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Article

Sustainable composites from nature to construction. Hemp and Linseed reinforced biocomposites based on biobased epoxy resins

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Abstract: The present manuscript describes the use of natural fibers as natural and sustainable reinforcement agents for advanced biobased composite materials for strategic sectors, such as construction. The characterization carried up have shown the potential of both hemp and linseed natural fibers and their composites to be used as insulation materials. Nevertheless, linseed shows better mechanical performance and hemp a higher fire resistance. Demonstrating that although natural fibers have similar properties each of them should be used specifically for a purpose. Besides the work also evaluates the use of bio matrixes in composites, demonstrating their feasibility and how they impact the properties of the final material, our bio resin enhances fire resistance and decrease the water absorption capacity of the natural fibers. Enabling the use of such composites as a final product. Therefore, it has been demonstrated that it is possible to manufacture a biocomposite with non woven natural fibers. In fact, for properties such as thermal conductivity, they are able to compete with current materials. Proving that biomaterials are a suitable solution for developing sustainable products fulfilling the requirements of the end user applications.

Keywords: Linseed; Hemp; biocomposites; bioepoxy; nonwoven reinforcements

1. Introduction

The European commission published in December 2019 the Green Deal, a document that gathered several environmental issues and goals, and that is guiding the European countries to move towards a more sustainable and circular economy [1]. Among all the different facts and references published in it, the commission showed that the construction sector is responsible for 20% of the European emissions of greenhouse gases and that together with the transport and energy sectors, they produce more than 50% of the total greenhouse emissions in Europe. Therefore, to reach the CO_2 neutrality set for 2050 and the reduction of 55% of CO_2 emissions by 2030, it is essential to tackle the environmental problem in these sectors by adapting their activities and increasing their environmental sustainability [2-4]. Besides, the pandemic and the current state of the global supply chain has demonstrated that new sources of material must be investigated and incorporated in the final product.

Among the different materials that must be tackled and improved in these sectors, composites are one of them as they can make a difference. A composite material is composed by two or more materials, achieving a performance that would not be achieved by any of the individual components. It is composed by a reinforcement, a material that enhance the mechanical properties and a matrix which is the component that enables a good impregnation and consolidates all the reinforcement together. The use of natural components in construction is not a novelty as composites materials reinforced with natural fillers were very common in the constructions of the Egyptians [5] who used straw fibers.

Nowadays, also in the construction sector composites are being used. Glass fibers are being used as reinforcement to get more resistant and insulating materials [6-9] allowing

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to reduce the amount of energy used to maintain a constant and comfortable temperature inside the buildings. Considering the European market, there are two potential sustainable solutions to substitute the glass fiber in composites, natural hemp and/or linseed fibers, due to their local availability and properties are the main alternatives, they have focused the interest of many researchers and industries [10-14].

Moreover, the implementation of natural fibers as reinforcement in composite materials is a valuable and strategic opportunity for the European agricultural sector. The use of hemp and linseed fibers would allow their valorisation while reducing the waste production, reaching the goals established at international level and moving towards a zero-waste goal. Nowadays, tons of natural fibers are being produced and wasted each year [15], therefore their valorisation could have a huge potential and could bring a real economic impact to rural agricultural regions in Europe, which is one of the objectives of the Green Deal strategy. This use of resources would imply the generation of new economic opportunities for these waste streams, such as their use in the construction sector.

Several studies have already proved a huge potential of natural fibers to be used as reinforcements, as the mechanical properties of their produced composites can reach similar outcomes to those composites of glass fiber [16-19]. These results are opening many market opportunities for the natural fibers but as their cost and reliability are still underevaluated, they are found mainly in non-structural parts and less demanded applications or products [20].

Therefore, there are still challenges and technical limitations that must be overcome for the use of vegetal fibers as valuable reinforcement in the composite market, at the same level than the current reinforcement materials. As reported in previous research, the adherence between matrix and reinforcement is a critical requirement to maximize the materials potential and their performances [21]. The use of binders and/or modification of the resin or fibers can be required, to reinforce the interactions between resin and fiber and so the final properties of the material, so a commercial level is achieved.

Thus, to achieve the circular economy premises in the whole composite systems, there is not only need to focus on the fibers but also on the resin. It is the aim of this study, where the resin formulation was optimized for its adherence to the fibers, its sustainability, carbon emissions and the reduction of the environmental footprint. In this sense plenty of work is showing the huge potential of natural fibers and resins and how their nature, structure and surface treatments impact the final properties of the composites. Some of these researches have not stopped on the mechanical performances or on the chemical properties, but they try take into consideration the environmental impact and the future of these newly developed composites [22].

One of the most common types of thermosets used in the construction sector are the epoxy resins [23-25]. The final thermoset chemical structure and properties are governed by the chemical crosslinking so by the monomer vs. hardener/initiator reactivity and compatibility [26,27]. Then, to prepare composites that enable the achievement of the carbon footprint reduction, new epoxy resins with high biobased organic carbon content must be developed [9,10].

The chemical industry is turning towards the great variety of molecules that can be found in nature, as source of raw materials in the production of thermoplastics, thermosets or other products with industrial use [28]. One of the most abundant and widely used resource for the preparation of bio epoxy resins are the unsaturated vegetable oils like: castor oil, linseed oil, soybean oil and cardanol oil. Their epoxidation by a simple and green oxidation of fatty acids unsaturation's, allow the synthesis of aliphatic biobased epoxy monomers [29]. In this study, the epoxidized linseed oil (ELO) has been selected due to its high functionality (~5.5 epoxy groups/triglyceride) and the large accessibility of linseed crops in Europe. In the last years many efforts have been focused on sustainable synthesis of ELO based thermosets [26,27,30]. Another, biomolecules that are attracting plenty of attraction are sugars [31] or biopolymers such as cellulose [32] and lignin [33], due to their properties and chemical structures these natural compounds can be used as raw materials for the fabrication of matrices. Besides, in the case of lignin, lignin-based

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carbon fibers can be generated [34] and combined with lignin-based resins [35] making possible to generate a whole lignin-based composite. The industry is more focused in the use of lignin and cellulosic fibers as source of reinforcement for the automotive and construction sectors through the fabrication of green composites, hybrid biocomposites and even biotextiles [36].

Another relevant compound used in this study, a biorefinery derived side-product, are the humins, which are generated in the production of furandicarboxylic acid) [37-40]. Humins are composed mainly of aromatic rings, containing different functionalities varying in function of biorefinery processing: aldehydes, hydroxyls, carboxylic and ketones. These reactive groups make the humins promising building block and an important compound for the development of thermosetting resins [30,37,38,40,41,42].

The objective of the present work is a proof of concept for the validation of the designed sustainable composites based on ELO, humins and natural fibers to be used in a key sector, the construction, as described in the frame of LIFE15 ENV/BE/000204 project "RECYSITE".

Nowadays the plastics are becoming a challenge for waste management, especially those involving composite materials, as these materials cannot be melted due to the cross-linking covalent bonds which link network chains, hindering the recycling. Therefore, most of the waste of thermoset composites, from production or end-of-life, are not currently properly recycled (incinerated 41.6%; landfill 27.3%). Nevertheless, new strategies are being researched to propose new ways that enable to recycle the composite materials.

2. Materials and Methods

2.1. Materials

The epoxidized linseed oil (ELO; average molecular weight = 980 Da; average functionality = 5.5 epoxides per triglyceride, viscosity ~ 1200 Pa.s) was purchased from Valtris Specialty Chemicals. CAPCURE® 3-800 is a mercaptan-terminated product used as a liquid curing agent with unique rapid-cure characteristics for epoxy resins at ambient temperatures supplied from Gabriel Performance Products. The humins were kindly provided by Avantium (Amsterdam, Netherlands).

The nonwoven hemp and linseed fibers were kindly supplied by CENTEXBEL (Gent, Belgium). All the different consumables used during the infusion process were purchased from MEL composites (Barcelona, Spain).

2.2. Resin composition and preparation

The resin was formulated by combining the two comonomers, i.e. humins and ELO, with the hardener, Capcure 3-800, in different ratios as given in Table 1.

Table 1. Compositions of designed formulations

Humins (wt%)	Capcure 3-800 (wt%)	ELO (wt%)
30	52.5	17.5
40	45	15
50	37.5	12.5
50	30	20
60	30	10

To reach these formulations, a deep study of systems reactivity was previously realized by the dynamic DSC evaluating the enthalpies of polymerization reactions and also the interval of reactions temperature [41, 42]. An important objective of this work was the valorisation of humins, therefore it was used as primary monomer, with the highest possible ratio (≥ 50%). With this reason, the selected formulation was the one containing 50% Humins, 30% Capcure, 20% ELO to be studied to prepare composites with hemp and linseed fibers, as this formulation has a good reactivity and a biobased content of ~70%. This formulation has also the advantage of a good viscosity allowing the fabrication of

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composites by liquid resin infusion. As, shown in Figure 1 the crosslinking temperature of the resin is ~119 °C with a viscosity of the system of around 1 Pa*s (1000 cPs), with the lowest value of viscosity between 80 °C and 90 °C, where the viscosity decreases to ~900 cps.

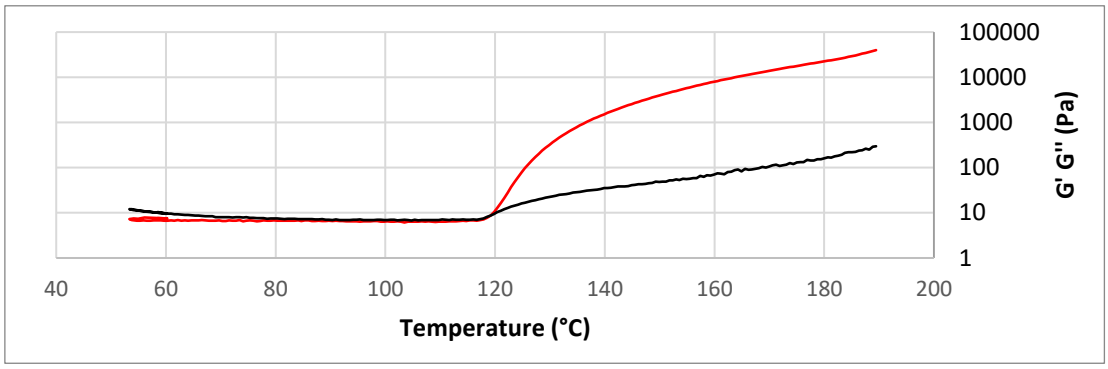

Figure 1. Evolution of storage (black) and loss moduli (red) with the temperature for the thermosetting resin 50%Hu/30%Cap/20%ELO.

To prepare the thermoset material, the humins were heated up to 75-80 °C, allowing them to flow and be mixed during 5 minutes with the corresponding quantity of ELO and under vigorous stirring with the Capcure at 75 °C. The final mixture was kept under continuous stirring during 10 minutes at 75 °C. Due to the slow polymerization rate, it was possible to proceed with the composites fabrication by LRI process and to maintain the composite for 3 hours at 130 °C achieving a complete curing [41].

2.3. Fabrication of composites by Liquid Resin Infusion (LRI)

There are several technologies allowing the production of thermoset composite materials such as pultrusion, resin transfer moulding or liquid resin infusion (LRI), among many others [37]. LRI was chosen since it is versatile from a technological point of view, and for its economic feasibility allowing to obtain a product that will be high competitive in the market. The LRI processing technology consists on the generation of vacuum in a covered mould where the reinforcement material has been previously placed, and to use this pressure gradient to pump the matrix into the mould until all the reinforcement is impregnated. At this point the entrance is closed and the vacuum maintained though the curing process. In Table 2 are given the compositions of 4 prepared composites with 1 or 3 fibers layers prepared. Once the infusion has been made the resin is trapped and cured within the mould [29].

The process allowed to prepare composites of ~0.16 m², based on hemp and linseed fibers with different densities: 600 g/m² (3 layers of reinforcement) and 1300 g/m² (1 layer of reinforcement). Therefore, the final composites vary in terms of fibers and also in the amount of resin that has been incorporated, as resumed in Table 2.

Table 2. Composites compositions based on different layers of hemp and linseed fibers

Composite based on 50%Hu/ 30%Cap/20%ELO	Fiber	Number of layers	Fiber density (g/m²)	Fiber weight (%)	Resin weight (%)	Thickness (cm)
A	Hemp	1	1300	29,9 ± 1,4	70,1 ± 1,4	5,8 ± 1,0
B	Hemp	3	600	31,1 ± 2,0	68,9 ± 2,0	7,1 ± 1,1
C	Linseed	1	1300	36,8 ± 1,3	63,2 ± 1,3	3,6 ± 0,5
D	Linseed	3	600	28,3 ± 2,3	71,7 ± 2,3	5,1 ± 0,5

*Deviations shown in the table are between specimens.

** Each of the specimens thicknesses have just a maximum deviation of 3%.

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2.4. Experimental Part

2.4.1. Thermal conductivity

The thermal conductivity of the prepared materials has been measured by the stationary methodology of the hot plate using a DTC-25 TA instrument (New Castle, UK). After reaching the thermal equilibrium, the temperature difference across the specimen is measured along with the output from the heat flux transducer. The thermal conductivity of the samples was determined applying the equation:

$$\Delta Q/(\Delta t*A) = -k*(\Delta T/\Delta x) \quad (1)$$

where ΔQ is heat gradient (W); Δt is time gradient (s); A is the sample area (m^2); k is the material constant thermal conductivity (W/(m*K)); ΔT is the gradient of temperature (K); Δx is the thickness of material (m)

2.4.2. Tensile testing

The Young's modulus and the tensile strength of the linseed and hemp non-woven composites were measured with an Ibertest STIB-200/W - 200 KN (Madrid, Spain) uniaxial test machine following ISO 527-5. As stated in the ISO, it was used a 1 mm/s speed and then the speed was increased to 5 mm/s. The tests were done with 8 specimens of 17.5 cm length x 2.5 cm wide from each composite and the values were averaged. The manufacture of the specimens was done through the LRI of a single plaque. It was afterwards cut with a saw to obtain the specimens with a geometry of 2,5 cm wide and 17,5 cm long observable in Figure 2. Taps were added to the specimens, made of glass fibre and maintained with a standard epoxy resin in order to ensure a proper load transfer from the tensile machine to the specimen.

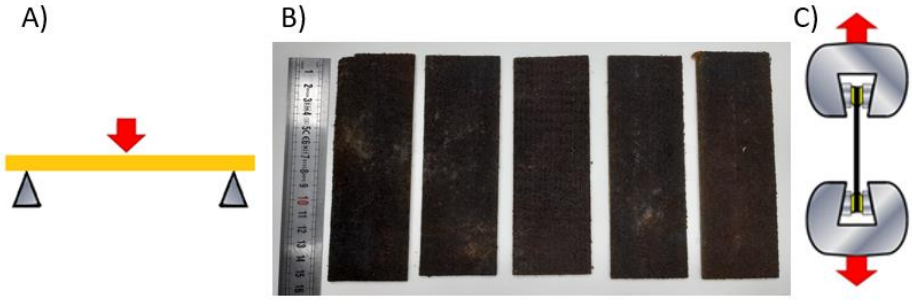

Figure 2. A) Scheme of bending tests; B) Nonwoven composites specimens for bending test C) Scheme of the tensile tests

2.4.3. Flexural testing

The flexural modulus of the composites was determined by using an Ibertest STIB-200/W - 200 KN (Madrid, Spain) uniaxial test machine, in three-points bending test method following the ISO 178, at a 1 mm/s speed and 2 mm/s. The tests were done on 8 specimens of 15 cm length, 5 cm wide and with a distance between supports of 10 cm, for each composite and the values were averaged (Figure 2)**.** The composites Young's modulus was calculated by using the equation:

$$E=(F/A)/(\Delta L/L) \quad (2)$$

F is the applied force (N); A is the specimens surface (cm^2); ΔL is the variation of length (cm); L is the initial specimen length (cm)

2.4.4. Cataplasma test

The cataplasma test was used to study the aging behaviour of the materials by measuring the physical changes caused in the samples (weight, shape and thickness) after their exposition at elevated temperature and high humidity . The measurements were performed with a Mirta-Kontrol equipment (Zagreb, Croatia) using ISO cataplasma test DIN EN ISO 9142. The samples were kept under a 100% humidity and 70 °C for a month, and the measurements were taken after 1, 7, 14 and 28 days. Before performing the flexural

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test (described in point 2.4.3) The samples were recuperated and dried during 12 hours at 60 °C. This drying process was applied in order to understand the aging effect, which has been simulated by the high humid conditions to which the samples have been exposed. In this way two sets of flexural measurements were differentiated: one after the exposition to the conditions defined in the cataplasma test, after cataplasma (AC) and one previous to the exposition, before cataplasma (BC). Hence, 6 different specimens were tested with dimensions 15 cm of length x 5 cm of width.

2.4.5. Scanning Electron Microscopy (SEM)

The adhesion between the natural fibers and the humins-based thermoset matrices, but also the morphology of fracture surface of the bio-composites were investigated by scanning electron microscopy (SEM). Fresh fractures of composites samples were mounted on a SEM stub and coated with platinum prior to observations and afterwards observed using a Tescan Vega 3 XMU SEM (Prague, Czechia) at an accelerating voltage of 5 kV.

2.4.6. Fire resistance test

To test the behaviour of the samples under fire conditions was used a Mirta-Kontrol equipment (Zagreb, Croatia). The reaction to fire tests method was EN ISO 11925-2 in which the samples are subjected to a direct single-flame source. The analyses take place inside a test chamber where the specimen is mounted vertically and subjected to a gas flame. During the test, time of ignition, burning droplets and whether the flames reach certain mark (defined by the ISO) within a prescribed time period, are registered. In this way it is possible to evaluate fire retardancy and generation of burning drops. Three specimens (25 cm length and 9 cm width) were tested from each sample.

3. Results and discussion

The first step towards the validation of a composite material is the quality of adhesion between the reinforcement and the polymeric matrix. SEM analyses were used to observe and evaluate the interaction between both components. The micrographs presented in Figure 3 confirm a good adhesion between the natural fiber and bio-resin. According with the SEM micrographs, the fibers surface is completely covered by the resin, proving the excellent compatibility between the two components of the biocomposite, the matrix and the biofiller. This is due to the excellent compatibility of vegetal fibers to the humins (hydrophilic macromonomer) as a consequence of the proper chemical affinity [21]. In the Figure 3 it is possible to observe that the fibers that come out of the matrix are impregnated with the resin, showing a good adhesion and compatibility between fiber and bioresin matrix. Besides, on the fractured composite can be noticed a good homogeneity in the fibers distribution and also it can observed a fibrillar breaking of the composite. Which is due to the fact that the fibers are in a non-woven structure, therefore once the matrix reach it limit force, the fibers start to break. Meanwhile, it is observed that after breaking, the fibers are completely covered in the matrix, meaning that the adhesion between fiber and resin is stronger than the force that the matrix is able to withstand. This observation strengthen the previous observation on the adhesion between fiber and matrix.

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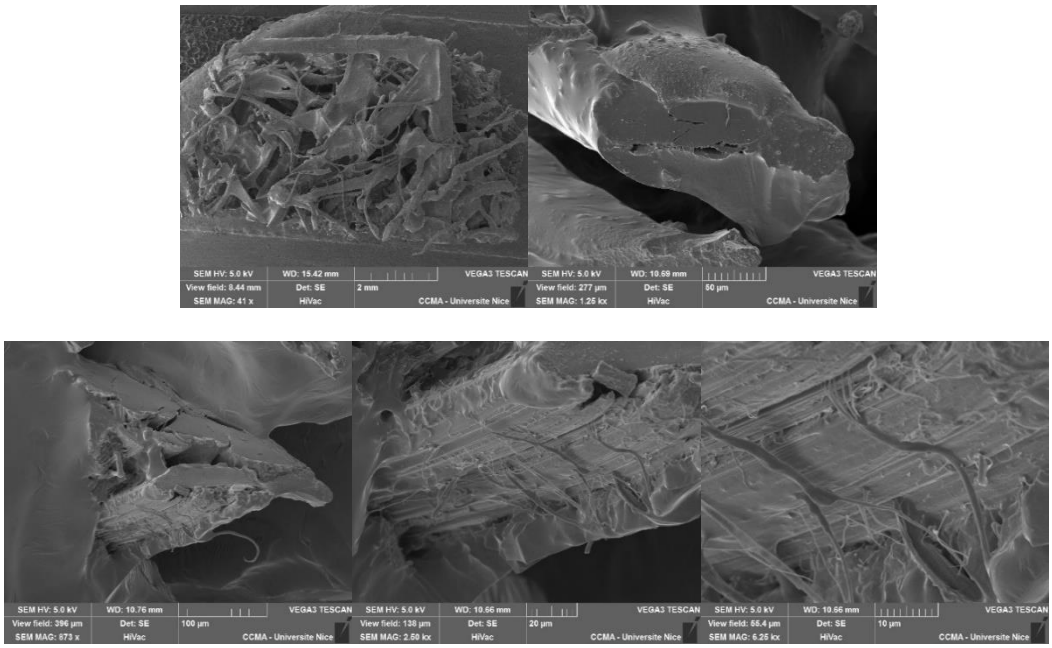

Figure 3. 50%Hu/30%Cap/20%ELO and hemp 1300 g/m2 composites: upper left, general look of the composite at a broken point; upper right, single hemp fiber covered in resin; lower row single hemp fiber covered by the resin in three successive magnifications.

3.1. Composites properties

The different biocomposite specimens were completely characterized following the conditions previously described.

3.1.1. Thermal conductivity

For the thermal behaviour of the composite materials, firstly the thermal conductivity of the natural fibers was measured. These measurements showed that the fibers thermal properties are in the same range as many other materials typically seen as good insulators such as sheep wool and glass wool with heat transmittance values of around 0.04 W/mK. It was found that the natural fibers of hemp and linseed have similar values of heat transmittance capacity, and that the density of these nonwoven structures do not affect the final capacity of the sample to transmit or isolate. Then, the four composite samples have superior values of the thermal transmittance compared to that of the neat fibers, multiplied by 2.5, reaching values of around 0.1 W/mK. This increment in the heat transmittance properties place the final composite materials in the range of other natural structures such as pine wood [43]. This result clearly shows the effect of the resin on the composites properties and that the thermal conductivity of the resin is higher than that of the reinforcement materials.

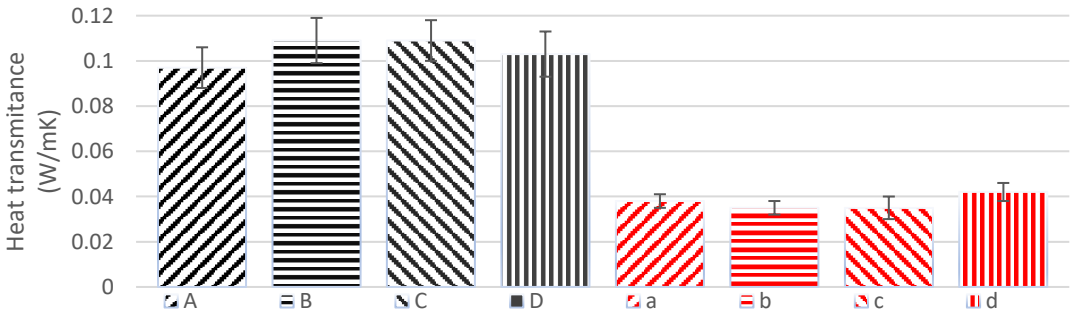

Figure 4. Heat transmittance of each of the different composites compared with the raw fibers (A: hemp composite 1300 g/m²; B: hemp composite 600 g/m²; C: linseed

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composite 1300 g/m²; D: linseed composite 600 g/m²; a: hemp 1300 g/m²; b: hemp 600 g/m²; c: linseed 1300 g/m²; d: linseed 600 g/m²).

With the date shown on Figure 4, it is possible to appreciate that the final properties of these composites are in line with other natural materials typically used in building structures. Although the densities and the source of the reinforcement is different, the values obtained for all 4 different composites are in the same range and therefore we can evaluate these composites made from natural reinforcement and biobased matrices a new possibility for the development of products with isolation properties.

3.1.2. Mechanical properties

The generated biocomposites have been tested mechanically by two different methods: tensile and flexural tests.

3.1.2.1. Tensile tests

The tensile strength and the elastic modulus have been studied comparing the prepared composites and the neat fibers. In these comparisons it is observed that the composite materials in which linseed fibers are used as reinforcement have a better mechanical performance than the hemp-based composites. This is aligned with the data reported by Padney et al. [44], research showing that the linseed is one of the most competitive natural fibers and that it can even go up to the same level as glass fiber. While comparing the tensile strength of linseed and hemp fibers it is possible to observe that the linseed shows twice the strength value of the hemp in both densities, and almost three times the elastic modulus of the hemp. Besides, in the base of the composites a significant difference is found depending on the fiber density, this difference is not dependant of the type of fiber as it is possible to observe it in both hemp (A, B) and linseed (C, D). In the case of the tensile strength the difference between the density of the two types of non-woven structures, provoked a drop of the tensile modulus value of a few MPa, more drastic in the case of the linseed and for the elastic modulus a drop of 100 MPa in the linseed case (Figure 5).

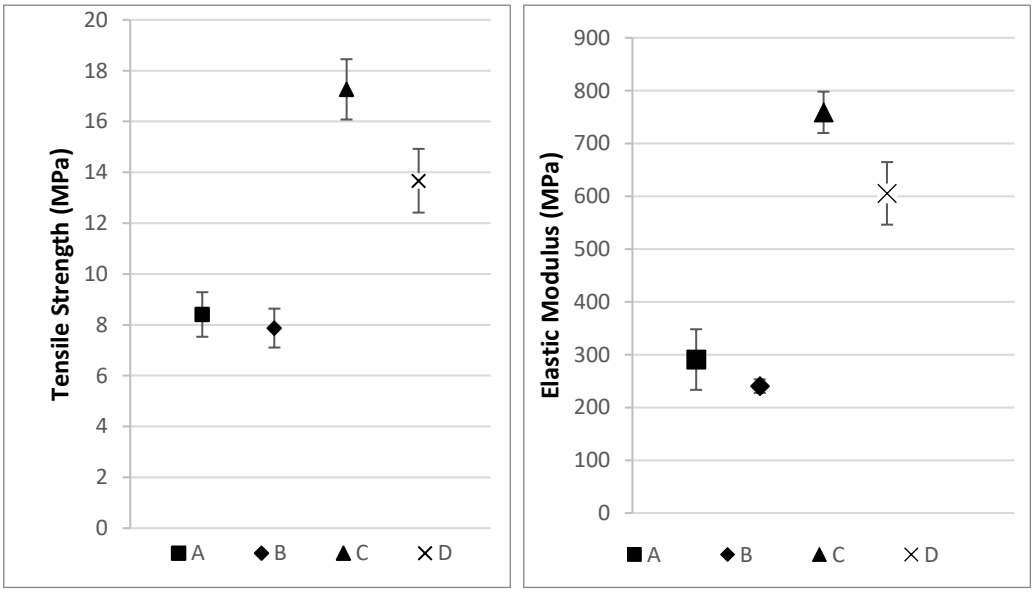

Figure 5. Tensile tests results (A: Hemp composite 1300 g/m²; B: Hemp composite 600 g/m²; C: Linseed composite 1300 g/m²; D: Linseed composite 600 g/m²).

The comparison of the shown data results with the reported tensile properties of woven reinforced composite materials as those gathered by Padney et al. [44] and Del Borello et al. [45], it is clear that the nonwoven structure cannot compete with the woven structures due to the lack of directionality of the fabrics. As it is shown by Bochnia et al. [46]

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the direction of the reinforcement has a direct impact on the mechanical properties, and this effect is the same for all kind of composite materials. The spread of results shown in the research depending on the orientation does not have any influence in these samples, as the fibers are randomly dispersed. These two points imply that the non-woven based composites can be used in any position as there is not a preferred direction.

3.1.2.2. Bending tests

The bending tests results are shown in the Figure 6 follow a similar behaviour as those reported for the tensile properties. The linseed fibers have a higher mechanical performance than the hemp fibers and high-density composites show higher bending modulus value. These results are in agreement with the previous data illustrated in Figure 5 in which the linseed has already shown higher mechanical performance than hemp. Nevertheless, it is remarkable that in the case of high-density hemp composites the bending modulus is quite close with that of the low-density linseed composite.

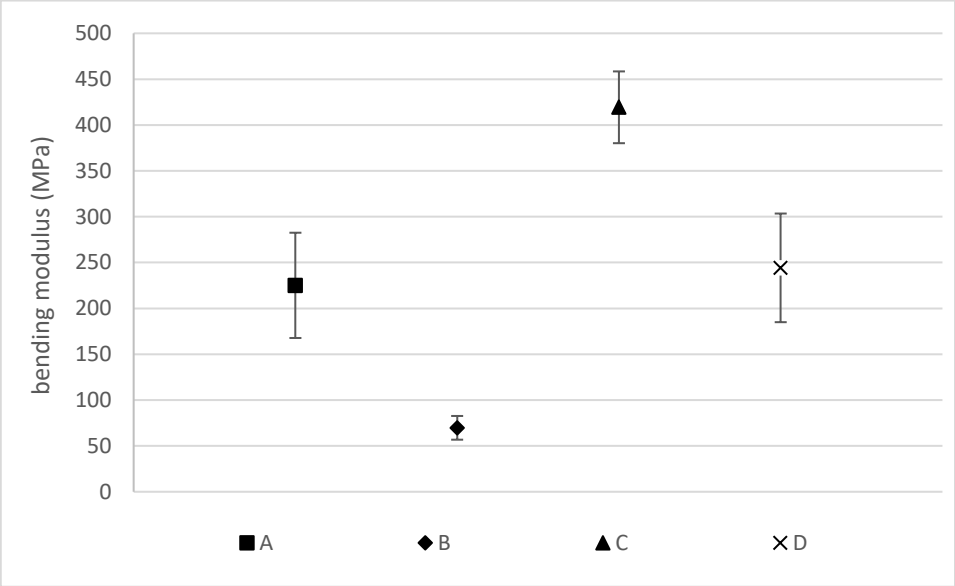

Figure 6. Bending tests (A: Hemp composite 1300 g/m²; B: Hemp composite 600 g/m²; C: Linseed composite 1300 g/m²; D: Linseed composite 600 g/m²).

3.1.2.3. Cataplasma tests

Physical changes in the composite specimens were measured during the exposure time. As specimens absorbed water physical changes in weight, width and thickness were monitored (Figure 7-Figure *9*).

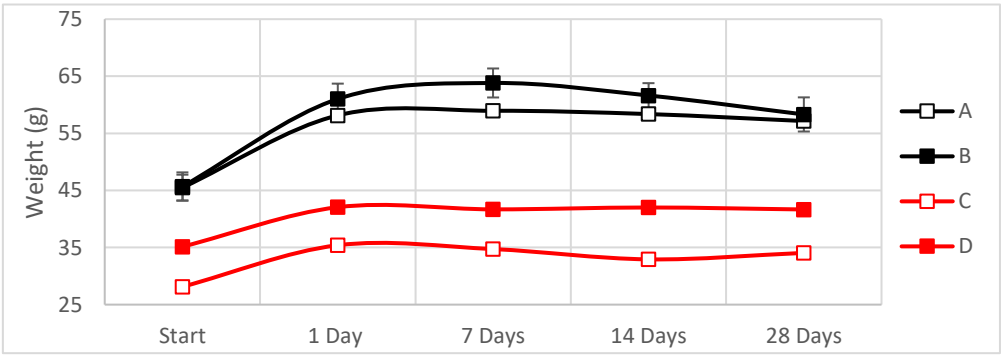

Figure 7. Variations in the weight during the cataplasma test due to the absorption of water (A: Hemp composite 1300 g/m²; B: Hemp composite 600 g/m²; C: Linseed composite 1300 g/m²; D: Linseed composite 600 g/m²). Raw data can be found in Table A 1.

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As shown in the Figure 8 and Figure 9 the dimensions of the hemp-based composites increased up to a 35% in weight and up to 15% in thickness, during the first 24h of exposure while their width increased with ~ 1% compared with the initial value.

In contrast, the weight increases during the first week for the linseed, up to a 40% of its initial value. While the width and thickness remain equal. Observing all these data and behaviours it is possible to say that in the case of both types of natural fibers all the water absorption is done after 1 day of exposure.

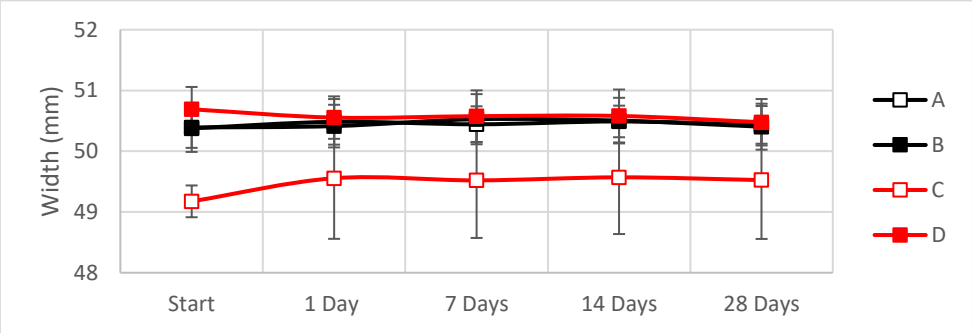

Figure 8. Variations in the width during the cataplama test due to the absorption of water (A: Hemp composite 1300 g/m²; B: Hemp composite 600 g/m²; C: Linseed composite 1300 g/m²; D: Linseed composite 600 g/m²). Raw data can be found in Table A 2.

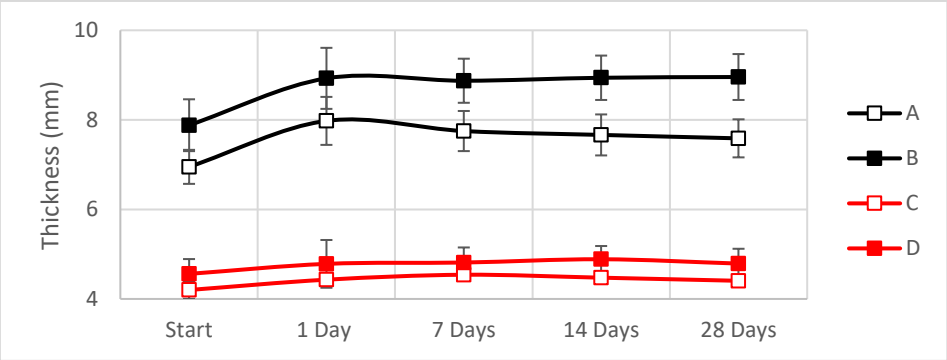

Figure 9. Variations in the thickness during the cataplasma test due to the absorption of water (A: Hemp composite 1300 g/m²; B: Hemp composite 600 g/m²; C: Linseed composite 1300 g/m²; D: Linseed composite 600 g/m²). Raw data can be found in Table A 3.

In Figure 10 values for the bending modulus for both composites before and after the exposure are compared. After the exposure, the low density fibers -based composites have increased values of the bending modulus by ~ 100 MPa, while in the case of high density fiber-based composites the bending modulus decreases ~ 200 MPa, ending both structures with similar bending modulus. The only point of the bending modulus that does not change, is the fact that the linseed fibers after the exposure still have values of around 550 MPa while for the hemp the values are down to 150 MPa. This implies that the linseed fibers are going to absorbed similar amounts of water than the hemp but due to their higher mechanical properties they will end up still having a higher mechanical performance. In the end the cataplasma test demonstrates that after the composite is saturated with water the mechanical performance of the linseed natural fibers has a bending modulus 4 times higher than the hemp, which means 400 MPa higher.

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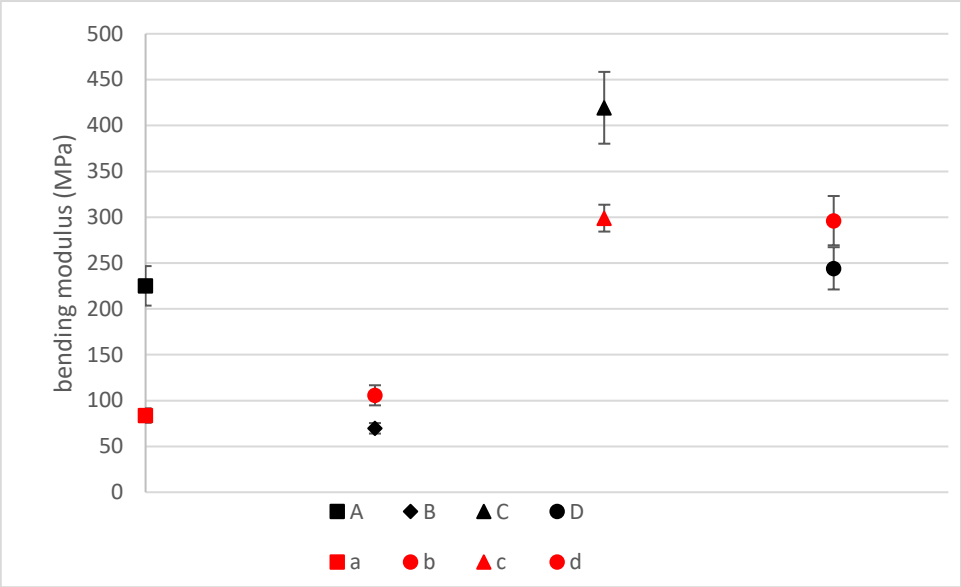

Figure 10. Variation of the mechanical properties before (BC) and after the cataplasma (AC) test (A: Hemp composite 1300 g/m² BC; B: Hemp composite 600 g/m² BC; C: Linseed composite 1300 g/m² BC; D: Linseed composite 600 g/m² BC; a: Hemp 1300 g/m² AC; b: Hemp 600 g/m² AC; c: Linseed 1300 g/m² AC; d: Linseed 600 g/m² AC).

3.1.3. Fire resistance test

All produced composite materials were tested for both their flame retardancy and the generation of drops. These tests show that none of the different materials generate burning drops while it is on fire.

Regarding the flame retardancy properties the composite materials have shown a lower capacity to spread the fire, in comparison with the natural fibers. As it is shown in Table 3, the presence of the resin has a flame retardancy effect on the final specimen. Making that while the natural fibers were not able to fulfil any of the test as in the case of the linseed or just the small burner during 15 seconds in the case of the hemp fibers. Whereas as the composite as a whole is characterized, the samples are able to fulfil the small burner during 15 seconds for the linseed, passing from a class F to a class E and in the case of the hemp it jumps to the next point where further characterization and techniques are needed in order to differentiate between class B, C or D.

Seeing all these points and how the different elements affect the fire propagation and therefore the final classification of the materials in the fire propagation classes. Two different conclusions can be easily made after observing the data gathered in Table 3. On one hand the presence of the resin, the composite as a whole, has higher fire resistance making the advance of the flame slower than in those cases in which no bioresin is incorporated in the sample. On the other hand, the most remarkable point is that even though all natural fibers are usually seen in the same way and similar fire behaviour are usually expected from them, the hemp has demonstrated to have lower fire transference than the linseed, favouring its use for this purpose.

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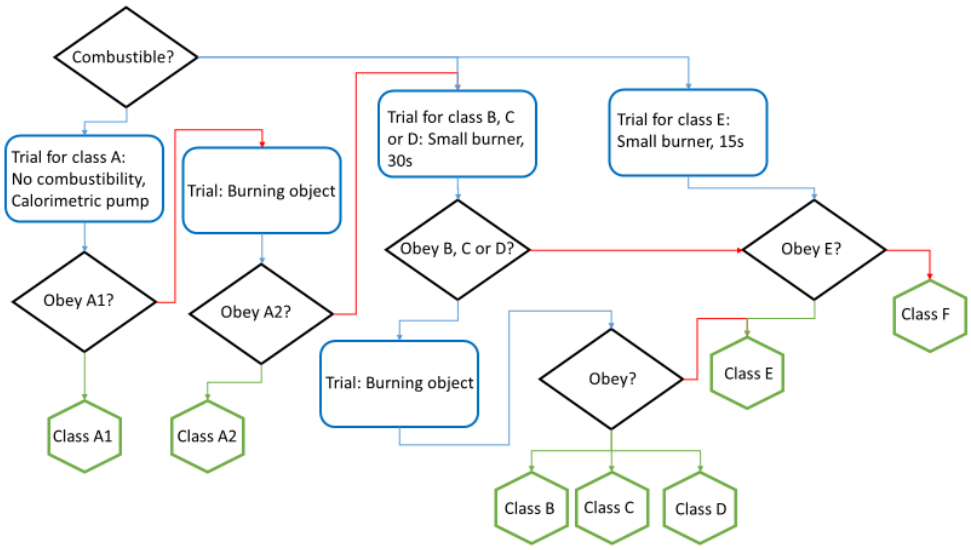

Figure 11. Scheme for the categorization of materials depending on their fire resistance

Regarding the propagation to other components through the generation of burning drops, it can be observed that none of the studied composites generate burning drops. This has a direct implication in the propagation of the fire towards other components or materials.

Table 3. Fire resistance classification of biobased non-woven epoxy composites

Material	Classification
Hemp	E
1 Layer of Hemp 1300 g/m²	B, C or D
3 Layers of Hemp 600 g/m²	B, C or D
Linseed	F
1 Layer of Linseed 1300 g/m²	E
3 Layers of Linseed 600 g/m²	E

4. Feasibility of the scaling up process

To demonstrate the feasibility of the fabrication of a 1 m² of composite, the LRI was upscaled to a mat of 1 m² with both types of fibers, demonstrating the capacity to manufacture bigger composite parts. On the other side, for comparison with commercial non-structural parts, a sandwich structure was manufactured with a PET core.

To manufacture sandwich structures, firstly, a 0.16 m² was fabricated to evaluate the best approach, which finally was a perimetral infusion process. For the large scale, a combination of strategies was used to reduce the impregnation time, the perimetral infusion with two entrances was supported by another four entrances within the geometry to speed up the impregnation process. The main difficulty of the sandwich structure was to assure the temperature on both sides of the sandwich (75-80 °C), to enable the resin to flow through the mats and PET's holes, joining all the components of the sandwich structure and avoiding possible delamination issues in the composite during its lifetime. Afterwards, it was possible to scale up the fabrication to a piece of 1 m². (Figure 12) At the end it was possible to manufacture several parts pre-industrial scale parts. These demonstrators had proven that the natural non-woven fibers can be used together with bio-epoxy matrix to generate a sandwich structure, similar to those commercially available for non-structural parts.

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Figure 12. Size comparison between the demonstrators for industrial purposes (1 m^2) and for material characterization (0.16 m^2) (left); Sandwich structure linseed-PET-linseed (right)

For the end of life of the composite, as mentioned in the introduction, incineration is not an option as nothing would be recovered. Nevertheless, mechanical grinding is a plausible solution. In order to validate this approximation some samples were grinded and introduced in other composite materials as reinforcement. Nonetheless, for composites with a sandwich structure the key point is the separation of components. For this thermoset and PET core were separated in a water bath, allowing to each of the materials to reach its specific recycling flow.

5. Conclusions

The transition towards the biomaterials in the composite industry is a real need together with the use of natural fibers as reinforcement. Within this research the focus has been placed in non-woven natural linseed and hemp fibers, with different mat densities reinforcing. Composites were produced using a bio-resin combining a biorefinery side-product, the humins, with an epoxidized linseed oil based monomer. The analysis of the obtained composites shown that the thermal conductivity properties compete with other typical materials used in the construction sector. The mechanical performances of the linseed based composites show superior values compared to that of hemp based composites. Nevertheless, the hemp based composites exceeded the performance of the linseed in terms of fire resistance where hemp have shown a better performance reducing the times for the fire propagation.

Hence, each of the nonwoven mats (linseed and hemp) has its own advantages, making the hemp fibers as the best option for those non-structural part that need an insulator material but have a higher risk of fire, while, for the case of the linseed fibers the applications should require a higher mechanical performance to the non-structural part.

Supplementary Materials:

Author Contributions: The work has been distributed among all the co-authors. Prof. Alice Mija has researched on the resin formulation, its characterization by rheological and SEM analyses. Dr. Monika Rymarczyk carried out the cataplasma and the fire tests. Dr. David Ponce has worked on the manufacturing of the final demonstrators and the experimental design. Julio Vidal has been working through the research as a whole, as the main investigator and analysing the data obtained from all the characterization techniques (Collaborating in those cases in which the measure has not been done in Aitiip) and finally Dr. Pere Castell as group leader in Aitiip has been supervising the research closely and analysing the conclusions before taking the experiments to the next step.

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Appendix A

Table A 1. Variation in the weight (g) during the cataplama test due to the absorption of water

	Start	1 Day	7 Days	14 Days	28 Days
1 Layer of Hemp 1300 g/m2	45,50 ± 2,26	58,15 ± 0,85	58,95 ± 1,05	58,38 ± 0,98	57,16 ± 0,91
3 Layers of Hemp 600 g/m2	45,69 ± 2,48	61,02 ± 2,68	63,82 ± 2,54	61,63 ± 2,16	58,31 ± 2,99
1 Layer of Linseed 1300 g/m2	35,15 ± 0,73	42,07 ± 0,51	41,69 ± 0,69	42,01 ± 0,33	41,67 ± 0,40
3 Layers of Linseed 600 g/m2	28,13 ± 0,55	35,40 ± 0,80	34,73 ± 0,76	32,93 ± 0,99	34,06 ± 0,71

Table A 2. Variation in the width (mm) during the cataplama test due to the absorption of water

	Start	1 Day	7 Days	14 Days	28 Days
1 Layer of Hemp 1300 g/m2	50,38 ± 0,32	50,48 ± 0,38	50,44 ± 0,30	50,49 ± 0,26	50,43± 0,31
3 Layers of Hemp 600 g/m2	50,39 ± 0,40	50,41 ± 0,35	50,53 ± 0,41	50,50 ± 0,38	50,40 ± 0,38
1 Layer of Linseed 1300 g/m2	49,18 ± 0,26	49,56 ± 1,00	49,52 ± 0,95	49,57 ± 0,93	49,53 ± 0,97
3 Layers of Linseed 600 g/m2	50,69 ± 0,37	50,55 ± 0,35	50,58 ± 0,42	50,58 ± 0,44	50,48 ± 0,38

Table A 3. Variation in the thickness (mm) during the cataplasma test due to the absorption of water

	Start	1 Day	7 Days	14 Days	28 Days
1 Layer of Hemp 1300 g/m2	6,95 ± 0,38	7,98 ± 0,54	7,75 ± 0,45	7,66 ± 0,46	7,59 ± 0,42
3 Layers of Hemp 600 g/m2	7,88 ± 0,58	8,93 ± 0,68	8,87 ± 0,49	8,94 ± 0,50	8,96 ± 0,51
1 Layer of Linseed 1300 g/m2	4,20 ± 0,20	4,43 ± 0,04	4,54 ± 0,03	4,48 ± 0,05	4,41 ± 0,02
3 Layers of Linseed 600 g/m2	4,56 ± 0,33	4,78 ± 0,53	4,81 ± 0,34	4,89 ± 0,30	4,79 ± 0,33

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