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BIOCOMPOSITE MANUFACTURING: THE ESTELLA PROJECT

The ESTELLA project aims to develop and produce sustainable thermoset epoxy composites, impacting the entire materials value chain, in particular by introducing covalent adaptable networks (CAN) in fossil- and bio-based matrices and fibres following the Safe-and-Sustainable-by-Design (SSbD) approach. This approach will enable the recycling of epoxy composites and redefine all manufacturing and recycling processes.

Introduction

Thermoset polymer, particularly epoxy resins-based composites, is widely used in the industrial sector. However, most thermosets are crosslinked using diamines, which does not allow recycling due to the formation of strong covalent bonds **[1]**. Therefore, they are currently mainly disposed of in landfills or by incineration. Moreover, 80-90% of the epoxy resins are composed of Bisphenol A, which is a harmful chemical **[1]**. The only way to achieve a circular economy is to rethink the life cycle of thermoset polymer composites using environmentally friendly chemicals. The ESTELLA project aims to develop and produce new thermoset epoxy resins that are inherently recyclable through the use of Covalent Adaptable Networks (CANs), a family of chemical bonds that allow the reshaping and reprocessing of polymers under certain stimuli, such as pH and temperature **[2, 3]**. In parallel, the resins will be formulated to fulfil the requirements for processability and biodegradability. The ultimate goal is the preparation of epoxy resins with CANs, starting from fossil- and bio-based raw materials to produce composite materials using lignocellulosic fibres to manufacture prototypes (a window frame and a scooter platform). To achieve these results, the ESTELLA consortium comprises 13 partners with different skills, with the Cidaut Foundation (CID **https://www.cidaut.es/**) as the coordinator. The results and achievements of the individual partners are described below.

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Fig. 1 - Examples of lignin-based epoxy resins

Key project results

Development of associative resins with Covalent Adaptable Networks

The National Institute of Chemistry (NIC, **https://www.ki.si/**) is involved in synthesising a bio-based epoxy resin containing associative-based CANs starting from renewable materials. To achieve this goal, lignin monomers (vanillin and syringaldehyde) were modified to prepare epoxide monomers containing imine bonds. Simultaneously, Kraft lignin was directly functionalised, increasing the carboxylic acid content to prepare an epoxy resin with a CAN-based on ester bonds (Fig. 1). This second approach was scaled up to 1 kg as the obtained resin allowed it to reach most of the required thermal and mechanical properties. Currently, the recycling tests are running to find the optimal conditions.

As a second approach, the Łukasiewicz Research Network - Institute of Heavy Organic Synthesis "Blachownia" (ICSO, **https://www.icso.lukasiewicz.gov.pl/**) is developing fossil-based epoxy vitrimers containing CANs using commercial epoxy resins and epoxidized soybean oil (ESO) as raw materials, with carboxylic acids and/or anhydrides serving as curing agents. The combination of these two hardeners, optimisation of the component addition sequence, and control of curing time have made it possible to achieve compositions with the desired mechanical properties, processing and recyclability. ESO improves viscosity and process control, making these compositions particularly attractive for industrial applications, especially in the manufacture of composites through lamination.

Development of Dissociative Dynamic Covalent Adaptable Networks

A third approach involves developing dissociative dynamic CANs. It refers to a class of materials based on dynamic covalent chemistry, where bonds can break and reform in response to external stimuli such as heat, light, or changes in pH. Dynamic covalent bonds are thought to significantly affect thermosets' thermal reprocessing and recycling potential. Diels-Alder (DA) bond is commonly used due to its thermal reversibility for creating dissociative CANs. Stichting Wageningen Research (WR, **https://www.wur.nl/en/research-results/research-institutes/food-biobased-research.htm**) focuses on developing a hybrid epoxy/DA system in this project. This combination of the beneficial properties of epoxy thermosets with the stimulus-responsive behaviour of DA bonds results in materials with a wide range of thermal and mechanical properties that can be repaired or reprocessed when needed. In addition, WR has studied the effect of position and concen-

Fig. 2 - Developed DA-containing formulations with progressively increasing DA concentration and bio-based content from left to right

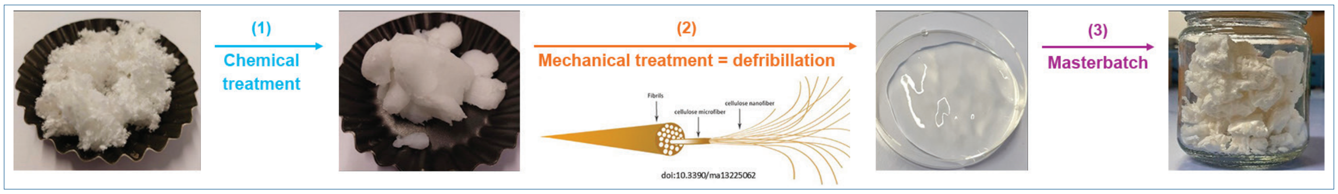

Fig. 3 - Process of production of cellulose nanofibers and specific compatibilization with the resin of the ESTELLA project (masterbatch)

tration of DA bonds as well as the effect of cross-link density on the material properties and behaviour. Thermoset formulations with high bio-based content have been developed and characterised on a lab scale (Fig. 2).

The rheological behaviour of these materials was studied to investigate the re-processability of these formulations. The viscosity behaviour of the epoxy resins by temperature cycling (40-140 °C) over time was studied. A high viscosity drop was observed with the biobased DA-containing thermoset over four cycles. This drop-in viscosity is necessary for reprocessing the thermosets.

Development of two natural fibre reinforcements

The production of biocomposites also requires the study and development of suitable fibres to reinforce the mechanical properties of the resins. Wood K Plus (**https://www.wood-kplus.at**) focused its research on the development of woven hemp fabrics and their functionalisation through physical and chemical treatment techniques. To improve the drapability of the fabric for 3D composite parts, twill weave was identified as the optimal choice, which was successfully achieved with hemp yarn from organic textiles. Both 3/1 and 2/2 twill weave patterns were easily woven with the hemp yarn. In a novel approach, sustainable chemical treatments were employed to avoid the use of toxic and corrosive chemicals. An advanced plasma coating with different precursors was used to functionalise the hemp fabric, ultimately achieving desirable properties for the intended application.

On the other hand, Celabor (**https://www.celabor.be**) developed specific cellulose nanofibers as bio-based and biodegradable reinforcement additives with high compatibility with developed resins. The main challenge was that the cellulose nanofibers were produced in an aqueous solution, and if dried, they aggregated irreversibly. Whereas most resin components should avoid contact with water because they would degrade. To overcome this issue, the following methodology was developed (Fig. 3): (1) cellulose functionalisation, (2) preparation of the nanofibers and (3) preparation of masterbatches to increase the compatibility of the nanofibers with each resin precursor developed by the project partners.

At the same time, FeyeCon (**www.feyecon.com**) used its proprietary knowledge to clean and functionalise the fibres for better reinforcement. Virgin

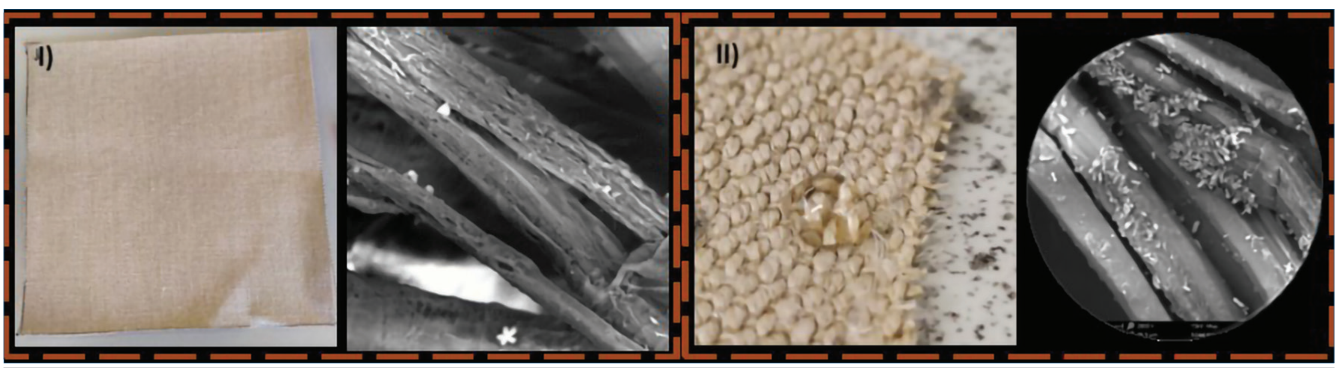

Fig. 4 - I) Hemp-woven textile and fibre after cleaning with $scCO_2$; II) hemp-woven textile after impregnation (more hydrophobic surface)

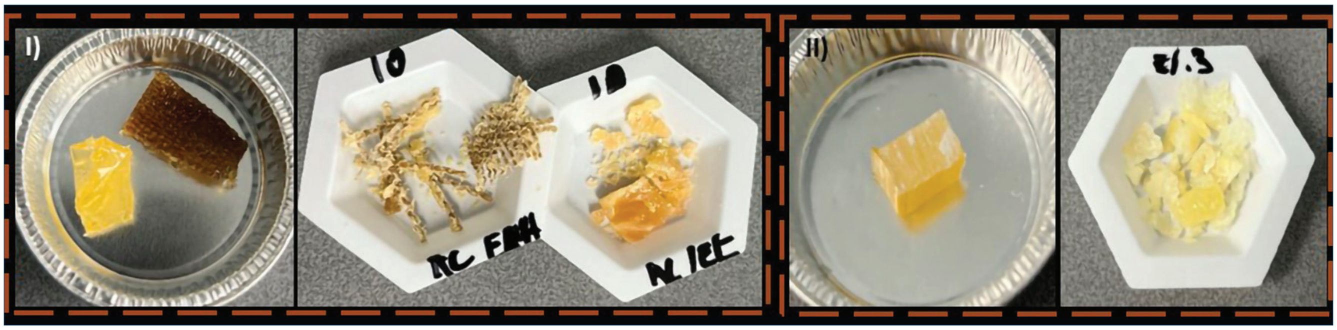

Fig. 5 - WR (I) and ICSO (II) resins and/or composites before and after $scCO_2$ treatment

hemp fibres and woven hemp textiles were first dried and cleaned to remove excessive water and spinning oils from these fibres without affecting their structural integrity (Fig. 4). These fibres (fabrics) require functionalisation for further usage as natural reinforcement structures in biodegradable composites. The functionalisation of these fibres was also achieved via supercritical carbon dioxide ($scCO_2$) impregnation (Fig. 4). Alkyl ketene dimers and oleic acid were used as reinforcement materials.

Bio-recyclability and degradability of designed resins

The biocomposites produced during the ESTELLA project must prove their recyclability. Andaltec I+D+i (**https://www.andaltec.org**) main role consists of evaluating the chemical recyclability of the developed composites through treatments with organic and aqueous solvents at varying pressures and temperatures, acidic and alkaline digestion, and catalytic and oxidative treatments. It is also responsible for optimising the process conditions and selecting the most efficient recycling treatment to recover both the polymer matrix and the fibres that make up the composites. In an attempt to recycle the newly produced epoxy resins, FeyeCon exposed these resins to $scCO_2$ at elevated temperatures and in the presence of co-solvents. The WR-resin and ICSO-resin were degraded, and their structure collapsed (Fig. 5).

In the next steps, Andaltec will assess the biodegradability of three selected developed materials under controlled temperature, aeration and humidity conditions according to the ISO 14855-1 standard. The solid recovered at the end of the treatment will be sent to SINTEF (**https://www.sintef.no/en/**) to identify and characterise any strains. Finally, the degradation by-products will be evaluated for their potential recyclability (feedstock and recovered fibres) and safety (environmental impact and toxicology).

At the same time, biodegradability is also being investigated, thanks to other three partners. University of León (**https://www.unileon.es/**) is focused on the isolation and characterisation of microorganisms capable of degrading epoxy resins. Thus, environmental isolates have been obtained from epoxy-based structures, resulting in the collection of 581 different microorganisms (Fig. 6), which includes a *Pseudomonas* strain from an industrial epoxydic sample. This microorganism has demon-

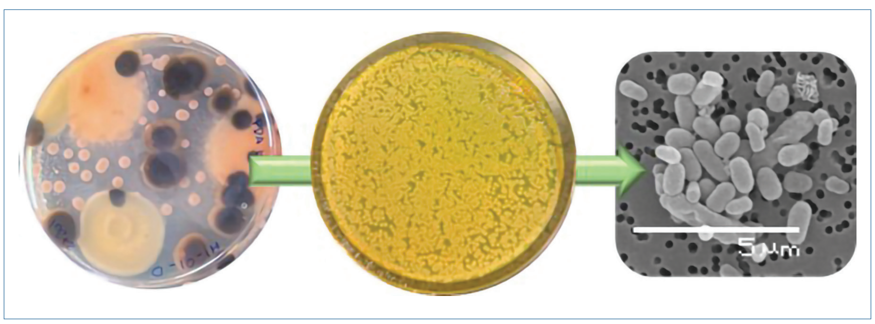

Fig. 6 - Isolation process of environmental microorganisms. Left: diversity of microorganisms present in the epoxy samples; middle: pure culture of a *Pseudomonas* strain isolate; right: Scanning Electron Microscope (SEM) image of *Pseudomonas* cells

strated a remarkable ability to survive for extended periods using an epoxy resin as a carbon source. Collaborative omics analyses (Genomics and Proteomics) with SINTEF are unveiling the mechanisms underlying its capacity to degrade epoxy composites. Nowadays, the team is assessing the morphological and chemical changes in the epoxy resins due to the microbial degrading action of the isolated strain.

The second partner is SINTEF. Its primary role in the project is to identify microorganisms and enzymes that can take part in the biodegradation and/or recycling of the produced ESTELLA materials. Microorganisms are acquired from strain collections based on their described properties or enriched by cultivation in the absence of other carbon sources for growth than the ESTELLA materials. So far, 27 bacterial isolates have been characterised by genome sequencing and mined for genes encoding enzymes that are proposed to catalyse relevant reactions, *e.g.*, laccases and peroxidases. The candidate genes will be expressed recombinantly in a host (typically *Escherichia coli*) and assayed on ESTELLA materials and homologues.

The third partner in biodegradation, IDENER (IDE, **https://idener.ai/**), has a role that encompasses several key aspects of enzyme-based composite material recycling, including identifying and screening enzymes, developing enzyme cocktails, conducting biodegradability tests, researching non-commercial enzymes, and drafting recycling strategies. Through an extensive literature review of 50 scientific articles, IDE identified 40 relevant enzymes. Three specific enzymes were selected for biodegradability assays: Celluclast 1.5L, Porcine Liver Esterase, and an esterase from *Bacillus stearothermophilus*. Experiments were conducted in controlled conditions and four different strategies: a) Celluclast 1.5 L biodegradability tests; b) *Porcine Liver Esterase* biodegradability tests; c) *Esterase from Bacillus stearothermophilus* biodegradability tests; and d) a combined Celluclast 1.5L + *Esterase from B. st.* biodegradability tests. IDE's focus is on developing efficient methods for degrading both fibres and resins in composite materials, aiming to advance sustainable recycling techniques.

Composite preparation and properties evaluation

In a further stage of the ESTELLA project, the target resins were produced at a higher scale (kg). CID is the coordinator of the Estella Project and is involved in the development and production of the final prototypes, *i.e.* a window frame for the construction sector and a scooter platform for the mobility sector, using the developed materials. To this end, trials have been carried out to test the processability of each of the selected composites, and flat specimens have been manufactured to perform mechanical tests to study their properties (Fig. 7). In parallel, simulation tests were carried out to predesign the prototypes and to design the moulds in which the final prototypes will be manufactured.

Safety, environmental and social assessment

The ESTELLA project wants to develop safe-and-sustainable-by-design (SSbD) criteria in polymers. Therefore, the impact of biocomposites on health, environment, and society is being studied.
Idener and NIC are responsible for predicting toxicity and assessing the exposure of the components and degradation products of the developed

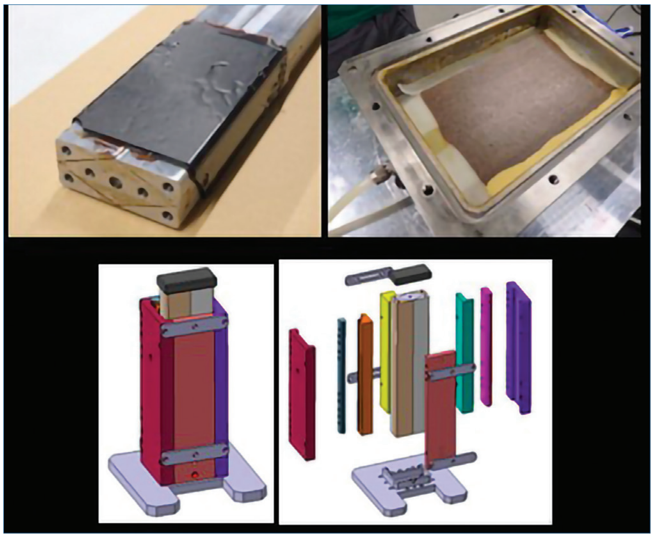

Fig. 7 - Manufactured and design prototype

materials. For toxicity prediction, QSAR modelling through a series of steps is used: collecting toxicity data from databases and experimental sources, pre-processing the data by cleaning and selecting relevant molecular descriptors, constructing mathematical models, and validating the models internally. For exposure assessment, indirect methods to determine human and biodiversity exposure to material components and degradation products are used. This involves describing exposure sources, pathways, and routes, as well as estimating exposure distributions within populations using fugacity models. Information on chemical degradation and accumulation from scientific literature and experimental data will be gathered. The results from both toxicity prediction and exposure assessment are integrated into a risk assessment to provide a comprehensive understanding of the potential environmental and health impacts of the materials and guide their safe design. At the same time, SINTEF is involved in evaluating the toxicity of ESTELLA materials, using MS-based analytics to assess what potentially harmful compounds are being released upon environmental exposure. In conclusion, Fraunhofer ISI (**https://www.isi.fraunhofer.de/en.html**) conducts a socio-economic analysis of ESTELLA alongside European composite recycling technology's (**https://ecrtechnology.com/**) LCA assessment. Key findings reveal that thermoset polymers possess significant socio-economic value in the EU and globally, with future demand expected to grow, particularly for fibre-reinforced composites. Innovative and scalable solutions are essential to compete with fossil-based materials. Economic success hinges on lowering energy consumption, enhancing material quality, reducing costs, and minimising environmental impact. The EU provides favourable conditions for the market uptake of both re-processible fossil and bio-based thermoset composites. However, challenges such as high production costs, performance uncertainties, and the need for stable demand for new materials must be addressed. In addition, ESTELLA's success is highly dependent on an efficient industrial waste management system, which requires improvements throughout the recycling value chain.

Conclusions

The ESTELLA project started in June 2022 and has lasted 3.5 years. Among several epoxy resins containing CANs in their chemical structure, three have stand out as the most promising ones. These resins have been combined with fibres to obtain biocomposites. Scaling-up tests are currently running, and the prototypes are under development (Fig. 7). At the same time, biodegradability and recycling tests are running together with the assessment studies to evaluate the impact of the proposed novel processes on the environment and society.

Acknowledgements

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Produzione di biocompositi: il progetto Estella

Lo scopo del progetto ESTELLA è quello di sviluppare e produrre compositi epossidici termoindurenti sostenibili, con un impatto sull'intera catena del valore dei materiali, in particolare introducendo un Covalent Adaptable Network (CAN) nelle matrici e nelle fibre a base fossile e biologica secondo l'approccio Safe-and-Sustainable-by-Design (SSbD). Questo approccio consentirà il riciclo dei compositi epossidici e ridefinirà tutti i processi di produzione e successivo riciclaggio.