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Chemical and mechanical reprocessed resins and bio-composites based on five epoxidized vegetable oils thermosets reinforced with flax fibers or PLA woven

Chiara Di Mauro [a], Aratz Genua [b], Monica Rymarczyk [c], Caroline Dobbels [d], Samuel Malburet [e], Alain Graillot [e], Alice Mija [a,*]

[a] *Université Côte D'Azur, Institut de Chimie de Nice, UMR CNRS 7272, 28 Av Valrose, 06108, Nice, France*
[b] *CIDETEC, Basque Research and Technology Alliance (BRTA), Paseo Miramon196, Donostia-San Sebastian, 20014, Spain*
[c] *Centexbel-VKC, Technologiepark 70, 9052, Gent-Zwijnaarde, Belgium*
[d] *Flipts & Dobbels, Groenestraat 220, B-8800, Roeselare, Belgium*
[e] *SPECIFIC POLYMERS, Parc Via Domitia, 150 Avenue des Cocardières, 34160, Castries, France*

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ABSTRACT

Bio-epoxy resins based on five epoxidized vegetable oils were formulated with an aromatic disulfide crosslinker with diacid functionality, 2,2′-dithiodibenzoic acid (DTBA), to obtain recyclable epoxy thermosets. Flax fibres (FF) and PLA woven were used as bio-based reinforcements for these matrices. Different percentages of reinforcement were tested and the effect of the natural fibres on the matrix's crosslinking reaction was studied by DSC analysis. Then, the obtained materials were analyzed by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA), water absorption and Scanning Electron Microscopy (SEM). The reinforcements improved the thermal and mechanical properties of the neat resins, with tan δ values varying from 91 to 148 °C showing a good compatibility matrix-FF but a reduced one in case of matrix-PLA woven. The dynamic nature of the networks crosslinking allowed the chemical and mechanical recycling of both resins and bio-composites. Moreover, the obtained results show the possibility to recuperate the natural FF filler for the preparation of second-life generation bio-composites.

1. Introduction

The use of natural reinforcements in the composites area has grown rapidly since the early 90s as a response to the growing demand for a sustainable development in the production chain. The strategy of using natural reinforcements in the automotive industry started in 1940 when Henry Ford produced external body panels car from hemp fibres and a resin based on soybean oil [1]. The great worldwide availability, the low cost and biodegradability have made the natural fibres generally suitable for reinforcing plastic (thermoplastic and thermosetting), thanks to their relative strength and rigidity [2–4]. Bledzki et al. [5] compared different vegetable fibres such as flax, jute, cotton, underlining the low density of these fibres (1.3–1.5 g cm^{-3}) compared to those of traditional fibres used as reinforcements such as glass and carbon, making them attractive for the automotive market and ensuring weight savings and cheaper transportation [6]. The study of the environmental impact of these materials revealed that the replacement of glass fibres with flax fibres (FF) guaranteed a 12% reduction in primary energy consumption [7,8].

The poly(lactic acid) (PLA) is a biopolymer, obtained from renewable and natural raw materials such as corn, known for its biodegradability and biocompatibility [9]. Its fibres find applications in the medical field or automotive interiors [10]. In the recent years PLA was used as filler in combination with a lignocellulosic flour providing bio-composites with excellent mechanical properties obtained by tensile testing, superior than those calculated and predicted by Halpin-Tsai model [11–13]. Composites based on PLA, modified PLA and woven FF textiles, with an increasing in impact resistance compared with that of unmodified PLA, therefore guaranteeing an ecological alternative to natural reinforced composites, were reported [14,15].

Green bio-composites, made with natural fibres and bio-resins, are offering a sustainable alternative to traditional composites. Epoxidized

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* Corresponding author.
E-mail address: Alice.MIJA@univ-cotedazur.fr (A. Mija).

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vegetable oils (EVO) have received attention in composites application, especially in the past two decades to produce bio-based reinforced materials. Liu et al. [16–18] explored composites from epoxidized soybean oil (ESO) reinforced with glass, carbon, mineral and natural fibres. Scanning electron microscopy (SEM) results reported by the authors confirmed the excellent adhesion fibres-polymer matrix, resulting in a composition with good flexural properties. High mechanical strength has been obtained in the case of the bio-composites based on ESO/maleic anhydride reinforced with FFs [19]. Shibata et al. [20] showed that the tensile strength and modulus are increased when a natural reinforcement based on micro fibrillated cellulose are added into the ESO and tannic acid matrix. Fejos et al. [21] studied the compounds prepared with epoxidized linseed oil (ELO) crosslinked with anhydrides or amines and reinforced with FFs. Although ELO allowed the formation of dense crosslinks, their composites have limited mechanical properties compared to similar petrochemical resins [22,23].

The bio-composites produced in this work were obtained using five EVOs with different epoxy contents crosslinked with a dynamic covalent hardener, the 2,2′-dithiodibenzoic acid (DTBA). ELO-based resin was used as reference. The synthesis and properties of EVOs/DTBA resins were reported previously [24–27], showing good thermo-mechanical properties of bio-based resins and recycled materials. As natural reinforcements, flax and PLA woven were used for the preparation of bio-composites. The details and the methodology implemented for the PLA woven production are reported elsewhere [28,29].

The influence of the fiber on resins curing was studied by Differential Scanning Calorimetry (DSC). The thermo-mechanical characterization of composites was done by Thermogravimetric analysis (TGA) and Dynamic Mechanical Analysis (DMA), and the obtained results discussed in correlation with the percentage of reinforcement. The morphological analysis of the interaction fibers-matrices were conducted by Scanning Electron Microscopy (SEM) analysis. The water absorption of the composites was investigated in order to evaluate their use in outdoor applications and the data were correlated with the network crosslink density. Finally, the recycling and repairing ability of the prepared composites were analyzed. The properties of the bio-composites were tested after mechanical recycling.

2. Experimental section

2.1. Materials

2.1.1. Bio-based epoxy resins, hardeners and initiator

ELO was obtained by Valtris Specialty Chemicals. The epoxidized perilla oil (**EPLO**), the epoxidized hemp oil (**EHO**), the epoxidized camelina oil (**ECMO**) and the epoxidized safflower oil (**ESFO**) were provided by SPECIFIC POLYMERS.

The resin formulations were made using 2,2′-dithiodibenzoic acid (**DTBA**), 95%, as hardener and imidazole (**IM**), 99%, as initiator, both commercially available and purchased from Sigma-Aldrich. All reagents were used without further purification. The characteristics of the selected reagents are given in Table S1.

2.1.2. Natural fibers

As reinforcement, the 100% FFs Basket 4/4 woven (Figure S1a) was provided by *Flipts & Dobbels*. The weave is essentially a plain weave with warp fibres interlaced with four fill fibres, based on long fibres (long brin), and a surface mass of 270 g m^{-2}.

The plain-woven PLA (Figure S1b) was supplied by *Centexbel.* The PLA fibers are characterized by a tenacity of 4.6–5.0 cN/dtex, elongation at break 25%, modulus between 9.4 and 9.94 GPa and hot air shrinkage 3.8–4.3% at 100 °C. For the woven preparation, two yarns were twisted in one, with 60 turns/meter, the warp and weft density were 18 yarns. cm^{-1} and a surface mass of 190 g m^{-2}. Both FF and PLA fibres were dried in oven at 90 °C for 2 h and used as received without further purification.

2.1.3. Formulation and curing of bio-based thermosets

The five EVOs thermosetting resins were formulated for composite preparation according to our previous work [19,20]. The formulations were prepared at a 1:1 ratio between epoxy and acid groups, according with Dusek et al. [30]. The EVOs were heated to around 80 °C to decrease their viscosity. Thereafter, the selected initiator was added at 1 wt% and mixed until homogenization. At this mixture was introduced the hardener. Each formulation was stirred at 80 °C for 10 min, then placed into a silicone mold and cured in oven, according to the curing protocol presented in our previous work and displayed in Table S2. The curing protocols were determined after a reactivity study by DSC and TGA to confirm the completion of reaction and that no thermal degradation occurred during the curing process. ELO-based resin was considered as reference. According to this procedure, the samples for DMA analysis were prepared in special rectangular molds (48 × 8 × 4 mm^3).

2.1.4. Bio-composites preparation

The composites were prepared by adding different percentages of FF and PLA to the uncured resins. The optimization of the fibre's percentage was performed using the ELO reference. The results are given in Figure S3 and S4(c). The optimal PLA woven percentage was chosen at 5 wt%, while for the FF two percentages were selected 5 and 20 wt%, respectively. The resin-coated fibre-mats were stacked in a silicon mold. Consequently, the mold was hot-pressed at 120 °C for 1 h under a pressure of 5 bars. Thereafter, the so prepared composites were post cured at the parameters given in Table S2. To test the thermal stability of the mixtures resin-fibre, thermogravimetric analyses were performed to verify that the samples are stable during the curing and post curing protocols.

2.1.5. Composites recyclability/repairability

2.1.5.1. *Mechanical.* To test the bio-composites repairability, a damage (scratch) was performed on the surface of the samples. Thereafter, the repairability test was performed in a hot press (at 170 °C for 30 min for FF composites and for 15 min for PLA composites, respectively), until the scratch was completely repaired. The properties of the reprocessed composites were analyzed and compared with those of the virgin ones.

2.1.5.2. *Chemical.* The dissociative ability of the S–S bonds in alkaline solutions was used to disintegrate the prepared composites and to recuperate the fibers for a second use. The composites were kept for 24 h in 1 N NaOH solution at 80 °C. At the end of the matrix dissociation, the fibres were dried at 50 °C for 12 h and used for a new composite preparation.

2.2. Characterisation

2.2.1. Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a Mettler-Toledo DSC 3 apparatus controlled by STAR^e Software. The instrument heat flow and temperature were calibrated in 3 points using water, indium and zinc standards. Samples of 5–10 mg were placed into 40 μL aluminium crucibles. The DSC technique was used firstly to study the curing behaviour, thereafter the glass transition (T_g) on the obtained resins using a heating rate β of 10 °C.min^{-1} over a temperature range from −60 to 180 °C.

The degree of crystallinity (χ) of neat PLA or of PLA included in composites was calculated according with the Equation (1):

$$\chi_{sample}\,\% = \left(\Delta H_m - \Delta H_{cc}\right)/\left(\Delta H_m{}^0\right)\cdot 100 \tag{1}$$

where ΔHcc and ΔHm are the respectively the cold crystallization enthalpy and the melting enthalpy after subtraction of the small exothermal event at the beginning of the melting peak of the samples.

ΔHm0 is the melting enthalpy of 100% crystalline PLA (93.7 J g^{-1}) [31, 32]. The maximum degree of crystallinity ($\chi_{\max}$%) was calculated as:

$$\chi_{\max}\% = \frac{\Delta H_m}{\Delta H_m^0}\cdot 100 \tag{2}$$

2.2.2. Thermogravimetric analysis (TGA)

TGA measurements were carried out on a Mettler-Toledo TGA 2. The microbalance has a precision of ± 0.1 μg. Samples of about 10 mg were placed into 70 μL alumina pans. To characterize the thermal stability of the thermosets, the samples were heated at 10 °C.min^{-1} from 25 to 1000 °C under 50 mL min^{-1} air flow.

2.2.3. Dynamic Mechanical Analysis (DMA)

Mechanical properties of the composites (storage modulus E', loss modulus E'' and damping factor tan $\delta = E''/E'$) were analyzed in a DMA 1 by Mettler-Toledo using a three-point bending fixture at an oscillatory frequency of 1.0 Hz and an amplitude of 20 μm. The rectangular samples with the dimensions of 48 × 8 × 4 mm^3 (length × width × thickness) were analyzed 3 times and the values averaged. The temperature ramp was selected from −30 to 220 °C at a heating rate of 3 °C.min^{-1}.

2.2.4. Water absorption tests

Water absorption studies were performed following the ASTM D 570-98 method. The absorption test of the bio-based resins and composites was determined during 48 h of immersion in distilled water at two different temperatures, 25 and 50 °C. The specimens were withdrawn from the water and wiped dry before the weight measurements. The samples were weighed in analytical scale Mettler Toledo balance accurate to 100 μg. The relative water absorption (WA) % was calculated using the equation:

$$WA\% = \frac{m_t - m_0}{m_0}\cdot 100 \tag{3}$$

where m_0 and m_t represent the specimen weighted at t = 0 and weight after t time, respectively.

2.2.5. Scanning electron microscopy (SEM)

The morphology of fractured surfaces of the composites but also the compatibility between the EVOs-based matrix and the fillers were investigated by SEM. The samples were analyzed using a Tescan Vega XMU SEM at an accelerating voltage of 5 kV. All samples were coated with platinum prior to observations.

3. Results and discussion

3.1. Reactivity study of the EVOs-based resins in presence of FF or PLA fillers

The DSC analysis was used to analyse the effect of fillers' presence during the chemical curing reaction Figures S3-S4(c) show the thermograms whilst the corresponding data, obtained during crosslinking reactions of ELO reference with DTBA in presence of FF and PLA woven, are reported in Table 1 and Table S4. These DSC results show a decrease in the reaction enthalpy as the percentage of fibres in the mixture increases. The normalized reaction enthalpy decreases from 174 J g^{-1} for the neat resin to 97 J g^{-1} and to 106 J g^{-1} for the blend with 20% of FF and PLA, respectively. In contrast, no sensible change in the T_{peak} was observed. Analysing the thermograms shape and the ΔH for the formulations with PLA, the blend with 5% is the least affected, with only 10% reduction in the reaction enthalpy. For this reason, the formulation EVOs/DTBA/5% PLA was chosen for the further analysis, since at this filler percentage their steric hindrance do not affect too much the chemical crosslinking. In Figure S3 we can notice that the dynamic DSC curing of the formulations with 10 or 20% PLA are accompanied by a small endothermic peak at around 168 °C, attributable to the PLA's melting. Fiore et al. [33] and Du et al. [31] explained that this PLA melting can be due to several aspects as the formation of a disordered phases in the PLA, or to a crystalline reorganization.

Table 1
EVOs reactivity vs. DTBA in presence of FF or PLA fibers. Temperatures of reaction onset, maximum, endset, total (ΔH_{tot}) and normalized to resin quantity ($\Delta H_{\text{normalized}}$) enthalpy of curing; values calculated from DSC experiments.

EVOs in EVOs/ DTBA	Fibres (%)		T_{on} (°C)	T_{peak} (°C)	T_{end} (°C)	ΔH_{tot} (J/g)	$\Delta H_{\text{normalized}}$ (J/g)
ESFO	–		142	158	184	172 ± 1	–
	FF	5	141	157	189	162 ± 1	154
		20	138	162	193	143 ± 1	114
	PLA	5	121	158	195	124 ± 1	118
ECMO	–		136	153	176	188 ± 1	–
	FF	5	138	153	178	162 ± 1	154
		20	136	156	188	135 ± 1	108
	PLA	5	136	153	187	135 ± 1	128
ELO	–		133	149	185	174 ± 1	–
	FF	5	132	150	186	164 ± 1	156
		20	132	150	171	121 ± 1	97
	PLA	5	134	150	175	164 ± 1	156
EHO	–		135	160	190	194 ± 1	–
	FF	5	129	155	196	167 ± 1	159
		20	155	161	192	148 ± 1	118
	PLA	5	136	155	193	155 ± 1	147
EPLO	–		126	152	187	207 ± 1	–
	FF	5	127	150	192	206 ± 1	195
		20	128	150	191	205 ± 1	164
	PLA	5	128	148	189	196 ± 1	186

Figure S4 and Table 1 display the influence of the two fillers on the thermal crosslinking of the EVOs based resins, compared with the reference ELO.

By adding 5% FF to the reactive mixtures, the normalized reaction enthalpies decreased from 172 to 162 J/g in ESFO/DTBA system and from 194 to 167 J/g in the formulation EHO/DTBA. EPLO/DTBA formulation recorded the smaller decrease in enthalpy, from 207 to 206 J/g with 5%FF and to 205 J/g with 20% FF. It can be observed that increasing the fibre percentage, also the interval of reaction, ΔT, increases, even if the reaction starts at comparable temperatures. Similar results were obtained for the reference ELO/DTBA systems (Figure S4 (c)). A decreasing in the exothermic reaction enthalpies was observed, as reported by Boquillon et al. [34] for ELO/methyl tetrahydrophthalic anhydride resin reinforced with 20% of hemp fibre. The EVOs/DTBA-PLA formulations have a similar trend as ELO/DTBA-PLA reference. As previously demonstrated by our team [35], higher reactivity was obtained for higher epoxy content of the starting monomer (EPLO), even in the composites formulations.

3.2. Thermo-mechanical characterization of bio-composites

3.2.1. Glass transition investigation

The glass transitions of the reinforced blends were determined using dynamic DSC measurements. Taking the ESFO/DTBA composites as example, the T_g shifts from 52 °C for the neat resin to 56 °C in the composition with 5% of FF, but in presence of 20% of FF the T_g decreases to 51 °C. In general, we can observe that the incorporation of 20% FF produces a small decrease of the T_g values for all the composites, excepting the EPLO/DTBA ones (Fig. 1). The results obtained with the ELO reference display intermediate glass transition values between ECMO and EPLO-based composites.

In the case of epoxide composites reinforced with 23–34% of FF, Muralidhar [36] explained that the shift of the T_g to higher temperatures in the reinforced composites, can be associated with the decrease in the mobility of the matrix, due to the incorporation of fibres. Boquillon et al. [34] observed a decrease of the T_g for thermosetting ELO resins reinforced with hemp fibres, explaining that the functional groups of the crosslinker might react with the hydroxyl groups of the fibres, to form covalent bonding.

A different trend can be observed for the composites made with PLA: ESFO, ELO and EPLO resins reinforced with PLA exhibit an increasing of T_g from 9 to 15% by adding the bio-filler, while the composites of ECMO and EHO resins with PLA show a decreasing of the glass transition compared with the corresponding neat resins. Figure S5-6 display the DSC thermograms of PLA and bio-composites. The decrease of T_g can be attributed to the contribution of PLA (Figure S5) that exhibits close values to the bio-composites transitions (57–60 °C). Yan et al. [37] reported for the PLA glass transition values in the range from 56 to 65 °C. The DSC data related to the biocomposites' T_g, or neat PLA related contribution on thermal events like cold crystallization temperature (T_{cc}) and enthalpy (ΔH_{cc}) melting enthalpy (ΔH_m) and melting temperature (T_m) are summarized in Table 2. As illustrated in Figure S7 a small endothermic peak of cold crystallization can be observed for the neat PLA and for all the composites, during the first heating. Several authors [31,33,38], correlated this peak to the physical aging of the PLA. More in detail, the T_{cc} seems not to be influenced by the type of EVOs, with a peak between 110 and 112 °C. Neat PLA and bio-composites show double melting peaks (T_{m1} and T_{m2}). Du et al. [31] manufactured composites with PLA and natural cellulosic and reported these double melting peaks in the range between 150 and 170 °C. The same authors explained that the double melting peaks can be attributed to less regular PLA crystals formed during composites fabrication.

The degree of crystallinity (χ_{sample}%) of the neat PLA or in composites are reported in Table 2. This value has an impact on the physical and mechanical properties, such as the stiffness, strength, and degradation rate. The low values obtained for the composites can be due to the fact that the matrix disrupt the crystallization and also due to the rapid cooling (during the composite fabrication). The maximum degree of crystallinity (χ_{max}%) for the neat PLA shows comparable value as Du et al. [31], with 40.5%.

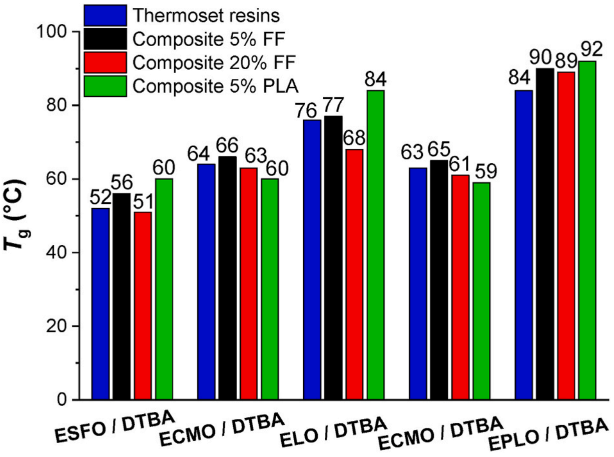

Fig. 1. T_g values of the resins and composites with 5 and 20% FF and 5% of PLA.

3.2.2. Dynamic mechanical analysis

The thermomechanical properties of EVOs-based resins and their bio-composites in presence of FF and PLA were analyzed. The results concerning the tan δ and storage moduli (E') *vs.* temperature are given in Fig. 2 and Table 3. We can notice that in general the composites exhibit higher storage modulii compared to those of neat resins, in the glassy plateau. Before the α transition, E' values are in the following order: Resins < Composites 5% FF < Composites 20% FF. For the Composites 5% PLA the modulii are in all cases lower than those of Composites 20% FF, excepting the case of EPLO-composites. The higher values of modulii in the composites show the reinforcement of the resin matrix by the FF or PLA fibers. Muralidhar [36] reported for epoxy-FF reinforced composites higher modulii in glassy plateau for the composites than for the epoxy resin. The authors explained this result by the stress transfer from the matrix to the fibres. Similar results were obtained by Liu et al. [39] for ESO resins reinforced with FF and by Manthey et al. [40] for ESO and EHO resins and theirs mixture with a commercial epoxy resin reinforced by jute fibres.

As summarized in Table 3 and according with previous results [35], the crosslinking density in the EVOs thermosets increases linearly with the epoxy content of the starting EVOs monomer. The values are ranging from 0.34 mmol cm^{-3} for ESFO/DTBA to 0.68 mmol cm^{-3} for EPLO/DTBA. Therefore, the network density obtained for the bio-composites varies in the same trend, with superior values compared to the neat resins. Adding 5% of FF a significant increase can be observed, from 12 to 380%, with for example for EPLO system an increasing from 0.68 to 3.26 mmol cm^{-3}. For the same system, the composite with 20 %FF reached an increasing with 7260% of the crosslink density (from 0.68 to 5.62 mmol cm^{-3}). The composites with PLA reached similarly an increase of crosslinking densities, at higher values compared with the FF at the same ratio (50%). The addition of PLA produced a decrease of the damping factor in the case of ESFO and ELO bio-composites. However, PLA allows to obtain higher modulus values in the rubbery state for all reinforced materials, compared with the neat resins. The composites based on EVOs with high epoxy content reached approximately double the modulus value of neat resins. Nonetheless, a more significant increase in crosslinking density was achieved by using 5% PLA fibers compared to same amount of FF. The composites network density are strongly affecting their thermomechanical properties, as for example illustrated by the amplitude of the loss factor (tan δ_{max}). Indeed, in Fig. 5 we can observe that the tan δ amplitude is decreasing in the composites systems, this decreasing being more pronounced for the systems with higher epoxy content, thus crosslink density. Concerning the damping factor, in the case of reference system the maximum value of tan δ is shifted toward lower temperatures for the bio-composites, which means that both FF and PLA fibres act as plasticizers for the matrix. The same behaviour was obtained for ESFO-based resin and composites. For the other systems, we can emphasize the high values of the tan δ, >100 °C, especially in the case of EPLO system. An increasing of the tan δ values can be observed for this system, from 135 °C (neat resin) to 142 °C (EPLO/DTBA/5% FF) and 148 °C (EPLO/DTBA/5% PLA).

3.2.3. Thermal stability

Figure S9 and Table 4 show the thermogravimetric results for the prepared resins and reinforced composites. Comparing all the results, no significative difference was obtained between all the materials that have similar behaviour as the reference system in Figure S9 (c). As general observation, we should notice that the PLA produces an increasing of the

Table 2
DSC results of neat PLA and EVOs-bio composites with PLA.

	PLA %	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	χ_{sample} %	χ_{max} %
PLA	100	110	163	168	30.60	37.99	7.83	40.50
EPLO/DTBA/PLA	5	111	164	170	27.40	6.91	4.45	7.37
EHO/DTBA/PLA	5	112	163	170	6.98	7.39	0.44	7.89
ELO/DTBA/PLA	5	110	162	169	2.78	3.24	0.49	3.46
ECMO/DTBA/PLA	5	112	164	170	8.13	8.85	0.77	9.44
ESFO/DTBA/PLA	5	112	164	170	11.50	12.44	1.03	13.3

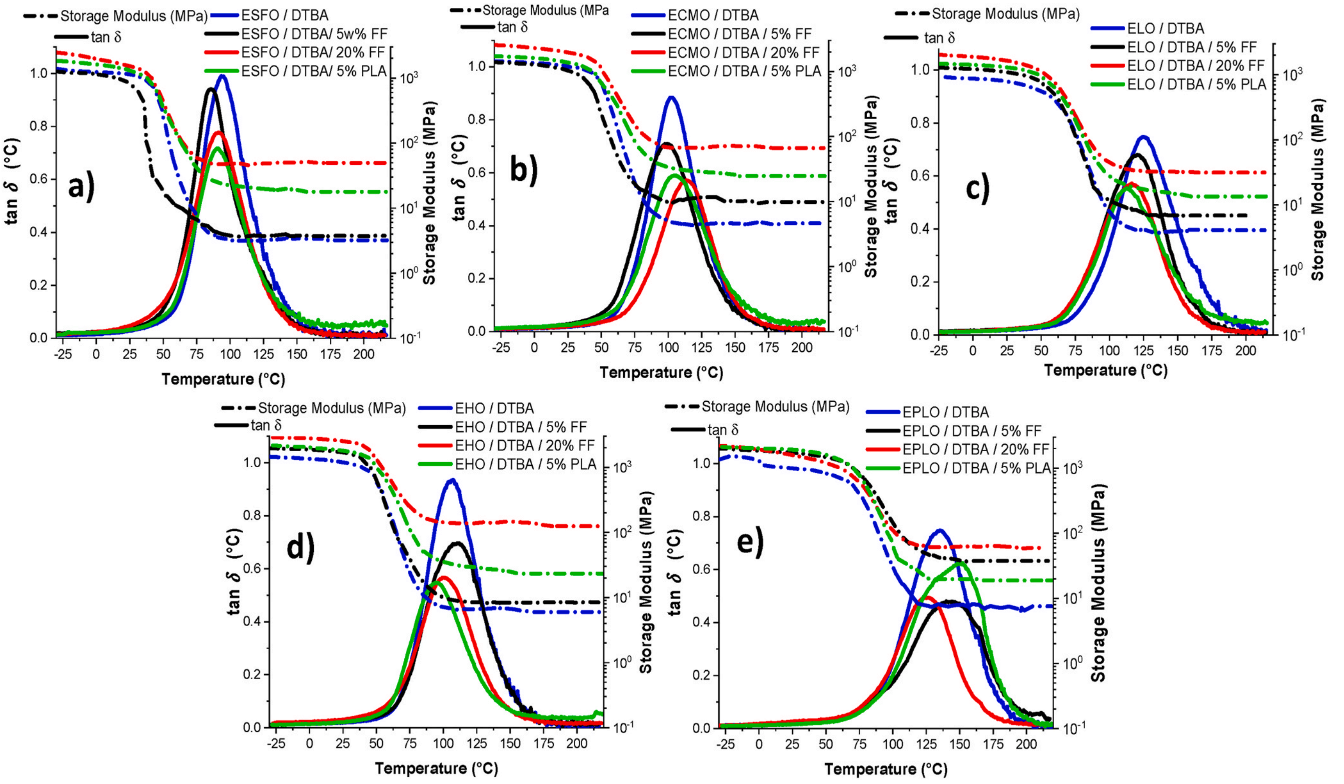

Fig. 2. Evolution of storage and tan δ vs. temperature for the EVOs-based resins (blue line) and their composites with 5% FF (black line), 20% (red line) and 5% PLA (green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$T_{5\%}$ values, with the higher increasing obtained for EHO/DTBA composite, with $T_{5\%}$ from 265 (neat resin) to 275 °C. The improved thermal stability of the composites is associated with the good thermal stability of the PLA fibres. Chieng et al. [41] reported higher thermal stabilities for the composites compared to the neat PLA (at 313 °C and 330 °C) when 5% of EPO (epoxidized palm oil) and ESO, respectively, are incorporated into PLA. The corresponding DTG (Figure S10) curves display the thermal decomposition peaks according to the major constituents of the natural fibres. In contrast with the PLA, by adding FF the thermal stability decreases, the lower values $T_{5\%}$ being obtained with 20% of FF (Table 4). These results were predictable since the FF have lower thermal stability ($T_{5\%}$ ~231 °C, Figure S2 and Table S3).

3.2.4. Fibre-resin interaction: SEM investigation

The wetting and compatibility between the fibres and the matrix are parameters determining the adhesion fibre–matrix and the composites' properties. In Figure S11 are presented the SEM results for the composites of ELO/DTBA reference system. It can be observed that the compatibility between resins and the FF is good, with few gaps and voids in both analyzed fibre percentages and that the matrix remains attached to the fibres. Comparable results were obtained by Manthey et al. [40] for the bio-composites from EHO mixed with a synthetic epoxy resin and jute fibre reinforcement. The authors justified the result by the absence of a chemical treatment of the fibers prior to the reinforcement. In contrast, a poorer interaction between matrix and the PLA fibres (Figure S11(c)) can be observed. The PLA yarns seem to be easily separated from the epoxy matrix, leaving voids close to the matrix. The composites based on the EVOs-based resins show comparable results as the reference. Fig. 3 shows the micrographs of EHO/DTBA composites. Increasing the FF from 5 to 20% no sensible changes were observed, showing in both cases a good adhesion FF-matrix. As in the case of the reference, a reduced compatibility can be observed for the composites with PLA (Fig. 3 (c)). All the analyzed composites presented in Figure S12-S14 show comparable results, whatever the type of the EVO in the matrix constitution. The interaction between ESFO or ECMO systems with PLA shows a better interaction and compatibility, probably due to the fact that a soft matrix is better impregnated. In general for EVOs, Chieng et al. [41] explained that a possible interaction between the hydroxyl group of PLA and the epoxy group of epoxidized palm or soybean oils through hydrogen bonding could occurred.

3.3. Water absorption analysis

Figure S15 illustrates the water absorption (WA) results for FF and PLA-epoxy composites performed at 25 and 50 °C in function of time. The introduction of FF produces an increasing in the absorption

Table 3
Thermomechanical properties of resins and composites with FF and PLA fibres.

EVOs in EVOs/DTBA	Fibres (wt. %)		tan δ (°C)	(tan δ) max	E′ in glassy state (MPa)	E′ in rubbery state (MPa)	Crosslink density (mmol. cm^{-3})
ESFO	–		95 ± 1	0.99	1385	3.1	0.34
	FF	5	85 ± 1	0.94	1264	3.8	0.38
		20	91 ± 1	0.77	2460	49.5	4.79
	PLA	5	91 ± 1	0.71	1836	17.9	1.73
ECMO	–		102 ± 1	0.88	1440	4.8	0.43
	FF	5	100 ± 1	0.71	1380	9.8	0.93
		20	113 ± 1	0.57	2550	70.0	6.43
	PLA	5	105 ± 1	0.60	1720	24.8	2.32
ELO	–		124 ± 1	0.75	920	4.0	0.55
	FF	5	120 ± 1	0.68	1290	6.8	0.62
		20	116 ± 1	0.57	2050	31.4	2.86
	PLA	5	113 ± 1	0.55	1500	13.4	1.23
EHO	–		106 ± 1	0.94	1460	6.0	0.60
	FF	5	111 ± 1	0.70	1970	8.3	0.77
		20	101 ± 1	0.57	2900	134	2.83
	PLA	5	95 ± 1	0.55	2170	23.3	2.22
EPLO	–		135 ± 1	0.75	1370	7.8	0.68
	FF	5	142 ± 1	0.48	2000	37.8	3.26
		20	127 ± 1	0.49	2200	63.1	5.62
	PLA	5	148 ± 1	0.63	2120	18.8	1.60

Table 4
Thermal characterization results for bio-based resins and the FF-PLA reinforced composites.

EVOs in EVOs/DTBA	Fibres (wt. %)		$T_{5\%}$ (°C)	1st Degradation peak (°C)	2nd Degradation peak (°C)
ESFO	–		270	318	518
	FF	5	270	318	540
		20	265	317	525
	PLA	5	275	318	555
ECMO	–		265	312	517
	FF	5	265	310	540
		20	265	310	520
	PLA	5	272	320	555
ELO	–		275	310	515
	FF	5	265	310	540
		20	260	310	520
	PLA	5	260	310	555
EHO	–		265	309	520
	FF	5	268	309	525
		20	260	302	515
	PLA	5	275	318	558
EPLO	–		265	305	518
	FF	5	265	315	540
		20	270	315	530
	PLA	5	275	320	550

percentage, higher for the composites made with EVOs with low epoxy content (Figure S15 (a)).This result is correlated to the lower crosslinking density: poorly crosslinked resins and bio-composites shows a higher WA or a higher swelling capacity [25,35]. The amount of WA increases linearly at the beginning of the test, to reach a plateau after 12–25 h. Higher values are observed for the 20% FF reinforcement. ESFO/DTBA systems present an increasing of the WA from 0.83, for the neat resin, to 4.9% at 25 °C and ~9% at 50 °C for the composite with 20% FF. The reference ELO composites show an intermediate behavior between ECMO and EHO-based composites (Figure S15 (c)). The low WA values for the FF composites, show comparable results as reported by Manthey et al. [40] for the bio-composites based on mixture of EHO-ESO reinforced with jute fibres.

3.4. *Recycling and repairing*

The recycling of fiber-reinforced composites has been growing in recent years, as for example investigating the effect of mechanical recycling [42,43]. Cicala et al. [44] recycled composites panels based on bio-based epoxy monomer (SuperSap) and the cure inhibitor INH by Entropy Resins mixed with cleavable amine (Recyclamine® 301) with hybrid flax/carbon fibers. The authors recycled chemically the cured laminated composites in mild acetic acid aqueous solutions, obtaining clean fibers and obtaining from the epoxy matrix a reusable thermoplastic. The presence of dynamic covalent bonds allows, as already demonstrated [25], to reach the recyclability of the EVOs-based thermosets. Depending on the nature of the disulphide bonds, the recycling can be achieved both chemically [45–47] and mechanically [45].

3.4.1. *Mechanical reprocessing*

For the mechanical recycling, damages in composites samples of ELO/DTBA/20% FF and 5% PLA were caused. The scratches were fully repaired in hot press at 170 °C for 30 min under 60 bars as illustrated in Fig. 4. For the ELO-based resin reinforced with PLA, due to the possible melt of the reinforcement, the repairing was done for 15 min under the same temperature and 30 bars (Figure S16).

Thereafter, the recycled and repaired composites were characterized to verify the effect of the reprocessing on materials' properties. For both tested composites, the T_g was analyzed by DSC, after the mechanical reprocessing. It was observed a decreasing from 68 °C for the virgin ELO/DTBA/20% FF, to 65 °C after the recycling, while for the ELO/DTBA/5% PLA composite from 84 °C to 73 °C (Fig. 5). The thermal stability of the virgin and reprocessed composites was investigated by TGA and the results are summarized in Fig. 5 and displayed in Figure S17. The reprocessed FF composites present equivalent thermal stability as the virgin ones, $T_{5\%} = 260$ °C, while the reinforced/recycled composite with PLA display an increase of the $T_{5\%}$ from 260 °C to 275 °C.

Figure S21 (a) shows the SEM micrographs of the ELO/DTBA/20%FF mechanically reprocessed composite. We can highlight from this result that the FF fibers are well incorporated into the matrix, the interaction fibers - matrix being similarly to that of the virgin composite (Figure S11 (b)). A different result was obtained for the reprocessed ELO/DTBA/5% PLA composite (Figure S21 (b)). It appears that the PLA fibers melted in the matrix, during the mechanical reprocessing, confirming that the higher thermal stability of this reprocessed composite could be connected to the PLA fully embedded in the matrix.

3.4.2. *Chemical*

Concerning the chemical recycling and according with the dissociative nature of disulphide bonds in alkaline conditions [25,47,48], the reference ELO-based composites reinforced with 20% FF and 5% of PLA, were immersed for different time in 1 N NaOH solution at 80 °C. After 18 h the matrixes were completely dissolved. At the end of 24 h, PLA fibers from composites presents significant damages and the woven is partially dissolved, not allowing subsequent uses (Figure S18). Different

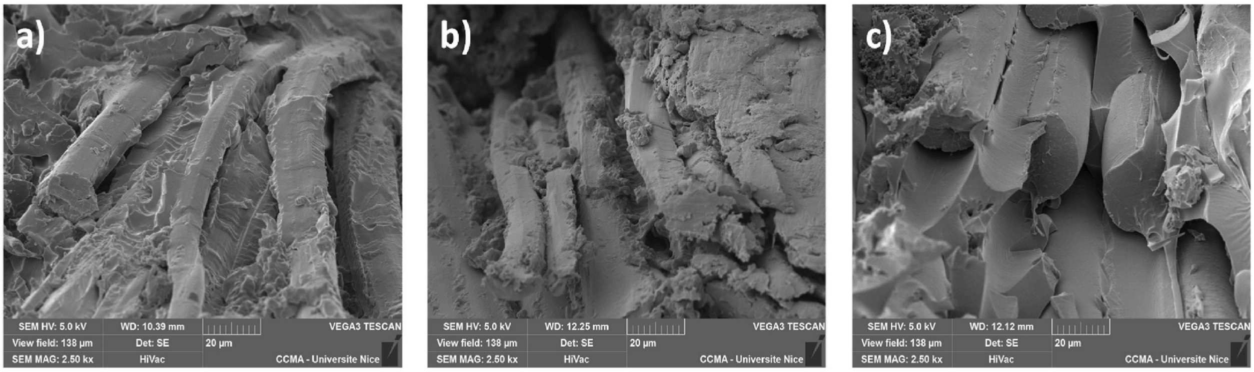

Fig. 3. SEM micrographs at magnifications of 20 μm for the cross-section of EHO/DTBA composites with **(a)** 5% FF **(b)** 20% F and **(c)** 5% PLA.

Fig. 4. Mechanical repairing of ELO/DTBA/20% FF: virgin **(a)**, damaged **(b)**, repaired **(c)**.

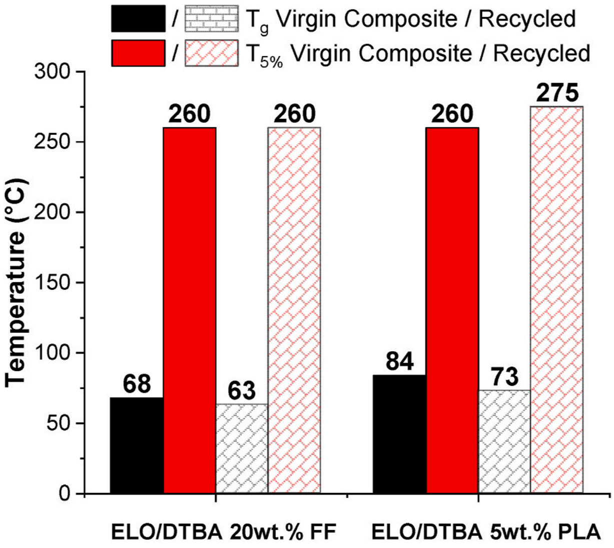

Fig. 5. T_g and $T_{5\%}$ comparison between virgin and mechanically reprocessed composites based on ELO/DTBA with 20% FF and 5% PLA fibres.

behaviour was obtained for FF that at the end of the test were dried at 50 °C for 12 h in oven (Fig. 6), and a tested to verify if the alkaline solution affected the thermal stability of the fibre. Figure S22 shows the SEM micrographs of comparison between the neat virgin FF fibers (Figure S22 (a-b)) and those recuperated after the chemical recycling of ELO/DTBA/20 %FF (Figure S22 (c-d)). From these results we can notice that the fibers do not present morphological differences, theirs surface do not show modifications, breakage, etc. We can just mention the presence of some small residue of the matrix that wasn't completely dissolved during the recycling process.

Thermogravimetric analysis (Figure S19 and Table S5) highlights that the chemical recycling affected thermally the FF, with a decreasing of the $T_{5\%}$ from 231 °C for the virgin natural fibre to 165 °C after the chemical reprocessing test. However, the chemically recycled FF were combined for a second life with the ELO resin for a new composite preparation. The obtained composite, cured according with the procedure displayed in Table S2, was tested again in DSC and TGA to evaluate the final properties of the second-generation composite. The obtained T_g value shift from 68 °C, for the virgin ELO/DTBA/20% FF, to ~73 °C for the bio-composite based on recycled FF. The second-generation composite exhibited $T_{5\%}$~260 °C, as the virgin one. These results show that the thermal properties of the "second life" composite are similar with the first ones, even if the FF fibre presented a decreasing in thermal properties after the chemical recycling (Figure S20 and Table S6). This explains that the thermal degradation of the bio-composite is strongly influenced by the thermal stability of the resin. The shifting at higher T_g, could be associated to the better interaction between matrix-fibre after the alkaline treatment. These results combined with composites chemical recycling can open a new scenario for the multi uses of the fibre, guarantying several applications minimizing the lost properties.

4. Conclusions

The effects of the quantity and types of FF and PLA fibre woven were studied when used as reinforcement in matrix based on five different EVOs having different epoxy contents. ELO-based resin and composites were used as reference. The increase in fibre percentage has led to a decrease in the T_g of FF-based composites with a sensible increasing of the storage modulus in the rubbery state than the EVOs-based resins. For PLA-reinforced composites the T_g of resins and composites are in the same range as the neat resins. All the composites exhibited comparable thermal stability as the respective resins with very low water absorption even at 50 °C, especially for PLA-based composites made with EVOs with high epoxy content as starting matrix monomers. SEM detection highlights good interaction FF-matrix with few gaps even and sensible

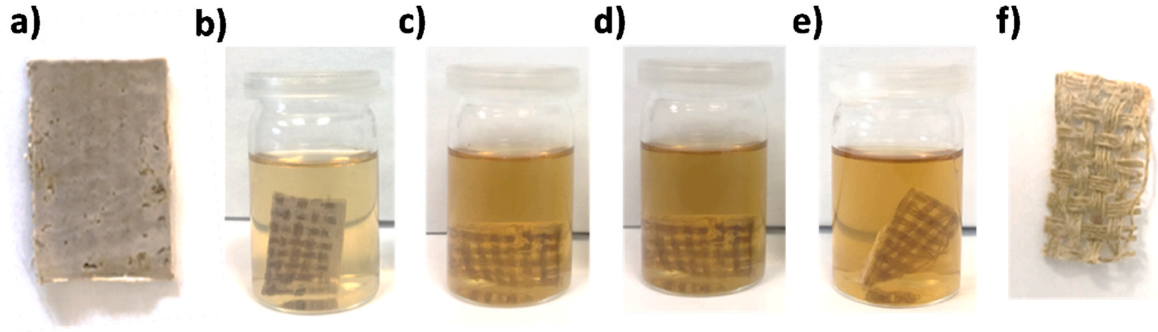

Fig. 6. Chemical recycling in 1 N NaOH at 80 °C of the composite ELO/DTBA with 20% FF: initial composite **(a)**, after 3h **(b)**, 9h **(c)**, 18h **(d)**, 24 h **(e)** end dried fibre **(f)**.

reduced compatibility between matrix-PLA.

Due to the dynamic nature of the disulfide hardener excellent mechanical recycling capabilities were achieved after causing damage to the composites, with comparable T_g and thermal stability. Chemical recycling, in a green solvent, made possible to use a second time the FF and recover them for next uses. These results open a scenario for the multi uses of the fibres, guaranteeing several applications without losing the final composite properties, opening to application in construction or automotive sectors.

Authorship statement

AM: Conception and design of study, analysis and/or interpretation of data, Drafting the manuscript, revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. CDIM: acquisition of data, analysis and/or interpretation of data, Drafting the manuscript, Approval of the version of the manuscript to be published. SM: acquisition of data, revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. MR: acquisition of data, Approval of the version of the manuscript to be published. CU: acquisition of data, Approval of the version of the manuscript to be published. AG: analysis and/or interpretation of data, revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. AG: revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

[1] J. Smits, Fiber-reinforced polymer bridge design in The Netherlands: architectural challenges toward innovative, sustainable, and durable bridges, Engineering 2 (2016) 518–527, https://doi.org/10.1016/J.ENG.2016.04.004.

[2] A.K. Bledzki, J. Gassan, Composites reinforced with cellulose based fibres, Prog. Polym. Sci. 24 (1999) 221–274, https://doi.org/10.1016/S0079-6700(98)00018-5.

[3] K.G. Satyanarayana, J.L. Guimarães, F. Wypych, Studies on lignocellulosic fibers of Brazil. Part I: source, production, morphology, properties and applications, Compos. Part A Appl. Sci. Manuf. 38 (2007) 1694–1709, https://doi.org/10.1016/j.compositesa.2007.02.006.

[4] G. Cicala, C. Tosto, A. Latteri, A.D. la Rosa, I. Blanco, A. Elsabbagh, P. Russo, G. Ziegmann, Green composites based on blends of polypropylene with liquid wood reinforced with hemp fibers: thermomechanical properties and the effect of recycling cycles, Materials 10 (2017) 998, https://doi.org/10.3390/ma10090998.

[5] A.K. Bledzki, S. Reihmane, J. Gassan, Properties and modification methods for vegetable fibers for natural fiber composites, J. Appl. Polym. Sci. 59 (1996) 1329–1336, https://doi.org/10.1002/(SICI)1097-4628(19960222)59:8<1329::AID-APP17>3.0.CO;2-0.

[6] P. Wambua, J. Ivens, I. Verpoest, Natural fibres: can they replace glass in fibre reinforced plastics? Compos. Sci.Technol. 63 (2003) 1259–1264, https://doi.org/10.1016/S0266-3538(03)00096-4.

[7] J. Bachmann, C. Hidalgo, S. Bricout, Environmental analysis of innovative sustainable composites with potential use in aviation sector—a life cycle assessment review, Sci. China Technol. Sci. 60 (2017) 1301–1317, https://doi.org/10.1007/s11431-016-9094-y.

[8] A. le Duigou, C. Baley, Coupled micromechanical analysis and life cycle assessment as an integrated tool for natural fibre composites development, J. Clean. Prod. 83 (2014) 61–69, https://doi.org/10.1016/j.jclepro.2014.07.027.

[9] Y. Tokiwa, B.P. Calabia, Biodegradability and biodegradation of poly (lactide), Appl. Microbiol. Biotechnol. 72 (2006) 244–251, https://doi.org/10.1007/s00253-006-0488-1.

[10] R.P. Babu, K. O'connor, R. Seeram, Current progress on bio-based polymers and their future trends, Progr. Biomater. 2 (2013) 8, https://doi.org/10.1186/2194-0517-2-8.

[11] R. Scaffaro, A. Maio, F. Lopresti, Physical properties of green composites based on poly-lactic acid or Mater-Bi® filled with Posidonia Oceanica leaves, Compos. Part A Appl. Sci. Manuf. 112 (2018) 315–327, https://doi.org/10.1016/j.compositesa.2018.06.024.

[12] R. Scaffaro, A. Maio, E.F. Gulino, B. Megna, Structure-property relationship of PLA-Opuntia Ficus Indica biocomposites, Compos. B Eng. 167 (2019) 199–206, https://doi.org/10.1016/j.compositesb.2018.12.025.

[13] R. Scaffaro, A. Maio, E.F. Gulino, G. Pitarresi, Lignocellulosic fillers and graphene nanoplatelets as hybrid reinforcement for polylactic acid: effect on mechanical properties and degradability, Compos. Sci. Technol. 190 (2020) 108008, https://doi.org/10.1016/j.compscitech.2020.108008.

[14] S. Siengchin, R. Dangtungee, Effect of woven flax structures on morphology and properties of reinforced modified polylactide composites, J. Thermoplast. Compos. Mater. 26 (2013) 1424–1440, https://doi.org/10.1177/0892705712475005.

[15] G. Cicala, D. Giordano, C. Tosto, G. Filippone, A. Recca, I. Blanco, Polylactide (PLA) filaments a biobased solution for additive manufacturing: correlating rheology and thermomechanical properties with printing quality, Materials 11 (2018) 1191, https://doi.org/10.3390/ma11071191.

[16] Z. Liu, S.Z. Erhan, D.E. Akin, F.E. Barton, "Green" composites from renewable resources: preparation of epoxidized soybean oil and flax fiber composites, J. Agric. Food Chem. 54 (2006) 2134–2137, https://doi.org/10.1021/jf0526745.

[17] Z.S. Liu, S.Z. Erhan, J. Xu, P.D. Calvert, Development of soybean oil-based composites by solid freeform fabrication method: epoxidized soybean oil with bis or polyalkyleneamine curing agents system, J. Appl. Polym. Sci. 85 (2002) 2100–2107, https://doi.org/10.1002/app.10763.

[18] Z. Liu, S.Z. Erhan, P.D. Calvert, Solid freeform fabrication of soybean oil-based composites reinforced with clay and fibers, J. Am. Oil Chem. Soc. 81 (2004) 605–610, https://doi.org/10.1007/s11746-006-0949-9.

[19] P. Tran, D. Graiver, R. Narayan, Biocomposites synthesized from chemically modified soy oil and biofibers, J. Appl. Polym. Sci. 102 (2006) 69–75, https://doi.org/10.1002/app.22265.

[20] M. Shibata, N. Teramoto, K. Makino, Preparation and properties of biocomposites composed of epoxidized soybean oil, tannic acid, and microfibrillated cellulose, J. Appl. Polym. Sci. 120 (2011) 273–278, https://doi.org/10.1002/app.33082.

[21] M. Fejős, J. Karger-Kocsis, S. Grishchuk, Effects of fibre content and textile structure on dynamic-mechanical and shape-memory properties of ELO/flax biocomposites, J. Reinforc. Plast. Compos. 32 (2013) 1879–1886, https://doi.org/10.1177/0731684413497277.

[22] D.P. Pfister, R.C. Larock, Cationically cured natural oil-based green composites: effect of the natural oil and the agricultural fiber, J. Appl. Polym. Sci. 123 (2012) 1392–1400, https://doi.org/10.1002/app.33636.

[23] D. Bertomeu, D. García-Sanoguera, O. Fenollar, T. Boronat, R. Balart, Use of eco-friendly epoxy resins from renewable resources as potential substitutes of petrochemical epoxy resins for ambient cured composites with flax reinforcements, Polym. Compos. 33 (2012) 683–692, https://doi.org/10.1002/pc.22192.

[24] T.N. Tran, C. Di Mauro, A. Graillot, A. Mija, Chemical reactivity and the influence of initiators on the epoxidized vegetable oil/dicarboxylic acid system, Macromolecules 53 (2020) 2526–2538, https://doi.org/10.1021/acs.macromol.9b02700.

[25] C. Di Mauro, T.N. Tran, A. Graillot, A. Mija, Enhancing the recyclability of a vegetable oil-based epoxy thermoset through initiator influence, ACS Sustain. Chem. Eng. 8 (2020) 7690–7700, https://doi.org/10.1021/acssuschemeng.0c01419.

[26] T.N. Tran, C. Di Mauro, A. Graillot, A. Mija, Monitoring the structure-reactivity relationship in epoxidized perilla and safflower oil thermosetting resins, Polym. Chem. 11 (2020) 5088–5097, https://doi.org/10.1039/d0py00688b.

[27] C. Di Mauro, A. Genua, A. Mija, Building thermally and chemically reversible covalent bonds in vegetable oil based epoxy thermosets. Influence of epoxy–hardener ratio in promoting recyclability, Mater. Adv. 1 (2020) 1788–1798, https://doi.org/10.1039/d0ma00370k.

[28] M. Kleščík, B. Bizubová, T. Zatroch, A. Balogová, L.A.R. Pedraza, P. Skalková, V. Krmelová, J. Krmela, E. Muks, L. v der Scheuren, Research and application of PLA fibres, IOP Conf. Ser. Mater. Sci. Eng. 776 (2020), 012091.

[29] C.L. Reichert, E. Bugnicourt, M.-B. Coltelli, P. Cinelli, A. Lazzeri, I. Canesi, F. Braca, B.M. Martínez, R. Alonso, L. Agostinis, Bio-based packaging: materials, modifications, industrial applications and sustainability, Polymers 12 (2020) 1558, https://doi.org/10.3390/polym12071558.

[30] L. Matějka, S. Pokorný, K. Dušek, Acid curing of epoxy resins. A comparison between the polymerization of diepoxide-diacid and monoepoxide-cyclic anhydride systems, Macromol. Chem. 186 (1985) 2025–2036, https://doi.org/10.1002/macp.1985.021861006.

[31] Y. Du, T. Wu, N. Yan, M.T. Kortschot, R. Farnood, Fabrication and characterization of fully biodegradable natural fiber-reinforced poly (lactic acid) composites, Compos. B Eng. 56 (2014) 717–723, https://doi.org/10.1016/j.compositesb.2013.09.012.

[32] E.W. Fischer, H.J. Sterzel, G. Wegner, Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions, Kolloid-Z. Z. Polym. 251 (1973) 980–990, https://doi.org/10.1007/BF01498927.

[33] V. Fiore, L. Botta, R. Scaffaro, A. Valenza, A. Pirrotta, PLA based biocomposites reinforced with Arundo donax fillers, Compos. Sci. Technol. 105 (2014) 110–117, https://doi.org/10.1016/j.compscitech.2014.10.005.

[34] N. Boquillon, Use of an epoxidized oil-based resin as matrix in vegetable fibers-reinforced composites, J. Appl. Polym. Sci. 101 (2006) 4037–4043, https://doi.org/10.1002/app.23133.

[35] C. Di Mauro, S. Malburet, A. Genua, A. Graillot, A. Mija, Sustainable series of new epoxidized vegetable oil-based thermosets with chemical recycling properties, Biomacromolecules 21 (2020) 3923–3935, https://doi.org/10.1021/acs.biomac.0c01059.

[36] B.A. Muralidhar, Study of flax hybrid preforms reinforced epoxy composites, Mater. Des. 52 (2013) 835–840, https://doi.org/10.1016/j.matdes.2013.06.020, 1980-2015.

[37] L. Yan, N. Chouw, K. Jayaraman, Flax fibre and its composites–A review, Compos. B Eng. 56 (2014) 296–317, https://doi.org/10.1016/j.compositesb.2013.08.014.

[38] L.C.E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier, New York, 1978.

[39] Z. Liu, S.Z. Erhan, D.E. Akin, F.E. Barton, "Green" composites from renewable resources: preparation of epoxidized soybean oil and flax fiber composites, J. Agric. Food Chem. 54 (2006) 2134–2137, https://doi.org/10.1016/j.msea.2006.12.186.

[40] N.W. Manthey, F. Cardona, G. Francucci, T. Aravinthan, Thermo-mechanical properties of epoxidized hemp oil-based bioresins and biocomposites, J. Reinforc. Plast. Compos. 32 (2013) 1444–1456, https://doi.org/10.1177/0731684413493030.

[41] B.W. Chieng, N.A. Ibrahim, Y.Y. Then, Y.Y. Loo, Epoxidized vegetable oils plasticized poly (lactic acid) biocomposites: mechanical, thermal and morphology properties, Molecules 19 (2014) 16024–16038, https://doi.org/10.3390/molecules191016024.

[42] M. Pietroluongo, E. Padovano, A. Frache, C. Badini, Mechanical recycling of an end-of-life automotive composite component, Sustain. Mater. Technol. 23 (2020), e00143, https://doi.org/10.1016/j.susmat.2019.e00143.

[43] P. Feraboli, H. Kawakami, B. Wade, F. Gasco, L. DeOto, A. Masini, Recyclability and reutilization of carbon fiber fabric/epoxy composites, J. Compos. Mater. 46 (2012) 1459–1473, https://doi.org/10.1177/0021998311420604.

[44] G. Cicala, E. Pergolizzi, F. Piscopo, D. Carbone, G. Recca, Hybrid composites manufactured by resin infusion with a fully recyclable bioepoxy resin, Compos. B Eng. 132 (2018) 69–76, https://doi.org/10.1016/j.compositesb.2017.08.015.

[45] A. Ruiz De Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez, I. Odriozola, Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites, Mater. Horiz. 3 (2016) 241–247, https://doi.org/10.1039/c6mh00029k.

[46] F. Zhou, Z. Guo, W. Wang, X. Lei, B. Zhang, H. Zhang, Q. Zhang, Preparation of self-healing, recyclable epoxy resins and low-electrical resistance composites based on double-disulfide bond exchange, Compos. Sci. Technol. 167 (2018) 79–85, https://doi.org/10.1016/j.compscitech.2018.07.041.

[47] Z. Ma, Y. Wang, J. Zhu, J. Yu, Z. Hu, Bio-based epoxy vitrimers: reprocessibility, controllable shape memory, and degradability, J. Polym. Sci. Polym. Chem. 55 (2017) 1790–1799, https://doi.org/10.1002/pola.28544.

[48] Z.Q. Lei, H.P. Xiang, Y.J. Yuan, M.Z. Rong, M.Q. Zhang, Room-temperature self-healable and remoldable cross-linked polymer based on the dynamic exchange of disulfide bonds, Chem. Mater. 26 (2014) 2038–2046, https://doi.org/10.1021/cm4040616.