

FROM BIOREFINERY BY-PRODUCT TO BIORESINS. THERMOSETS BASED ON HUMINS AND EPOXIDIZED LINSEED OIL

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*Dedicated to the 70th anniversary of the Department of Pulp and Paper,
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Resource depletion is one of the hardest challenges facing humanity today. Reuse, repurposing and waste management are valid strategies in order to relieve some of the pressure on natural resources. For the first time, in this work, we propose to study the properties of bioresins synthesized by the combination of a lignocellulosic based by-product, humins (Hu), and a vegetable resourced comonomer, epoxidized linseed oil (ELO). The copolymerization of these two bio-based products was conducted with the help of a common hardener, Capcure. The synthesized bioresins display a range of mechanical properties, from elastomers to rigid thermosets, showing their ability for industrial applications.

Keywords: renewable resources, biorefinery by-products, humins, epoxidized linseed oil

INTRODUCTION

The European strategy of development envisages a bio-based economy founded on locally sourced and produced plant and waste derived materials, chemicals, fuels, food and feed. This global paradigm shifting from oil-based towards bio-based materials represents a unique opportunity for Europe to kick-start a world leading competitive bio-economy with significant financial, environmental and societal benefits. The EU, with its strong agricultural, agro-food and forest-based sectors and world leading companies in the plant breeding, biotech, renewable energy and chemical/biochemical industries, is technologically poised to spearhead the development of a bio-based economy with a global market value of € 200bn by 2020. Therefore, the research and innovation in the bio-based materials area have the aim to support the transition towards more efficient energy building by means of reducing the dependence on fossil resources. For this application, the target is to obtain bioresins with the higher amount of bio-based percentage. In this study, we focus on the elaboration of by-products based resins and their elaboration by applying the principles of green

chemistry and circular economy. This study was done in the frame of LIFE15 ENV/BE/000204 project "RECYSITE",¹ which aims to demonstrate the recyclability and reuse of a new generation of high-performance fibre-reinforced thermoset composites from renewable resources (bio-waste). In this perspective, we have focused on developing bioresins starting from renewable products for the eco-design of novel biobased materials.

The design of the bioresin materials has been done by choosing the main components: humins (Hu), a by-product from bio-refineries, and epoxidized linseed oil (ELO), an epoxy derivative of natural polyunsaturated linseed oil. The main component of these designed formulations is represented by humins, a biorefinery side product. Despite the fact that this product, resulting from prolonged sugar degradation reactions in the caramelisation process, is known for almost a century,²⁻³ its applications are limited to energy and heat conversion.⁴⁻⁶ Recently, we have shown in our initial work that humins can be successfully used to produce polymeric foams.⁷⁻⁸ The polyfuranic structure of humins and its high

functionality are important structural factors that should be considered and even exploited in order to develop interesting bio-based thermoset materials,⁹⁻¹⁰ or as a matrix for impregnations and composites.¹¹⁻¹²

Humins are heterogeneous amorphous biomacromolecules, with a model structure constituted by furan rings connected *via* alkylene moieties, as proposed by van Zandvoort *et al.*¹³ and schematized in Figure 1. Although the interest is high, rarely materials have been elaborated from humins or humin derivatives, such as humin foams.⁷ In one such case, they have been employed as a low-cost complement for polyfurfuryl alcohol (PFA) in thermosetting resins. The resins were used to impregnate filter paper, and composites were obtained. The composites presented twice the tensile strength of composites elaborated using neat PFA or a PFA/lignin blend. Bio-based and bio-sourced materials employing epoxidized vegetable oils are much more prevalent. Vegetable oils are valuable platform chemicals for high performance materials due to their global availability and diversity.¹⁴⁻²⁰ ELO was employed as the main component for thermosetting resins by crosslinking with anhydrides.²¹⁻²⁶ Resins with bio-sourced content of up to 60% for MHPA and to 70% for BTDA were obtained.²⁷ Bio-sourced resins present decomposition temperatures similar to those of commercially available DGEBA-based epoxy resins.

Taking into account these previous results, the strategy proposed in this work is a next step, *i.e.* the design and manufacturing of a bioresin based on humins and ELO. To copolymerize the two products, a third component was included in the formulations as a common hardener: Capcure 3-800. Capcure 3-800 is sold as a low-temperature, industrial epoxide hardener. One of its main characteristics is that a tertiary amine-based initiator is not required with this hardener. This property allows the conception of eco-friendlier materials, since no initiators/catalysts are required. Figure 1 displays the chemical structure of the feedstock used in the conception of the bioresins.

In order to optimize the maximum humins content in the bioresin formulations, different HU/ELO/Cap ratios were tested, as presented in Table 1.

Structural insights into the copolymerization mechanism of Hu/ELO/Cap have been thoroughly provided in a previous work (not yet published), showing the formation of a bioresin terpolymer.

In this study, the thermo-mechanical properties of the obtained bioresins are studied, in order to highlight their ability to generate materials with industrial application potential. The thermomechanical properties of the bioresins have been analyzed by rheometry, dynamic mechanical analysis (DMA), Shore tests and the thermal resistance of these polymers has been evaluated by thermogravimetry (TGA).

EXPERIMENTAL

Materials

A commercially available bio-based epoxy molecule was obtained from Valtris Ltd. It is an epoxidized linseed oil (ELO), which is viscous-liquid at room temperature, having a viscosity of about 1200 mPa.s. ELO has a molecular weight of about 980 g.mol⁻¹ and contains about 5.5 epoxy groups, on average.

Humins (Hu) were provided by Avantium Chemicals, as produced at the Avantium pilot plant in Geleen (Netherlands). These humin oligomers have molecular masses that generally range from 270 to 650 g.mol⁻¹.

CAPCURE® 3-800 (CAP) is a mercaptan-terminated product used as a liquid curing agent with unique rapid-cure characteristics for epoxy resins at ambient temperatures provided by Gabriel Performance Products.

Sample preparation

For the synthesis of the resins, multiple formulations and parameters have been assessed. The aim of this research was to accommodate formulations with a large content of humins. The humins were preheated at 80 °C, then the hardener, in the specified proportions, was added to the humins and the mixture was well homogenized for 5 to 10 minutes. Thereafter, it was heated to 130 °C and stirred at this temperature for 20 minutes. To the hot mixture, ELO was added and incorporated. The homogenous mixture was then poured into the molds and kept in an oven at 130 °C for four hours. This crosslinking protocol is consistent with the results of curing, postcuring followed by DSC analyses.

To prepare the DMA specimens, the pre-polymer was put in a mold of 48 x 8 x 4 mm³ (length x width x thickness) and heated firstly to 80 °C under pressure of 10 bars for two hours. Then, the material was heated to 130 °C for 60 min to ensure completion of the curing.

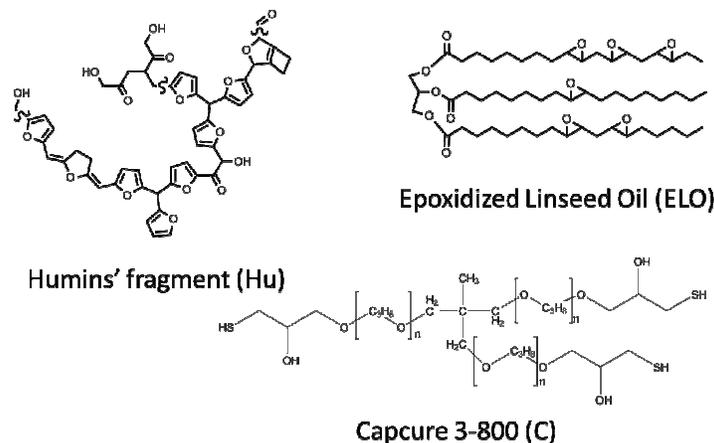


Figure 1: Chemical structures of humins (Hu), epoxidized linseed oil (ELO) and Capcure 3-800

Table 1
Resin formulations based on humins, ELO and Capcure

Humins, wt%	Capcure, wt%	ELO, wt%	Sample code
30	52.5	17.5	30 Hu
40	45	15	40 Hu
50	37.5	12.5	50 Hu
60	30	10	60 Hu

Experimental techniques

Rheometry

Rheological measurements were performed using an Anton Paar MCR-302 rheometer, using disposable plate-plate geometries (25 mm diameter and 1 mm gap). The measurements were carried out at a scan rate of $0.2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ over a temperature range from $80\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. Complex viscosity, storage modulus (G') and loss modulus (G'') were measured by oscillatory shear experiments with an angular frequency of $10\text{ rad}\cdot\text{s}^{-1}$ and a deformation of 0.2%. The temperature of crossover of the values of storage (G') and loss (G'') moduli was considered as the temperature of gelation (Tgel).

Thermogravimetric analysis

The thermal stabilities of the obtained bioresins were analyzed using thermogravimetric analysis (TGA). The thermal degradation, mass loss and its derivative as a function of temperature were evaluated using a Mettler-Toledo TGA2 between $25\text{ }^{\circ}\text{C}$ and $1000\text{ }^{\circ}\text{C}$ under oxidative (air) flow ($50\text{ mL}\cdot\text{min}^{-1}$) at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Samples of about 5-10 mg were placed into $70\text{ }\mu\text{L}$ alumina pans and tested.

Dynamic mechanical analysis

DMA measurements were performed in a Mettler-Toledo DMA1, equipped with a three-point bending assembly, at an oscillatory frequency of 1 Hz and an

amplitude of $20\text{ }\mu\text{m}$. The analyzed samples had rectangular dimensions of $48 \times 8 \times 4\text{ mm}^3$ (length x width x thickness). Each resin formulation was analyzed 3 times and the values were averaged. The DMA was operated in the temperature-scanning mode with a constant displacement amplitude and frequency. The temperature ramp covered a range from -50 to $120\text{ }^{\circ}\text{C}$, at a heating rate of $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere. The loss (E''), storage (E') Young moduli and damping factor ($\tan \delta = E''/E'$) were determined.

Shore hardness test

A Zwick Roell 3116 hardness device was used to determine the hardness according to ISO 7619-1 ASTM D2240 and ISO 868. To avoid errors, five samples of each bioresin formulation were tested, and three measurements have been done for each sample.

RESULTS AND DISCUSSION

Rheometry analysis during crosslinking

Chemo-rheological studies were done in order to follow the chemical reactivity of the elaborated mixtures and also to identify the physical phenomena accompanying network formation, *i.e.* gelation and vitrification. The results of this study for the four formulations are presented in Figure 2, showing the evolution of G' and G'' moduli during crosslinking of the systems. We can

observe that the humin-based reactive mixtures start to react in the interval of 117-149 °C, when heated at 0.2 °C.min⁻¹, depending on the formulation composition. Also, it can be noticed that the system with the higher content of humins (60%) starts reacting at a lower temperature, around ~100 °C, with a gelation point at ~117 °C, in contrast with the system richer in ELO (30% of humins), which starts reacting at around 120-130 °C with a gelation at around 150 °C.

Investigation of bioresins properties

Thermomechanical properties

DMA analyses were performed to analyze the molecular dynamics of the humin-based bioresins, especially the α relaxation phenomenon. Depending on the bioresin formulation/composition and temperature, some events can occur during mechanical solicitation, such as energy dissipation and mechanical transition. The values of maximum $\tan \delta$ are assigned to the α relaxation (T_a) phenomenon, related to cooperative chain motions and associated with the macroscopic T_g . As presented in Figure 3 and Table 2, the synthesized bioresins

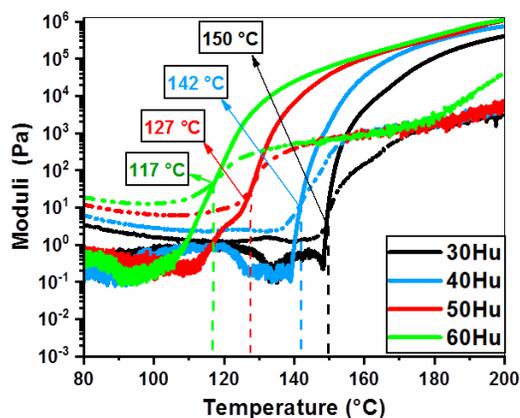


Figure 2: Evolution of moduli of humin-based mixtures during heating from 80 to 200 °C at 0.2 °C.min⁻¹

The DMA results were compared with those of DSC (second curing heating to measure the T_g) and with the hardness test results, as presented in Table 2. We can observe that the three techniques conduct to results that are in agreement, T_g values measured by DSC and the hardness of the bioresins follow the same trend as the $\tan \delta$ values. By Shore hardness tests, the resistance of

have a broad interval of $\tan \delta$, from ~ 10 to 60 °C, showing the potential of the proposed formulations to produce materials from elastic to rigid ones.

The symmetrical Gaussian shape of the $\tan \delta$ peak of “30 Hu” and “40 Hu” bioresins is an indication of the homogeneous distributions of relaxation times in the chain motions of the polymer. Increasing the humin content in the formulations produces an increase of the chain relaxation times, which is reasonable, considering the particularities of the humin structure. Then, the presence of a single $\tan \delta$ peak in each DMA curve is also a sign of homogeneous networking during terpolymerization. Then, we can observe in Figure 3 that the bioresins with lower content of humins (30%) have higher amplitude of damping, *i.e.* higher peak height that could be related to the facility of chain motions, the high content of triglyceride chains of ELO playing the role of plasticizer between the humins core and increasing the energy dissipation by internal frictions. In consequence, the impact strength increases due to better dissipation of vibrational energy during impact.

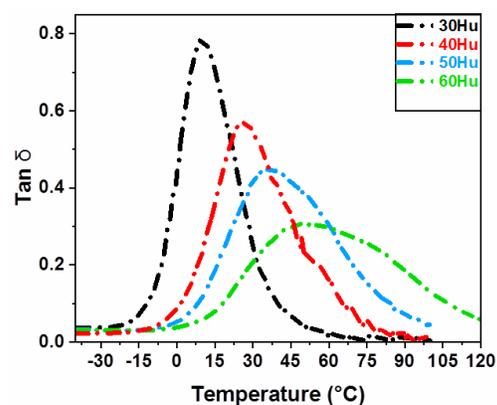


Figure 3: DMA plot for humin-based bioresin systems from -50 to 120 °C at 3 °C min⁻¹ and 1 Hz

the bioresins was measured upon the penetration of a spring-loaded needle-like indenter. The Shore hardness results of the synthesized bioresins show values from 64A to 49D. According to the Shore hardness scale, the first value corresponds to a more elastic material, while the hardness of the bioresins with higher content of humins (60%) corresponds to more rigid, hard materials.

Table 2
Comparison of mechanical properties of humin bioresins according to DMA, DSC and Shore hardness test analyses

Bioresin	$\tan \delta$	T_g , DSC	Hardness
30 Hu	10	-3	64A
40 Hu	28	11	74A
50 Hu	37	17	40D
60 Hu	60	30	49D

Thermal stability of the networks

Thermogravimetric analyses were carried out to measure the thermal stability of the fully crosslinked materials under oxidant (air) flow. The TGA results of analyzed bioresins are given in Figure 4. The temperature of degradation was considered at 5% of the weight loss, $T_{5\%}$. The thermal degradation of the four bioresins involves complex chemical and thermo-oxidative multistep mechanisms. Surprisingly, the obtained results

reveal a higher thermal stability for the ELO rich systems. We would expect that the presence of humins in the bioresin formulation should increase the thermal stability by the polyfuranic network. It wasn't the case, since the bioresin with 60% humins content had a lower thermal stability with a $T_{5\%}$ value of ~ 250 °C, compared with ~ 300 °C for the 30% humins bioresin. Perhaps, we can explain this result by the high content of oxygen functions in humins, so we would expect an easier cleavage of ether links.

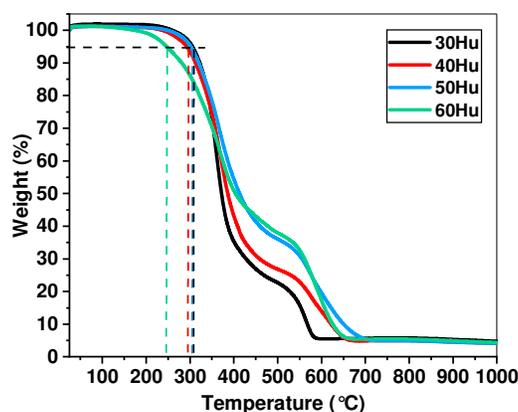


Figure 4: Thermogravimetric analysis of humin-based bioresin systems at 10 °C. min^{-1} under air

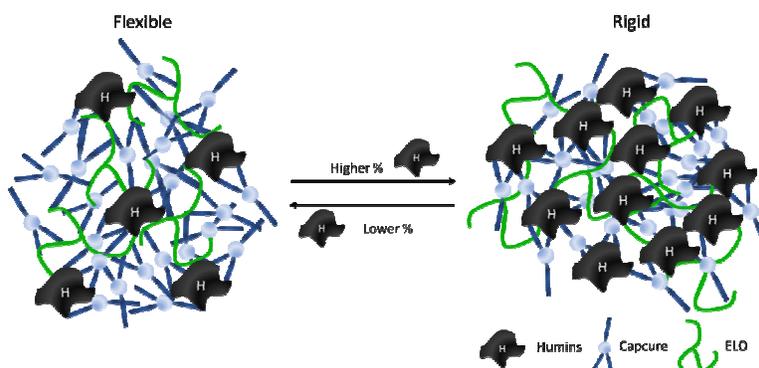


Figure 5: Humins-Capcure-ELO schematized networks

As presented in our previous study (not yet published), regarding the reaction mechanisms part, there are several possibilities of chemical

reactions between the humins, ELO and Capcure. This freedom of each component to form chemical bonds with other components implies

that the ratio of the reagents can be varied over a wide interval, between 30 and 60% weight in humins, yielding bioresin materials in each case. This variety of compositions allows a very good control over the final properties of the resulting material. The mechanical properties of the resin formulations vary with the proportion of humins present in the material. A formulation rich in humins is more rigid, while a formulation with a lower percentage of humins is more flexible, as schematized in Figure 5. The tuning of mechanical properties in the formulation phase is a very enticing advantage for thermosetting resins, as they can be optimized for the desired purpose.

CONCLUSION

Bioresins incorporating up to 60% weight of humins as a biorefinery by-product have been designed and synthesized. These formulations also feature ELO, a vegetable epoxidized oil, leading to resins with a bio-sourced content up to 70% in weight. The humin-based bioresins present a broad tan δ interval from ~10 to 60 °C, showing the potential of the proposed formulations to produce materials from elastic to rigid ones. They also have good thermal stability, with $T_{d5\%}$ values from 250 to 300 °C. The hardness of the resulting materials can be controlled, and in the synthesized bioresins, it varies between 64A and 49D, from elastomers to rigid thermosets. This type of materials adheres to the principles of circular economy, in which a by-product finds a new life as the main component of high value-added materials.

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