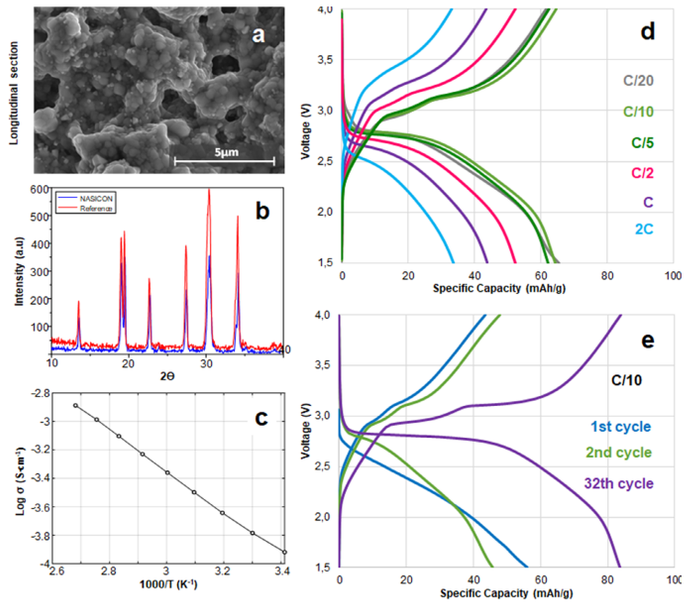
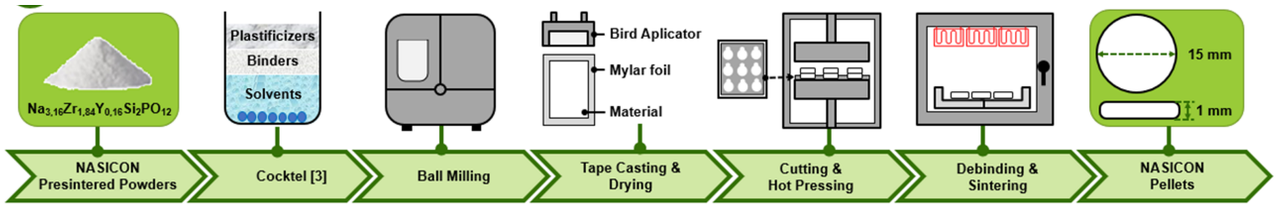
The intermittent behavior of renewable energies requires efficient and sustainable storage systems [1], [2]. Given its abundance, low cost and physical-chemical similarities with lithium, sodium-ion batteries are being re-visited as the alternative. In this work, we propose a new methodology to develop NASICON ($Na_{3.16}Zr_{1.84}Y_{0.16}Si_2PO_{12}$) based electrolytes (Figure 1) in order to solid-state sodium batteries, which allows increasing safety (elimination of flammable organic liquids and establishment of a mechanical barrier to prevent dendritic growth), the electrochemical window and the volumetric density.

Scanning electron microscopy (SEM) shows a material well sintered, with a highly porous and uniform microstructure (Figure 2.a). Hardness has been evaluated by Vickers micro-hardness, giving a value of 325±20 HV, a value higher than that reported for similar electrolytes processed by uniaxial pressing [4]. X-ray

diffraction (XDR) verified the presence of the monoclinic NASICON phase (Figure 2.b). Ionic conductivity (Figure 2.c) was characterized by electrochemical impedance spectroscopy (EIS) as a function of temperature, with values from 0.12 $mS{\cdot}cm^{-1}$ (20ºC) to 1.25 $mS{\cdot}cm^{-1}$ (90ºC). The manufacturing process allows to obtain a robust, strong, and uniform solid electrolyte with a improve interface with the electrodes. This presents high hardness, which not only avoids fracture during coin-cells assembling but also hinders dendritic growth, increasing safety and extending the life of the battery. The capacity at slow c-rates is ~80mAh/g (Figure 2.e) so the NASICON-based solid-state sodium battery can be a potential alternative for static storage applications, getting safer, efficient, sustainable, and environmentally friendly energy storage systems that promote an appropriate transition to cleaner energies.





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Modification and structural characterization of different aniline derivatives to be used as electrolytes in calcium ion batteries

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Li-ion batteries have been widely used in electrical power supply networks from renewable energies to reduce fluctuations in supply. They are characterized by their high energy density; nonetheless, in 2018 lithium was classified as critical raw material due to its abundance (20ppm on the Surface of earth) and its distribution (71% of global reserves are found in the lithium triangle: Argentina – Chile – Bolivia, leading the scientific community to develop rechargeable batteries using

more abundant and better distributed elements. [1]

The replacement of lithium by calcium in the negative electrode brings with itself important advantages such as the increase in the capacity, voltage and energy density of batteries, it also improves safety in the operation of battery [2]. To make possible the CaBs batteries implementation, it is necessary to design calcium-based electrolytes that successfully allow the reversible calcium plating/stripping at room temperature.

Different attempts of modifying the substituents in 3,5-difluoraniline y 2,6-dichloro-4-nitroaniline to insert linear chains of PEGME were tried in order to enhance mechanical properties. Diverse conditions of base, temperature, nucleophile and solvent were proposed without any success.

Three anilinyl-perfluorosulfonamides were synthesized, two of them: N-(3,5-diclhorophenyl)-1,1,1-trifluoromethanesulfonamide and 1,1,1-trifluoro-N-(4-nitrofenyl) methanesulfonamide were obtained as pure substances; nonetheless, the yields of their synthesis were 17% and 31.9% respectively; the third anilinyl-perfluorosulfonamide synthesized (N-(2,4-dinitrofenil)-1,1,1-trifluorometanosulfonamide) could not be separated from its bis-substituted byproduct.

From anilinyl-perfluorosulfonamides, calcium salts were synthesized using THF as solvent and $Ca(OH)_2$ as calcium source, thermal stabilities of respective salts were studied between -100 and 120°C, in this temperature range no melting point was observed. Based on these results it can be concluded that a possible electrolyte material, stable in the operation temperature range for calcium ion batteries was synthesized.

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Using metal-organic framework MIL-88a for green energy technologies

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Electrochemical energy storage (batteries, supercapacitors) and conversion (fuel cells, FCs) are currently the best solutions to reduce global CO_2 emissions from fuel combustion. Hydrogen fuel cells have been proposed as promising energy sources for a variety of applications such as transportation, stationary energy, and even portable devices [1, 2]. One of the most promising types is proton-exchange membrane fuel cells (PEMFCs) based on cathode, anode and electrolytic proton exchange membrane (PEM) [3]. The functions of membranes in PEMFCs are to afford channels for proton migration and transport, to separate gas reactants, and to insulate electrons [4]. An ideal membrane would be one with high proton conductivity under low humidity conditions and good electrochemical and mechanical stability. The most important property of membranes is their ability to retain water, because the conductivity of membranes directly depends on the level of hydration of the membrane. The use of metal-organic frameworks (MOFs) in the synthesis of polymeric membranes can improve its properties due to their high specific surface area and large pore size. For example, MOF MIL-88a is composed

of iron trimers (Fe_3O) that are linked together by fumaric acid. The honeycomb structure and composition allow MIL-88a to change its crystal structure and pore diameter from 13Å to 10Å by changing the temperature of the MOFs and the presence and type of guest molecules. This property allows to control the sorption capacity of MIL-88a, a requirement to be used for filtration, storage and separation of liquids and gases.

In this work, metal-organic framework structure MIL-88a was used to modify novel proton exchange membrane composed of Polysulfone (PSU) and Polyphenylsulfone (PPSU) poly(ether sulfone) segments (SPES). A complete characterization of obtained material was carried out to determine the efficiency of using this material in fuel cells and batteries. Thus modification of SPES membranes with MIL-88a increase it water uptake from 24% to 53% at 30°C and ion conductivity from 15,8 mS/cm to 26,5 mS/cm at 90°C and relative humidity equal to 90%. At the same time, the synthesized membrane was tested on a hydrogen fuel cell, where the power density reached 1040 mW/cm² under operating conditions (Figure 1). So these hybrid membranes can be proposed to be used as solid electrolyte in hydrogen fuel cells.

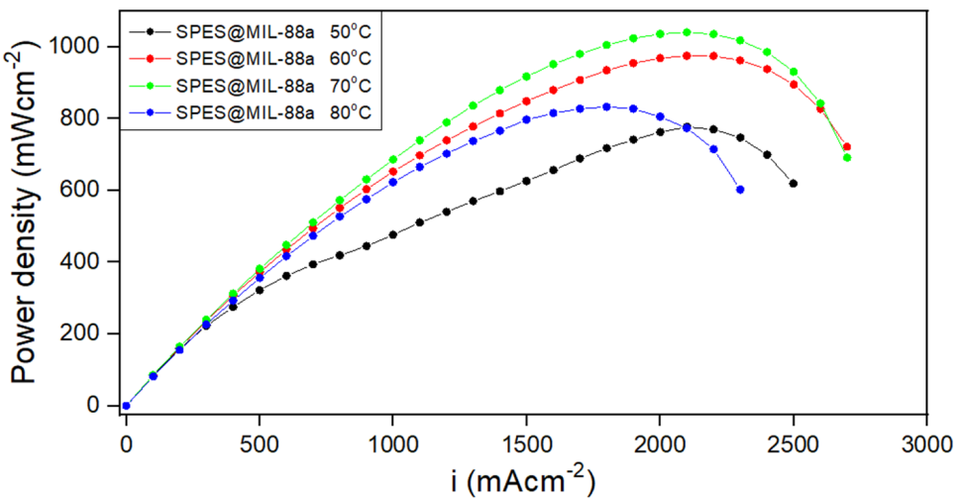

Figure 1. Power density curves of SPES@HKUST-1 membrane at 50, 60, 70, and 80 °C and 100% RH.

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Manufacture of $LiFePO_4$ electrodes for lithium-ion batteries by 3D

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The additive manufacturing technique known as Fused Filament Fabrication (FFF) is an interesting method for manufacturing ceramic parts with complex shapes. A conventional plastic printer is used to produce pieces starting from a filament made with ceramic powder and a sacrifice polymer, which is subsequently removed, and finally, the piece is sintered. The simplification of the manufacturing process reduces operating costs and production times, while also increasing design flexibility.

The main objective of this work is the fabrication of thick ceramic electrodes for Li-ion batteries by 3-D printing. With these electrodes, the amount of electrochemically inactive components is reduced, which reduces the amount of waste generated by a battery at the end

of its useful life. In addition, having fewer components simplifies the recycling process. Reducing electrochemically inactive components increases the energy density of the electrode and also reduces the steps of cutting and stacking the electrode sheets.

$LiFePO_4$ (LFP), a cathodic material, will be used as the active component of the electrode. For this purpose, we will carry out the design and manufacturing of thermoplastic filaments to the assembly and launching of the batteries with printed electrodes.

LFP filaments were extruded with high dimensional accuracy (Figure 1) (1.760 ± 0.004 mm in diameter) and were capable to be coiled on reels. Several printing tests were carried out until the optimal conditions for the manufacturing of the electrodes were established.

The removal of the binder system and sintering was carried out in an inert atmosphere. The extruded filaments and the green and sintered pieces were microstructurally characterized by scanning electron microscopy (SEM) (Figure 2).

Finally, its electrochemical behavior in lithium half-cells was studied using LFP discs of different thicknesses.

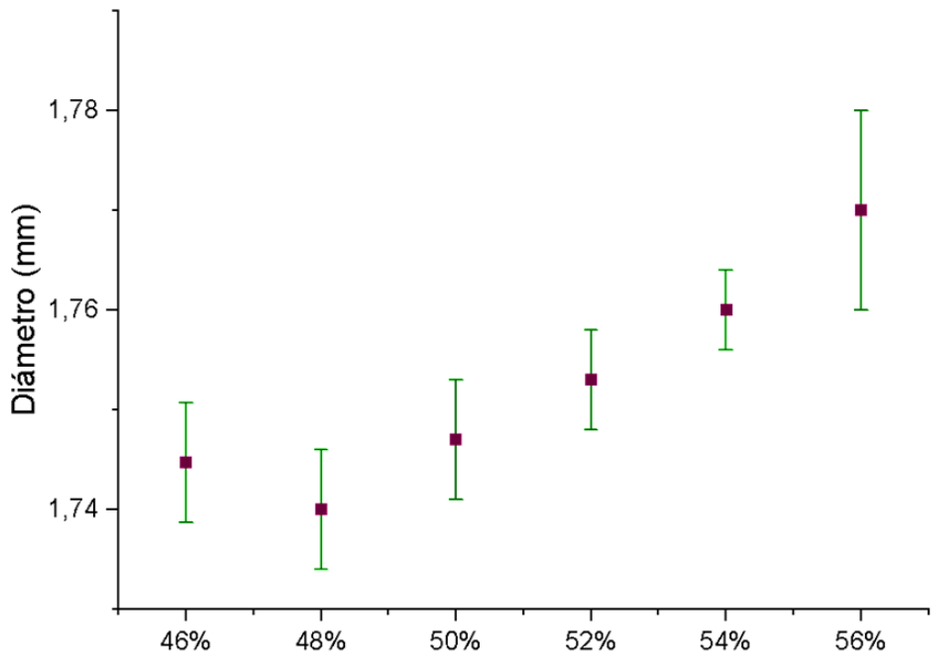

Figure 1. Average diameter of filaments at different percentages of ceramic load.

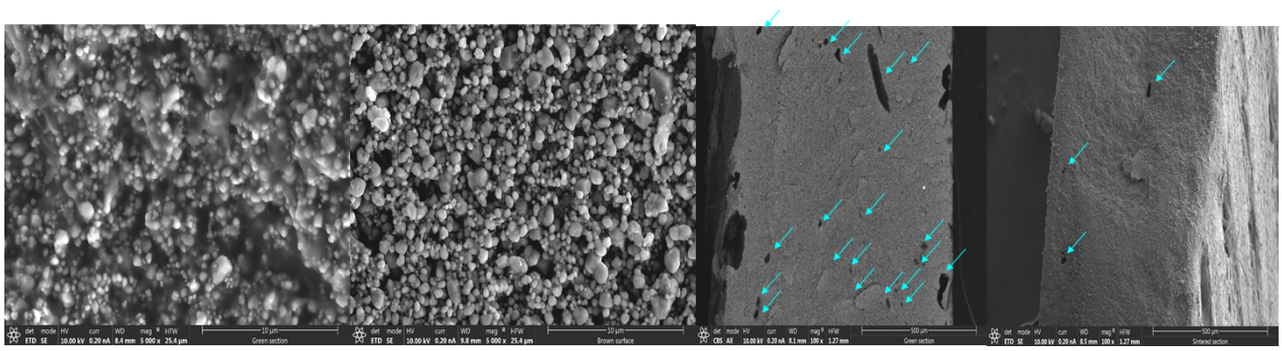

Figure 2. Microstructure of printed electrodes (5000 x).
a) Green; b) Brown. Cross section (100x). c) Green; d) Sintered.

Carbon-based monoliths with improved thermal and mechanical properties for methane storage

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Porous materials have been widely applied for a number of cutting edge processes, from gas adsorption/separation, sensors, drug delivery, etc [1,2]. The excellent performance of these materials is based on the presence of a widely developed porous structure and, in some cases, a perfectly tailored surface chemistry. However, bridging the gap from fundamental studies to a potential industrial application of these materials is not straightforward and, indeed, some limitations are still on the ground and require further investigation [3]. One of these limitations concern the densification of these powder samples into pellets, monoliths or any other shape. The conformation of these porous networks is mandatory i) to minimize pressure drops in gas and liquid-phase adsorption processes, ii) to facilitate the manipulation of the material (charging and discharging), iii) to densify the samples and iv) to minimize environmental and health issues due to particulates. For instance, the conforming step is extremely important for gas adsorption/storage applications due to the necessity to trap a large amount of a target molecule (e.g., CH_4, CO_2 or H_2 storage in porous solids) in a

minimum volume (for instance, in automotive applications) [4,5].

A series of activated carbon monoliths have been prepared from petroleum residue using KOH as activating agent. Activated carbon powder have been conformed into monoliths using a small amount of a binder (5 wt.%), either carboxymethyl cellulose (Figure 1a) or polyvinyl alcohol (Figure 1b), with proper mechanical properties. Incorporation of graphite or graphene in the initial formulation does not alter and/or modify the textural properties of the original activated carbon. However, once conformed into monoliths, the presence of graphite or graphene allows to improve i) the packing density of the monolith (up to 0.52 g/cm^3), ii) the mechanical properties of the monoliths (compressive strength up tp 12.3 MPa) and iii) their thermal conductivity (up to 0.49 W/mK) without compromising the methane storage capacity (ca. 100 V/V).

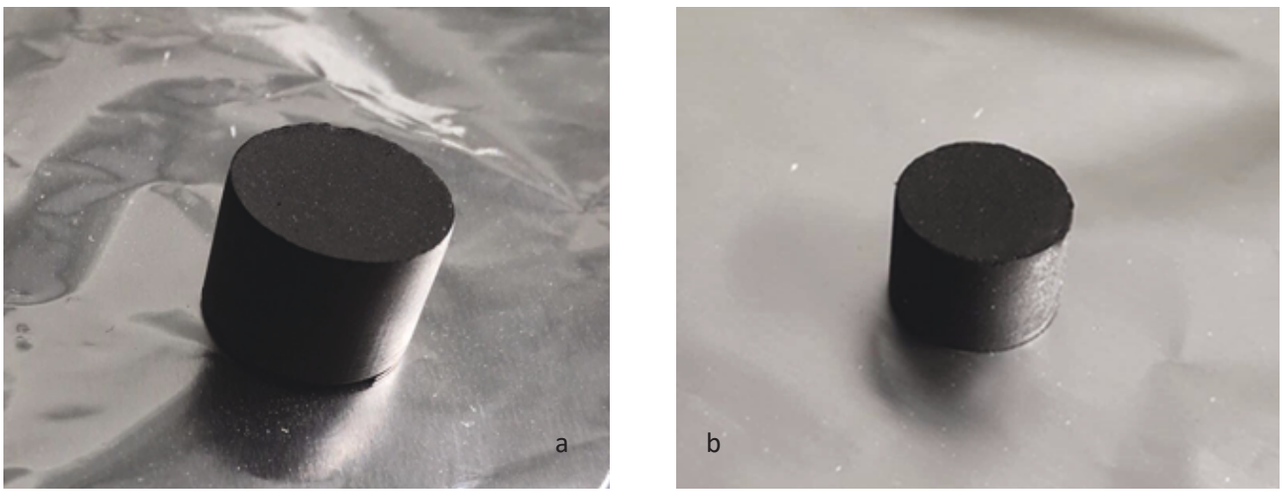

Figure 1. Images of a typical carbon monolith synthesized using 5 wt.% of carboxymethyl cellulose (a) or polyvinyl alcohol (b) as a binder (i.d. 1.3 cm; height 0.7-0.8 cm) and 74 MPa of conforming pressure.

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Dynamic analysis of Mobility as a Service using Big Data (MaaS)

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City densification processes has led, and could continue to increase dispersed development patterns, known as urban sprawl, making it more difficult to serve and cover all areas with public transportation. Consequently, poorly-served areas will tend to have an intense use of private automobiles, causing more congestion/pollution. To tackle this unsustainable pattern, new strategies and development models have emerged. Transit oriented and smart city development, as well as the sharing economy are all frameworks were public policy uses a fully-user, rather than car-oriented, perspective. In this context, a high ssmartphone penetration, fast development of mobile payment systems, positioning systems (GPS and geolocation) and the internet of things (Big Data, cloud computing, information processing and widespread data connectivity) that have enabled new apps and services to thrive in many sectors, and especially in transportation with shared mobility.

Shared mobility has been defined as the short-term access to shared vehicles according to the user's needs and convenience, instead of requiring vehicle ownership (Shaheen, Cohen, & Zohdy, 2016). Shared mobility services increase travel options, offering the possibility to rent motorcycles, bicycles and scooters for a certain amount of time, without the need to own a car or reducing car-dependency. Moreover, with the introduction of new

applications, there is an increasing need to have a centralised, easy-to-use application to handle all the different transport services. This need has given birth to the concept of Mobility as a Service (MaaS). Nevertheless, with both concepts (shared mobility and MaaS) still in its nascent stage, the analysis of their demand is scarcely addressed in scientific literature, providing a burgeoning new sub-field with numerous avenues of exploration, which conforms the main contribution of this investigation. This topic is of high relevance, especially after the COVID-19 pandemic, which has radically changed our mobility patterns and travel behaviour. Therefore, the objective of this research is to conduct spatiotemporal analyses based on GPS trip datasets from different shared mobility services in order to understand their demand and spatial patterns. Based on this knowledge, we could better inform public policy oriented to offer adequate infrastructure to achieve more sustainable mobility patterns.

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Hierarchically organized catalytic materials to obtain high added value products

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This research group reported a method for producing hierarchically nanodispersed catalysts by means of nanodispersion and anchoring of nanoparticles or nanoparticulate clusters (<100 nm) on the surface of micrometric scale supports, using a process of low energy dry dispersion, free of residues and without organic solvents. The catalysts prepared at room temperature made by mixing oxides of different nature are characterized in that they have novel nanoparticle supporting interfaces capable of generating new reactive surfaces that promote high activity and catalytic selectivity in the production of fine chemical intermediates (Figure 1). The thermal treatment of these catalytic systems induces the formation of stable crystalline species, generating catalytically inactive interfaces and reducing the number of free active sites.

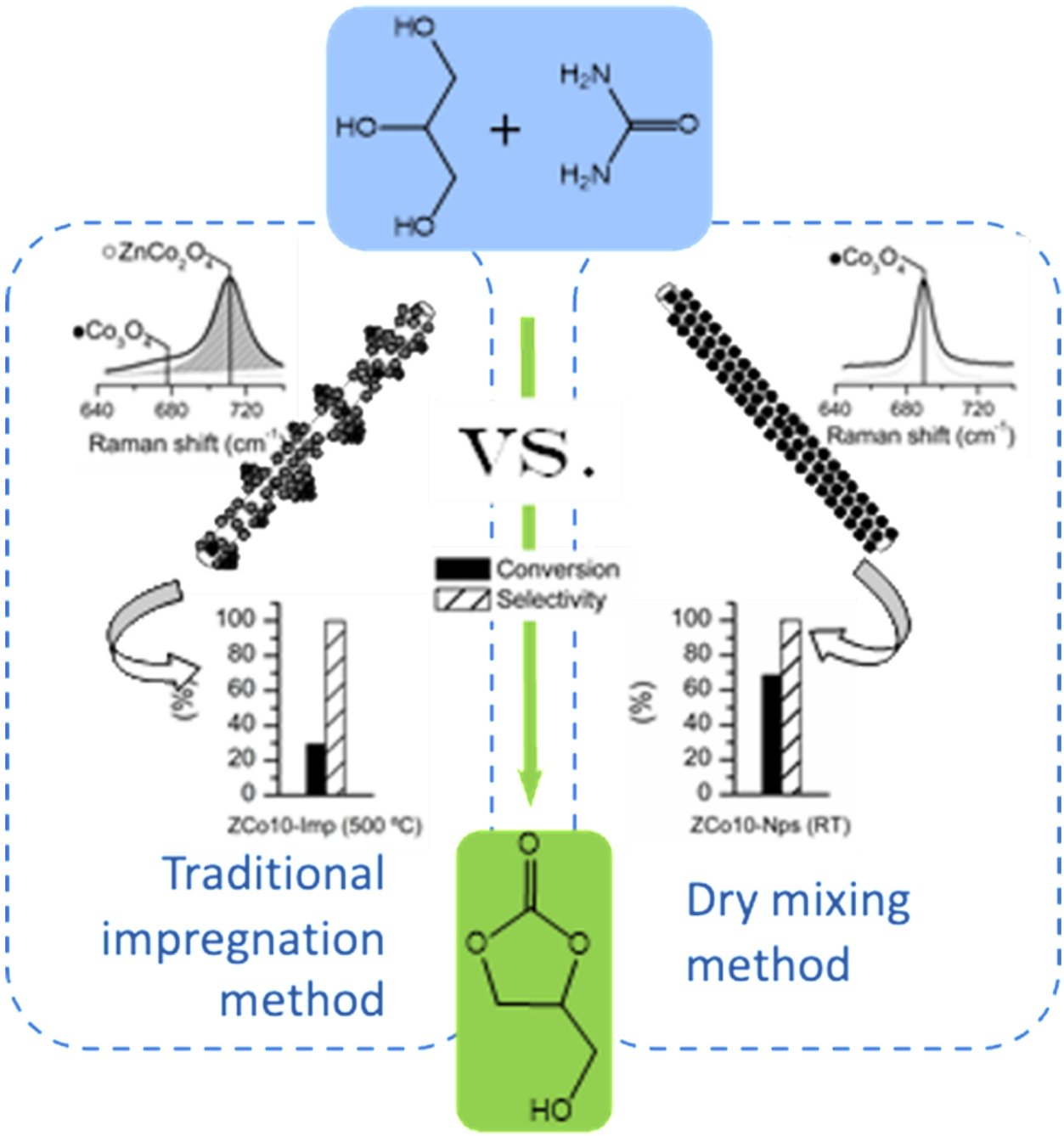

Figure 1. Co_3O_4/ZnO system prepared using a novel dry mixing method at room temperature is very promising catalytic materials for the transformation of renewable materials via carbonylation of glycerol with urea. The activity can be modulated by the interaction of CO_3O_4 nanoparticles with ZnO support, which remarkably depends on the preparation stage.

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WASTE TREATMENTS AND RECOVERY

Recycling of urban waste caps and the importance of antioxidants addition

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Single use plastics are considered a key environmental problem due to their massive utilization and non-biodegradable character. In 2018, production of plastics in Europe reached almost 62 million tons: 29.1 million tons were collected, and only 32.5% of them was used to give a second life [1]. This fraction should grow in the next future, since The New Directive (EU) 2018/852 on packaging and packaging waste establishes a minimum target of 50 % by weight for plastic recycling by ending of 2025 and of 55% in 2030 [2]. The transformation of current linear model to a circular economy is mandatory, aiming to use materials, energy and wastes more sustainable and efficiently. Many recycling initiatives have been thus developed from private and public companies as well as local collectors to favor plastic supplies chains in this circular economy. An example

of these proposals has been initiated by municipalities and by several companies in relation to collect the caps of different containers from packaging wastes.

Recycled materials often show partial degradation from their previous service life, which can affect the properties of the plastic items created from their reprocessing. Addition of antioxidants is then necessary to ensure a proper performance, playing a fundamental role in the recyclates [3][4]. The aim of this study is to evaluate the benefits of incorporation of these additives to recycled caps. Resultant polymeric material based on these urban recycled caps was prepared by melt extrusion and processed by compression molding. A comparison between the additivated and non-additivated recyclates, submitted to an accelerated aging test is carried out in terms of the durability and mechanical properties, (see Figure 1 for thermal transitions).

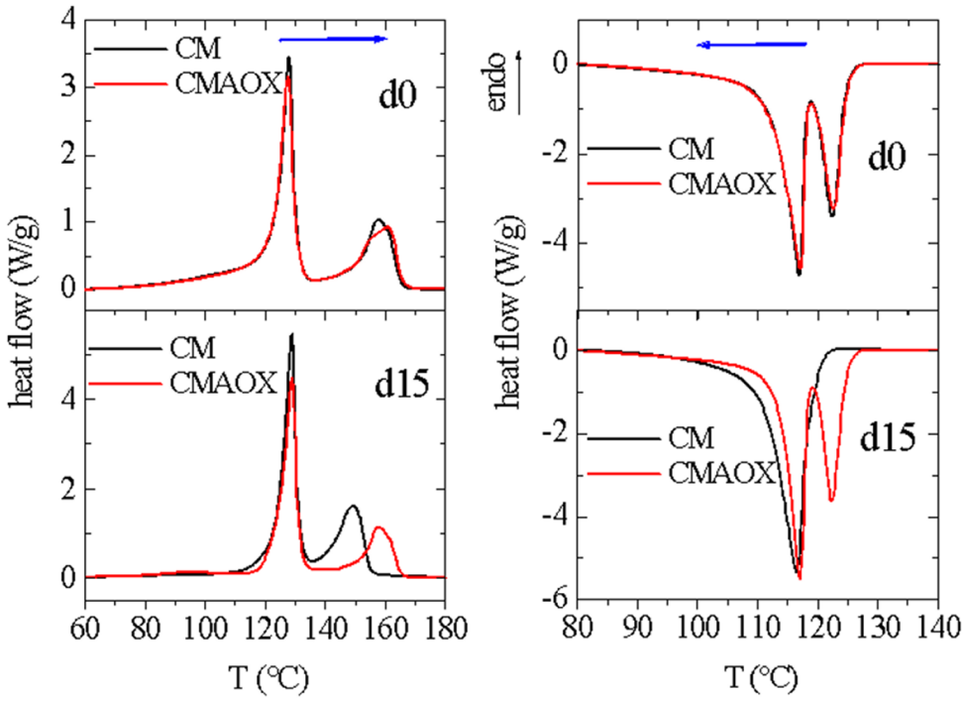

Figure 1. DSC curves for the first melting (left) and crystallization (right) processes in the non-additivated and additivated recyclates.

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Valorization of secondary products generated during the industrial production process of Electrolytic Manganese Dioxide (EMD)

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AUTLAN EMD is a company focused on the production of electrolytic manganese dioxide (EMD). EMD is used as cathode material in primary alkaline batteries that use Zn as anode and KOH as electrolyte. The industrial process consists of several steps from reducing, leaching and purifying the Mn-rich ore to the final electrodeposition and post-treatment of the EMD product[2] During the purification process, secondary products rich in different mix oxides, oxy-hydroxides,

sulphates and silicates of Ca, Fe, Mg and Mn are generated. The objective of this work is the valorisation of these secondary products. Different routes have been proposed, such as their reinsertion into the industrial process given their Mn content [3], their use as construction materials given their Ca, Fe and Si content [4] or their use in the manufacture of NTC thermistors, given its composition in mixed oxides of Fe and Mn [5]. In this work, a valorisation route towards high-value applications has been studied. The secondary products have been used as precursors of electrode materials for Li-ion batteries. Firstly, the synthetic routes of the compounds $LiMn_{1/3}Fe_{2/3}PO_4$ and $LiMn_{1.5}Fe_{0.5}O_4$ [6][7], starting from the previously synthesized pure spinel $MnFe_2O_4$, was adapted and optimized. X-ray and neutron diffraction confirmed the purity of the obtained. Next, different treatments were carried out to purify the spinel $MnFe_2O_4$ in the secondary products. The lithiated high-voltage spinel $LiMn_{1.5}Fe_{0.5}O_4$ was successfully obtained starting from the treated secondary products. The optimisation of the electrode preparation currently carried out to improve the electrochemical performances of the synthesized compounds will be presented.

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Circular economy approach for conversion of waste textiles and biomass into textile-based adsorbents for contaminant removal

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Over the last 30 years the demand for textile products has increased with population growth and changing economic and fashion cycles leading to high levels of high value waste products. Since 1996, the clothes purchased in the EU has increased 40% with, on average, 26 kg per person per year: 11 kg are discarded. The magnitude of this problem can be seen from estimated values reported for China, USA and the UK of 26, 12.4, and 1 million tonnes, respectively [1]. Furthermore, if this waste is not correctly disposed of, it occupies large volumes of space, creates odours, attract pests and promotes diseases. The best alternative to this is to reuse this textile waste, ideally without downgrading its value according to circular economy (CE) principals.
Another product of interest is chitosan

(CH), one of the world's most abundant biopolymers, derived from the shell waste of crustaceans, insects and molluscs etc., with an estimated annual global production of ~10^{11} tonnes in 2021 [2]. CH is not only cost-effective, non-toxic, biocompatible and biodegradable, but also contains many -NH_2 and -OH groups that can act as coordination sites. It has therefore been widely used as an adsorbent to purify water, and can be produced in film, coating, bead and fabric forms [3]. However, pure CH has poor mechanical properties.

Herein we present on-textile supports coated with chitosan and activated carbon (AC) for the adsorption of an herbicide contaminant (see Figure 1). Combining these two products adds value to a waste product and rectifies some of the deficiencies of CH all within a CE context.

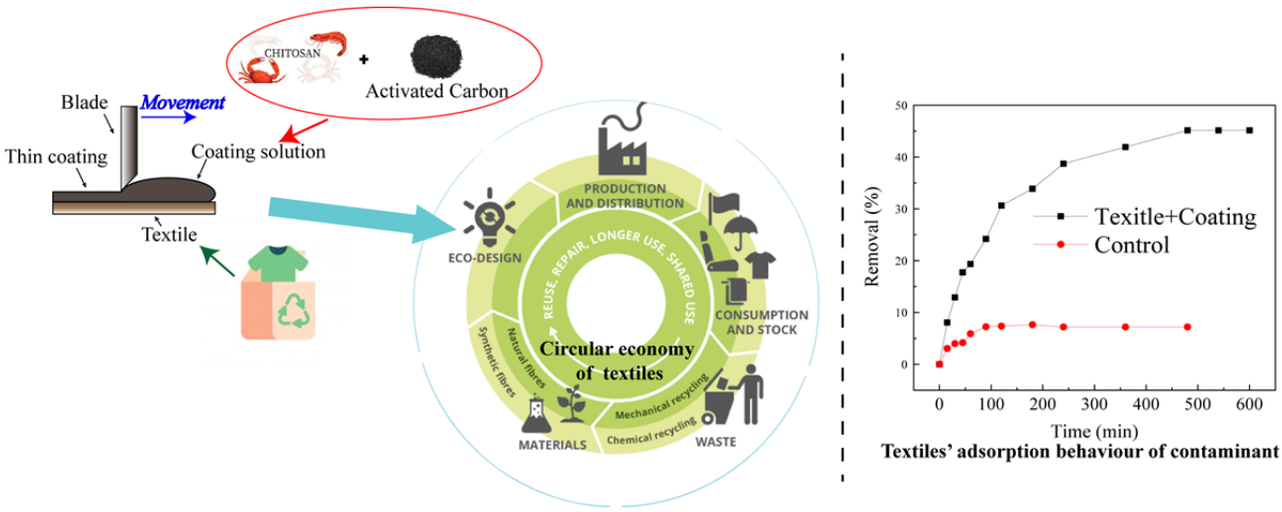

Figure 1. CH/AC textile coatings within a CE basis. Graph demonstrating herbicide removal.

CH/AC slurries were prepared and coated onto various textiles (polyester, cotton etc.) using a doctor blade, washed and dried. The adsorption removal efficiency of these materials was then tested and performed very well compared to standards. This may provide a promising route to upcycling of textile and biomass waste into valuable functional materials, and further work is ongoing.

This work is supported by the MICINN project **SPoNaFun** (PID2020-117573GB-I00) and MHY thanks the China Scholarship Council for a doctoral scholarship (CSC Nº. 202008440497).

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Life cycle analysis of precast mortar with the addition of wastes

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In Europe, almost 26 million tons of plastic are generated each year, which is why the EU intends to promote initiatives to reuse and recycle these plastic products and move towards a sustainable economy, there are currently several previous studies that propose the incorporation of waste in construction products.

For all these reasons, this study proposes the reuse of polymeric wastes in construction products, developing prefabricated mortar blocks in which wastes from the automobile industry are incorporated, replacing part or all of the aggregates. To evaluate the environmental performance of the products throughout their life cycle, a life cycle analysis of these products is carried out, according to the UNE-EN ISO 14040 standard.

Once these block-shaped prefabricated products were manufactured, composed of cement, aggregate, additive, water and

industrial waste from shredded car roofs, resulting in a lighter and more fire-resistant recycled product and with the valorization of the waste, their viability was evaluated from an environmental point of view, carrying out a life cycle analysis of these products, according to the UNE-EN ISO 14040 standard. This study was carried out at the product manufacturing stage, in order to compare the impact of using industrial waste in construction. Several parameters have been evaluated, such as global warming, ozone layer depletion (ODP), human toxicity, abiotic depletion and aquatic eco-toxicity in fresh water. Most of the above parameters increase, although it is true that in a minimal proportion with respect to the traditional mortar, except for abiotic exhaustion, which decreases. This is due to the use of waste, which requires a previous crushing treatment before being incorporated into the mortar, which makes the environmental balance slightly negative, and greater the more waste is incorporated into the mortar.

However, and despite the fact that in general, at an environmental level the results are not as positive as expected, the use of revalorized waste and the reduction of the use of natural resources such as aggregates in the construction sector, generates important environmental and economic benefits, making these new materials viable, increasingly favoring a circular economy.

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Plasma technology for the revalorization of organic gaseous waste: a preliminary result

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Biogas is a mixture of different gases produced by the breakdown of organic matter obtained from raw materials such as agricultural waste or food waste, among others. It is composed by greenhouse gases, fundamentally, methane (CH_4) and carbon dioxide (CO_2) which have a huge heat capacity, so it is often employed as combustible for energetic exploitation. However, the potential of biogas goes beyond its use as fuel. In this research it is proposed plasma technology to not only eliminate CO_2 and CH_4 harmful gases to relieve atmospheric pollution, but also revalorize biogas gaseous waste. Biogas can be utilized as a source of other high-value products [1][2]: hydrogen (H_2), syngas (a mixture rich in H_2 and CO) or graphene.

Microwave plasma technology is proposed to be a powerful technique for the decomposition of biogas produced during

the agricultural activity into the above-mentioned high-value byproducts, then converting this waste into a resource of high environmental interest (Fig. 1). It has been recently discussed the suitability of plasma technology to achieve the decomposition of CO_2 [3] (a biogas component) and it offers a promising skyline due to its high conversion yield, low cost, overall flexibility… As a preliminary result, it has been obtained the decomposition of CO_2 molecules by a microwave plasma device (surfatron [4]). By the optical emission spectroscopy (OES) analysis of the radiation emitted by an Ar-CO_2 plasma, it is observed the emission of C, O, CO and C_2 plasma species which certainly proves CO_2 decomposition through the plasma process. Thus, despite the high energy input needed to break CO_2 bonds, it is remarkable the success of the plasma processing for this purpose. This

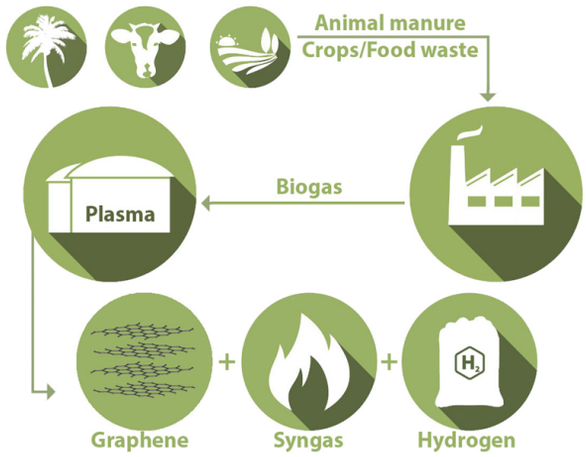

Figure 1. Innovative plasma technology for the revalorization of biogas (CO_2 and CH_4) scheme.

fact confers two advantages at a time of plasma technology framed in the UE Circular Economy Action Plan: not only a greenhouse gas is being eliminated, but it also opens the way to revalorize organic gaseous waste when CH_4 is also injected to the plasma.

Research co-financed by the Operational Program FEDER 2014-2020 and by the Regional Government of Andalusia within the context of the project Ref. 1380678-F.

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Circular Economy in Timber Construction

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Reuse of building waste materials in timber construction follows the Circular Economy principles and improves the high level that represents wood as building material for carbon sequestration and climate change mitigation. The demolition sector generates a large amount of timber products among others that could be reused directly or recycled for structural purposes. However, nowadays there is no established recovered timber market due to the lack of a standardized classification system for this product. The grading standards for new sawn timber are not suitable for grading recovered timber due to their particularities, e.g. aging, distortion, notches, cracks and checks, variable cross-section, nails, biological attacks; thus most of the recovered pieces are rejected as not valid for construction. Nowadays wood waste created from demolition is reduced to

chips and either used for energy production, wood panel manufacturing or other minor uses (pallet blocks, composting, mulching, animal bedding…). Potential structural end-uses were explored recently in two European research projects (CaReWood and InFutUReWood) [1][2] recycling recovered timber in Engineered Wood Products (EWP) e.g. CLT and Glulam. Furthermore, the timber source influences the reuse possibilities. In Central and Northern European countries mid cross-sections from light-frame construction systems are mainly recovered, these are of similar size than timber needed for EWP. However, in Southern and Eastern European countries, with a rich existing timber construction heritage, recovered timber is mainly large cross-sections from post-and-beam construction systems. Recycling it in EWP generates much wood waste and will be preferable to reuse it in refurnishing heritage buildings [3]. Based on the cascading principle of sequential reuse of recovered materials, reuse is preferable than recycle. When timber dimensions are reduced for EWP production a significant amount of wood waste is generated, energy consumption and restricts a possible third, fourth, fifth… live of the recovered timber. Through a Marie Curie fellowship, the main goal of the REusing COnstruction Wood through a common EuRopean Standard (RECOWERS) project [4] is to develop a standardized grading system for recovered timber to enhance the secondary timber market.

The RECOWERS project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 101025786. The InFutUReWood project was supported under the umbrella of ERA-NET Cofund ForestValue and has received funding from MICIU-Spain [PCI2019-103544].

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Mechanical study of mortars with gypsum/plaster matrix with addition of fibers from CDW

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Since ancient times a bast number of civilizations have use the gypsum as a building material. Archaeologists have been dated the oldest applications of stucco or plaster mortar to 7000 B.C. [1] in what we now know as Israel. In Spain the use of gypsum and plaster is widely used in construction because its good behaviour as a humidity regulator, retaining in wet seasons and evacuating in dry seasons and behaviour to fire. Different studies of gypsum have been performed, with additions of natural and artificial fibers such as fiberglass [2], recycled rock wool [3] or made of polymers as polypropylene [4], polyethylene, recycled plastic. The building sector generates a huge amount of construction and demolition waste "CDW". Within this waste are plastics and, in this group, we find single-use slings made of PE, PU, PP, used to transport rebar to the construction site.

In this study, fibers from CDW have been collected from construction sites, superficially cleaned, cut to 12mm in length, homogenized and stored for incorporation into the plaster mortar. The objective of this study is to compare the properties of gypsum mortars with the incorporation of recovered fibers and mortars with polyethylene fibers of 12 mm length commercialized in the construction field. The tests carried out are those established in the application standard, the percentage of fibers incorporated is from 1 to 4% by weight. The specimens have been executed according to the UNE-EN13279-2/2014 standard and cured for 7 days at room temperature and 24 hours of oven drying at 40°±2° C until constant weight. The results obtained indicate us in the hardness that: the incorporation of recovered fibers maintains the initial hardness while the commercial fiber generates an initial reduction, improving as a function of the percentage of incorporation of fibers. Regarding bending, recovered fibers have a direct relationship with the percentage of fiber incorporation, while with commercial fibers this relationship has a lower dependence. The compression values show a decrease in strength in terms of the incorporation of commercial fibers and this trend is maintained while the incorporation of recovered fibers presents an inverse relationship with the percentage of fibers. Main conclusion, it is obtained that mortars with the incorporation of recovered fibers have better properties to mortars with commercial fibers.

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Recycling and valorisation of carbon fibre reinforced aluminium composite materials

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Composite materials are nowadays widely used, and their demand is growing over the years thanks to their exceptional mechanical properties such as high fatigue strength or high stiffness, as well as their low density. They are found in different sectors such as aeronautics, automotive, defence, wind power and others. The most commonly used metal matrix in composite materials is aluminium due to its lightweight, high thermal conductivity and wear resistance [1].

However, when these composite materials reach the end of their useful life, they are mainly forgotten in landfills. At present, there are no definitive methods for their recycling and recovery, as these materials are very difficult to treat due to the need to separate the two components and because there is little research on the subject. It is therefore necessary to develop an effective treatment methodology

to transform this type of waste into new resources in order to continue to meet the needs of industry within a circular economy model.

The aim of this work focuses on the development of treatments for aluminium matrix composites reinforced with carbon fibres at the end of their useful life cycle, contributing to their circularity by giving them a new life. To do this, firstly, most of the aluminium is recovered through smelting [2] processes by separating the aluminium from the aluminium-impregnated carbon fibre. Then, for complete recycling, three lines are proposed: (i) use of the aluminium impregnated fibre for the manufacture of new aluminium matrix composite materials, (ii) complete removal of the aluminium surrounding the carbon fibre by acid and base treatments [3] and (iii) search for new applications in industry, of this recovered carbon fibre, after a study of its mechanical and thermal properties, as well as its structure, revaluing this material by giving it a new function.

This study shows that the aluminium-impregnated carbon fibre is highly adhesive to the matrix and, although its structure is slightly damaged, it still improves the mechanical and thermal properties of aluminium, justifying the manufacture of new aluminium composite materials reinforced with carbon fibre from the recycling of components already in use.

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Mechanical characterization of gypsum mortars with waste from the automotive sector

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The construction sector is one of the main sectors generating greater environmental impacts. In this sense, the European Commission is forcing the sector to implement alternative measures and strategies to tackle this situation and bring the sector to a circular economy. One of the adopted measures is the use of recycled materials to produce construction materials and products. In this sense, many research works have been conducted analyzing the incorporation of different waste categories in gypsum products. In this sense, the main objective of this research is to characterize new gypsum-based materials that incorporate waste from the automotive sector. For this, waste from the production of cars has been used, containing a mixture of polyurethane foam, cardboard, and fiberglass (PCF) through different size scales. A total of 123 gypsum samples were made incorporating

up to 11% of waste addition. These samples were tested according to the density, superficial hardness, mechanical resistance, and thermal behavior. Results show that it is possible to incorporate up to 11% of waste overpassing the minimum strength values established by the regulations. In addition, the lightness of the material and its compression and flexion behavior improved considerably compared to the reference values. Finally, the use of the automotive waste analyzed can be used in the manufacture of gypsum mortars for construction, reducing the consumption of natural resources and, at the same time, recovering an industrial waste that is otherwise difficult to recycle.

Keywords: plaster, waste, recycling, building, circular economy, polyurethane, fiberglass, cardboard.

WATER TREATMENT AND CO_2 CAPTURE

Circular economy in membrane technology: upcycling end-of-life reverse osmosis membranes for sustainable electrochemical water treatment

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The increasing number of end-of-life (EoL) Reverse Osmosis (RO) membrane modules yearly dumped in landfills comprises an important environmental concern. In this context, the development of innovative membrane reuse and recycling alternatives can help reducing the waste generation and fostering the transition towards a circular economy in the water sector. Previous studies have been devoted to the development of membrane reuse and direct recycling alternatives. Whilst, in the case of excessively damaged membranes, an indirect recycling approach could be a more suitable alternative. Indirect recycling entails the de-

construction of the RO module, allowing for the individual management of membranes and plastic components. In this work, a new methodology to enable the indirect recycling of EoL RO membranes as Anion-Exchange Membranes (AEMs) has been developed. The technical feasibility of the prepared membranes has been validated for different water treatment processes, including brackish water desalination by electrodialysis [1,2], selective nitrate separation [3], and nitrate removal by an Ion-Exchange Membrane Bioreactor [4].

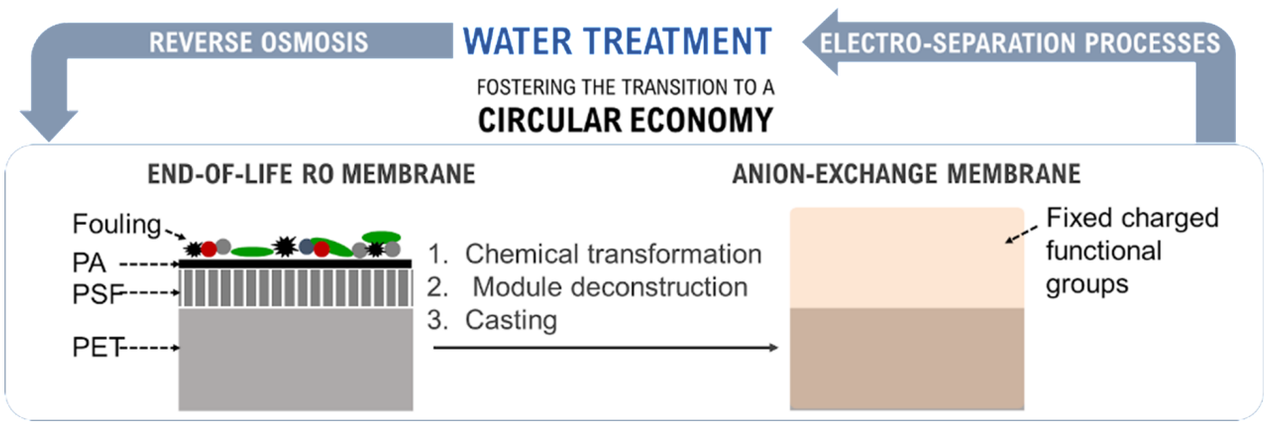

Figure 1. Schematic representation of indirect RO membrane recycling into AEMs for water treatment. PA, polyamide; PSF, polysulfone; PET, polyester.

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Microbial Desalination for Low Energy Drinking Water

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Seawater desalination and the reuse of treated water have been proposed to overcome water scarcity worldwide. Reverse Osmosis (RO) is the most widely implemented desalination technology, but new approaches are still necessary to decrease its high energy consumption (3-4 kWh m^{-3}). With this aim, the MIDES project has developed the world's largest demonstrator of the low-energy Microbial Desalination Cell (MDC) technology as a pre-treatment step for RO to reduce the desalination energy of the RO process and increase drinking water production using wastewater as a renewable energy source[1]. The MDC technology is a sustainable and energy-efficient bioelectrochemical technology that treats waste-

water, produces energy, and desalinates water simultaneously in the same device without external energy input[2,3]. The desalination process in the MDC device **(Figure 1)** is driven by the energy provided by electroactive microorganisms via the degradation of the organic matter contained in the wastewater.

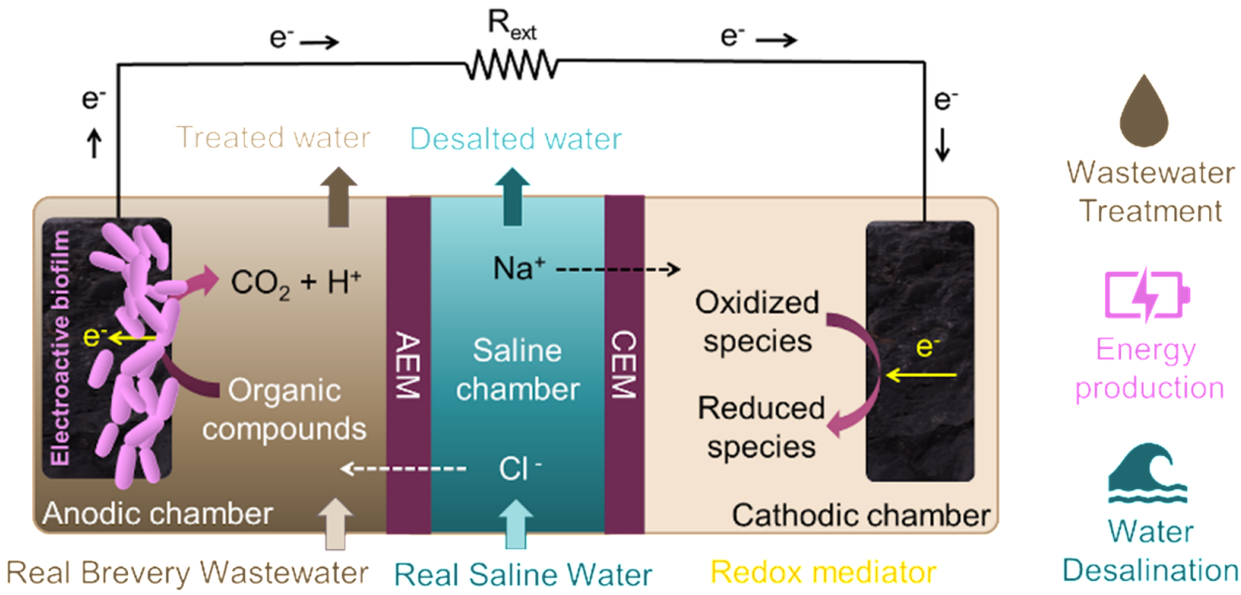

Figure 1. MDC concept scheme. AEM/CEM: Anionic/cationic exchange membrane. Electroactive biofilm on the anode provides an electric potential for ion migration from saline to other chambers.

Prior to the scale-up of the MDC system in the project, studies of the behaviour of the laboratory-scale MDC system under actual conditions were carried out. The MDC device achieved the complete desalination of different natural saline waters using real brewery wastewater as system fuel, under ambient temperature and pressure conditions and neutral pH.

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Use of Recycled Reverse Osmosis Membrane Modules in Membrane Distillation and Forward Osmosis Technologies

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Reverse osmosis (RO) is a well-established worldwide water treatment industrial membrane technology, especially in desalination field. More than 840,000 end-of-life RO membrane modules are discharged annually all around the world. This fact, together with the continuous growth of the number of RO desalination plants, induces a chronical and irreversible increase of the number of discarded membrane modules. The most common management of the discarded RO membrane modules is their deposition in municipal landfills near desalination plants. The objective of the present research is to study the possibility to reuse different parts of discarded RO membrane modules in membrane distillation (MD) and forward osmosis (FO) separation processes for the treatment of high saline aqueous solutions including RO brines and wastewaters, respectively.

Passive RO module cleaning protocols in pilot plant and laboratory scale were followed using sodium hypochlorite (NaClO) at different concentrations and exposure time. The cleaned RO membranes and both the feed and permeate spacers are not suitable for their direct application in MD technology. Therefore, a hydrophobic nanofibrous polyvinylidene fluoride (PVDF) layer was electrospun over them increasing their hydrophobic character and rendering them suitable for MD separation process as recycled RO composite hydrophobic/hydrophilic membranes (i.e. the cleaned RO membranes and spacers act as hydrophilic supports). These membranes prepared using the recycled RO membrane and the permeate spacer as hydrophilic supports exhibited interesting characteristics suitable for MD desalination (i.e., 18.1 and 43.2 kg/m^2 h permeate fluxes, respectively; with very high salt rejection factors, greater than 99.95 %).

The cleaned RO membranes were also reused in FO for the treatment of humic acid (HA) aqueous solutions. To improve their FO performance, the cleaned RO membranes were modified by interfacial polymerization technique. Different polyamide and polyester thin active layered membranes were prepared (i.e. thin film composite, TFC, FO membranes). The best FO performance (15.12 kg/m^2h, with a specific reverse salt flux of 0.014 kg/m^2h, and a HA rejection factor greater than 99%) was achieved by the TFC membrane prepared with a mixture of m-phenylenediamine (MPD) / trimethylamine (TEA). These values were comparable to those of TFC commercial membranes (Hydration Technology Innovations (HTI)) used under the same FO conditions.

In general, this study opens new ways to extend the lifetime of RO discarded membrane modules contributing to a circular economy and sustainability in membrane science and related materials.

The authors gratefully acknowledge the financial support of the Ministry of Economy and Competitiveness of Spain (CTM2015-65348-C2-2-R) and the Ministry of Science, Innovation and Universities of Spain (RTI2018-096042-B-C22).

Reprocesing of TPUS into foams using supercritical CO_2. Influence of pressure, temperature and time

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Polyurethanes (PU) are part of the "big six", a group gathering the six most important plastic materials worldwide for their use and economic value. PU is well-known for its outstanding properties such as high resilience, excellent resistance to wear, and long useful lifetime combined with the inherent great tunability of the PU chemistry.

Although recycling of thermoplastic PU is possible by heating and reprocessing in a liquid form, those processes usually need high temperatures (it is necessary to reach the melting point of the polymer). Also, the number of times that a polymer can be recycled is limited. Therefore, we propose the foaming of thermoplastic polyurethanes as an alternative to traditional PU recycling., This alternative not only can provide a new method of PU recycling but also can lay the groundwork for the thermoset polyurethane polymer

recycling (which can't be reprocessed by heating).

The present work is focused on the study of the influence of temperature, pressure, and contact time with the supercritical CO_2 in the foaming of TPU. To carry out the study of those variables a commercial TPU was selected. The TPU selected was 1080A from Desmopan catalogue of Covestro.

To determine the influence of temperature, pressure and contact time in this process. The following conditions were studied:

Temperature: 100 ºC – 120 ºC
Pressure: 100 bar – 200 bar
Contact time: 1 h – 3 h

The results obtained showed that the variable with higher influence in this process is the pressure. The increase of pressure leads to an increase of expansion ratio, cell density and a decrease of average cell size of the foams. Meanwhile the increase of temperature and time did not show a clear effect in the properties of the foams obtained as can be observed in Figure 1.

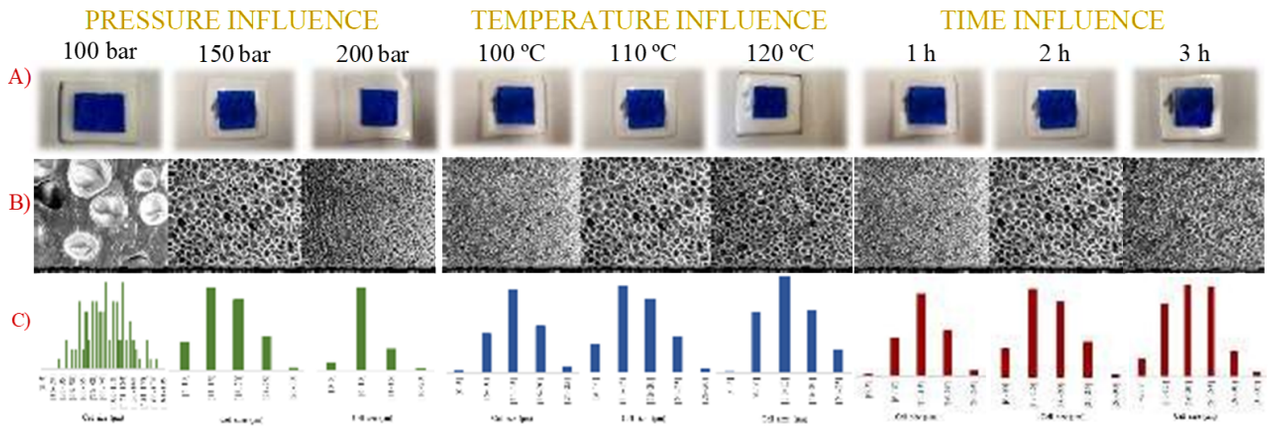

Figure 1. A) Foams obtained and reference elastomer size (blue square). B) SEM images of the corresponding foamed sample. C) Distribution of cell size of the foamed sample.

Microwave Plasma Technology for the conversion of CO_2/CH_4 mixtures: Closing the Loop

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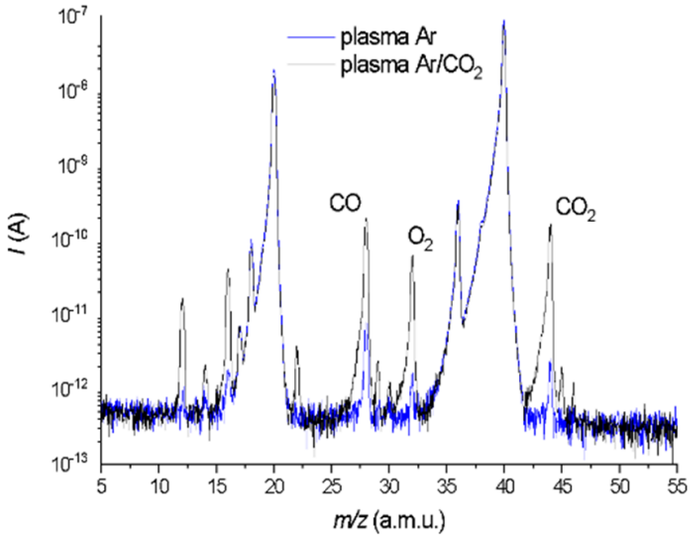
Greenhouse gas emissions is one of the biggest problems that humanity is dealing with nowadays. Spain was the sixth biggest greenhouse gas emitter country in Europe [1] due to its meat industry among others. Furthermore, El Pratt (Barcelona), the second Spanish most transited airport during 2019, emitted during this year 600 times less than the equivalent of CO_2 that all the macro farms did in the same period. At this point microwave plasmas at atmospheric pressure arise as a solution [2]. Plasma internal processes are energetic enough to favour the breakdown of greenhouse gas molecules like CO_2 and CH_4, main components of biogas emission from agricultural waste. It is worth remarking that this plasma can break high-stable molecules, e.g., CO_2. In the other hand, the fact that we are working at atmospheric pressure benefits the facility of implementing the

process at an industrial scale.

In this work, the decomposition of CO_2 molecules in an Ar/CO_2 plasma is researched using a surfatron microwave energy source [3] (200 W). As it can be observed in the mass spectra shown in Fig. 1, when a flow of 0.01 L/min CO_2 is introduced into a 3.00 L/min Ar plasma, CO (28 a.m.u.) and O_2 (32 a.m.u.) gases are formed while CO_2 signal (44 a.m.u.) is also detected. Therefore, it can be concluded that CO_2 molecules are partially dissociated reaching a decomposition rate higher than 50%. To improve this result, experiments with another more robust microwave torch, namely TIAGO [3], are being carried out. TIAGO plasmas are capable to withstand higher concentrations of CO_2 leading to larger decomposition rates.

It is worth remarking that in forthcoming experiments, biogas decomposition will be researched since, due to its high carbon content, nanostructured carbon material can be obtained [4]. This can potentially lead to the production of high valuable products using the large quantity of the said gas thus closing the loop framed in the European Commission Circular Economy Action Plan where the materials they contain are highly valued.



Research co-financed by the Operational Program FEDER 2014-2020 and by the Regional Government of Andalusia within the context of the project Ref.1380678-F.

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CO_2-AFP STRATEGY: Circular Economy archetype

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Over the last decade, there has been a significant rise in global greenhouse gas (GHG) emissions. According to GRP Report, the annual anthropogenic global emissions had increased from 22 Gt in 1990 to 37 Gt CO_2 in 2018. Among the most effective strategies for combating global warming and climate change are those based on the negative-emissions approach. Under this context, we propose the so-called "CO_2-AFP Strategy", based on the Carbon Capture and Utilization processes. In this research, we focused on capturing biogenic carbon from relatively small but highly enriched sources of CO_2 emissions derived from Alcoholic Fermentation Processes (AFP). This strategy is based on mineralization procedure

whereby the captured CO_2 reacts with caustic soda solution (NaOH) to produce sodium carbonate (Na_2CO_3). This product is in the top ten most demanded commodities list in the chemical industry. In global terms, it has been estimated from a theoretical angle that the application of this strategy to the most significant worldwide AFP organizations, could produce more than 30.6 Mt of Na_2CO_3, capturing 12.7 Mt of CO_2, thus achieving a reduction of up to 56 Mt of negative CO_2 emissions per year. This study presents the strategy development corresponding to a real case: a medium-size company in Spain, where the "CO_2-AFP Strategy" has been successfully tested and scaled-up. Detailed and tested carbon capture and utilization schemes are used to evaluate the overall carbon footprint balance via an improved hybrid multiregional input-output-lifecycle assessment model (MRIO-LCA). The carbon footprint balance assessed in this study shows how the implementation of this strategy may compensate neutralize the Scopes 1 and 2 and 17 % to the overall CF. The benefits go beyond the reduction of carbon footprint in the fermentation industry. The application of the "CO_2-AFP Strategy" implies a revolution, in terms of Circular Economy, in the sodium carbonate industry, as the symbiotic process between the different stages of the value chain will allow downstream carbon footprint reductions, facilitating a greener sodium carbonate production.

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Green synthesis and study of magnetic-luminescent bifunctional materials for biomedical and metal ions water removal

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In recent decades, numerous samples of materials with different compositions and structures at the nanometric scale have been synthesized. Some of these samples have been extensively investigated due to their great scientific and technological interest. Knowledge of their specific characteristics such as its composition, structure, size or morphology of its constituent particles, as well as their properties and the interrelation between these properties has made its use possible in certain applications. Currently, the "Materiales Híbridos Inorgánicos-Orgánicos" (GMHIO) research group is studying samples of new lanthanide-doped orthovanadate compositions exhibiting efficient upconversion luminescence for application in bioimaging. In this case, the orthovanadate host lattice offers good mechanical and thermal resistance, which allows the hosting of lanthanide ions [1-2].

In the synthesized Ln^{3+}: YVO_4 samples, the good location of lanthanide ions in low symmetry allows the generation of down-conversion (DC) and up-conversion (UC) processes after their photoexcitation, as a consequence of the electronic transitions occurring between the 4f-4f or 4f-5d levels [3-4]. In samples doped with a single lanthanide ion that leads to down-conversion (DC) processes, the inorganic lattice acts as a host crystal to accommodate the Ln^{3+} ions and, in turn, as a sensitizer of their luminescence [1-2]. The GMHIO group is working on samples doped with two lanthanide ions that are capable of generating upconversion (UC) processes for use in imaging biological cell cultures. In these compositions, one of the lanthanide ions acts as a sensitizer of ions with higher absorption coefficient and the other as an activator [5-6]. Near-infrared excitation has been found to produce a much more efficient luminescence emission minimizing cell damage and allowing deeper tissue penetration [5,7]. The potential application of such samples as fluorescent thermometers has also been studied [8]. Furthermore, it is now possible to study samples prepared as mixtures of orthovanadate and coated Fe_3O_4 nanoparticles [9,10]. However, the aim is to obtain samples of bifunctional magnetic-fluorescent materials that not only allow their use in bioimaging, but they can also be directed by means of an external magnetic field and, suitably functionalized, they can be directed to diseased tissues or cells for their treatment [9].

In addition, the GMHIO group has found the possibility of using iron oxide nanoparticles functionalized with $-NH_2$ groups in the adsorption and further removal of metal ions from polluted water. All tests were carried out with great success, which makes it possible to apply ferrites in water purification [11,12].

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Sustainable and economic solution for H_2 and CO_2 recovery in the petrochemical industry

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Membrane separation is one of the most promising, economic, and eco-friendly approaches for gas separation, mainly in the petrochemical and pharmaceutical industries. The incorporation of porous organic polymers (POPs) as fillers to commercial polymer matrices like polycarbonate [1], polysulphone, matrimid and polyphenylene oxide [2] has been recently investigated. The results indicated that 20% biphenyl-based knitting aryl polymer (K2Ph) to the pristine polymers had different influences on the selectivities and gasses permeability (P) depending on the polymer phase and on the gasses.

In this work, we used polysulphone (**PS**) as matrix and 20% w/w of a new brominated POP (**K2Ph4Br**) as filler. Thermal, morphological and gas transport properties have been investigated and the results are compared with those ob-

tained with the membrane containing the no-brominated filler (**PS@K2Ph**).

Porous polyphenylenes fillers, **K2Ph** and **K2Ph4Br**, have been prepared by the Friedel-Craft reaction using commercial and cheap monomers, and showed high surface area (SBET=1034 and 1483 m^2/g). Mixed matrix membranes have been obtained following an easy procedure recently reported by us [1], using an accessible and economic matrix such as PS. A homogeneous dispersion of fillers through the membrane can be observed in SEM images of the cross-section of **PS@K2Ph4Br** (Figure 1A), which also showed good compatibility between both phases and no remarkable voids. The decomposition temperature of the membrane was higher than the neat polymer which indicates that the organic filler increases the thermal stability of PS.

P coefficients of O_2, N_2, CO_2, H_2, CH_4, and C_2H_4 for **PS@K2Ph4Br** were 2-3 times higher than the P for neat PS and 1.5-2 times higher than the gasses permeability for **PS@K2Ph** membrane (Figure 1B). These results were attributed to the increase in the solubility parameters. As it is shown in Figure 1C, the selectivities of the MMMs were higher than the neat polymer, mainly H_2/CH_4, H_2/C_2H_4, and CO_2/CH_4, making them good candidates for recovering CO_2 and H_2 from petrochemical industries.

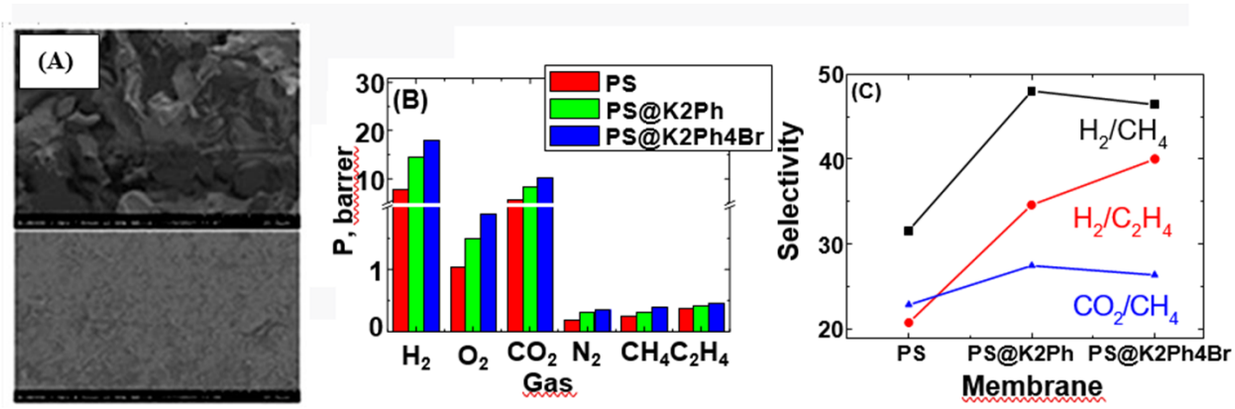

*Figure 1. (A) SEM images of the cross-section of pure **PS** (down) and **PS@K2Ph4Br** (up); P coefficients at 30ºC and 1 bar (C) Some selectivity coefficients of MMMs compared with neat polymer.*

Acknowledgments to MINECO of Spain PID2019-108552GB-100 for financial support.

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This book collects some of the most prominent advances in terms of circular technologies and materials exhibited at the CIRMAT symposium. The editors want to thank the contributions of all the participants who wanted to join us, and especially all the collaborators for all their work and support.

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