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Sustainable Series of New Epoxidized Vegetable Oil-Based Thermosets with Chemical Recycling Properties

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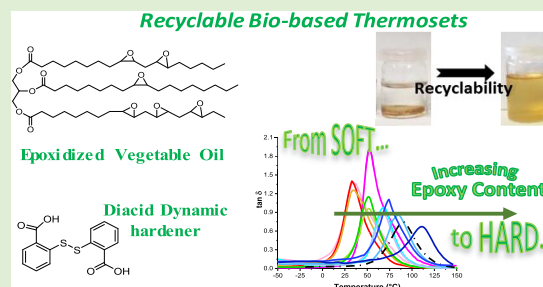


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ABSTRACT: This work reports for the first time the copolymerization studies of 11 newly synthesized epoxidized vegetable oils (EVOs) that reacted with a disulfide-based aromatic dicarboxylic acid (DCA) to produce thermoset materials with recyclability properties. These new EVOs' reactivity and properties were compared with those of the two commercial references: epoxidized linseed oil (ELO) and epoxidized soybean oil (ESO). The structure–reactivity correlation is proposed by differential scanning calorimetry (DSC) analysis, corroborating the epoxy content of EVO monomers, the initiator effect, the copolymerization reaction enthalpy, and the temperature range. The thermomechanical properties of the obtained thermosets were evaluated and discussed in correlation with the structure and reactivity of monomers by dynamic mechanical analysis (DMA), tensile testing, and thermogravimetric analysis (TGA). It has been found that the higher the EVO functionality, the higher is the reactivity, cross-linking density, and final performances, with $\tan \delta$ values ranging from 34 to 111 °C. This study investigates the chemical recycling and the solvent resistance of these vitrimer-like materials that have a high bio-based carbon content, from 58 to 79%, with potential application in coating or composite materials in the automotive sector.



INTRODUCTION

Accumulation of plastic waste is becoming one of the major threats to our ecosystem. With a level of production of around 140 million tons of synthetic polymers each year and with less than 10% being effectively recycled, the growing amount of plastic waste ending up in oceans or landfills raises several concerns. Developed countries, as the main consumers of energy, for a long time, started planning and managing new renewable and alternative energy sources to solve the current problems related to air quality linked to ozone, carbon monoxide, or particulate matter. The sustainable use of natural resources is one of the strategies to ensure the development of renewable materials and a sustainable economy. In the last few decades, the use of bio-based raw materials has led to the development of green chemistry by integrating minor toxicity¹ and biodegradability,^{2–4} offering a different scenario for coal as a basic feedstock.⁵ However, most of these products still do not offer a competitive alternative compared with the products coming from the petrochemical industries. In the case of thermoset materials, this problem is further duplicated since they cannot be recycled. Although relentless efforts are dedicated to reduce the use of petro-based resources, the ecological impact of thermosets at the end of the lifetime remains a crucial challenge that needs to be addressed to limit the greenhouse emissions and the associated footprint. For this reason, important strategies are the replacing of petro-based raw materials and also the synthesis of recyclable, reusable, and reshapable vitrimer-like thermoset materials based on rever-

sible disulfide bond and carboxylate transesterification (vitrimer).^{6–8}

Considering the growing amount of fiber-reinforced composite materials due to their outstanding properties in terms of lightweight, high weight-to-strength ratio, and long durability, the next generation of bio-based thermosetting resins need to be cost-effective and based on nondepletable bio-based resources. Within this scope, the valorization of vegetable oils through the synthesis of thermoset materials is supported by advantages like diversity, abundance, and low price, promising to be a sustainable alternative for the chemical industry.⁹

Commonly, vegetable oils (VOs) are extracted from fruits or seeds by solvent extraction or by the pressing process. More than 95% of VOs constitute triglycerides,¹⁰ containing three fatty acids branched to a glycerol unit. Nevertheless, VOs are a complex, variable, and thus very interesting mixture. The diversity in VO composition depends not only on the nature of the oil but also on the geographical origin of the plants, maturity, species, and the method used for its extraction. As a

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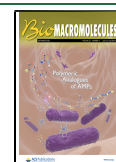


Table 1. Chemical Composition of VO Raw Materials and Corresponding EVOs

EVOs	fatty acid				epoxy index (mequiv·g ⁻¹)
	saturated ^c	monounsaturated ^d	diunsaturated ^e	triunsaturated ^f	
karanja ^a	22	56	21	1	2.77
castor ^a	3	92 ^d	5		2.85
St John's wort ^a	21	63	16		2.97
peanut ^b	20	53	27		3.35
rapeseed ^a	7	62	25	7	3.99
soybean	11	24	54	8	4.20
rosehip seed ^a	17	20	57	5	4.7
safflower ^c	12	18	70		4.93
grapeseed ^b	11	22	67		4.94
camelina ^c	10	30	28	32	5.29
linseed	6	22	16	52	5.61
hemp ^c	10	12	65	13	6.09
perilla ^c	3	21	18	58	6.77

^aNonedible oils. Rapeseed oil is the high erucic fatty acid compared to canola, which has low erucic fatty acid. ^bEdible oils. ^cEdible but nonvaluated.

^dMonounsaturated fatty acids of castor oil comprised 90% of ricinoleic acid. ^eMainly comprised of palmitic and stearic fatty acids. ^fMainly comprised of oleic fatty acid. ^gMostly linoleic fatty acid. ^hMostly linolenic fatty acid.

matter of fact, the length of the main fatty acids is in the range of 4–28 carbons and unsaturated bonds or functional groups such as hydroxyl (castor oil) or epoxy (vernonia oil) can be encountered alongside the alkyl chain.¹¹ According to the unsaturation degree of fatty acids, they can be generally classified into saturated, mono- and polyunsaturated fatty acids, which may have different configurations, resulting in different physical and chemical properties. For instance, vegetable oils can be either liquid or waxy at room temperature. This property is mainly linked to two major criteria, which can help to understand the composition of the oil. First, the vegetable oil is certainly poor in unsaturated fatty acids, which allow them to crystallize by self-organization, as in the case of coconut oil or palm oil, for instance. Also, the fatty acids having a long alkyl chain length will promote self-organization and crystallization. In fact, the higher the melting point of the vegetable oil, the higher is its content in saturated fatty acids with long alkyl chains. Finally, the unsaturation degree, also known as the iodine value, has a major importance for the production of monomers and thermosetting resins. High iodine values indicate a high aptitude for functionalization and polymerization.¹²

Usually, the industrial process to synthesize the commercial epoxy resins is based on epichlorohydrin as the main reactant, allowing the conversion of hydroxyl,¹³ phenol,¹⁴ or acid¹⁵ functions into epoxides. Vegetable oils have been used for long time as paints, lubricants,¹⁶ and coatings, but in the last few decades, polymeric systems based on these raw materials have been developed using a variety of polymerization techniques.¹¹ One considerable advantage of the use of VOs as raw materials is their potential of double-bond functionalization, as for example, into epoxies using oxidizing agents and, thus, avoiding the very hazardous epichlorohydrin, the usual reactant for diglycidyl ether of bisphenol A (DGEBA) synthesis.

Therefore, based on a wide variety of VOs, we were able to develop and implement a robust, sustainable, and harmless synthetic pathway giving access to fully bio-based epoxidized vegetable oils exhibiting a wide range of epoxy content from 2.77 to 6.77 mequiv·g⁻¹. The details and the methodology implemented for new epoxidized vegetable oil (EVO) synthesis are reported elsewhere.^{17,18} It has been then important to evaluate the potential of synthesized EVOs as

precursors for thermoset materials and to highlight how the thermomechanical properties of the obtained materials can be influenced by their epoxy content. The latter is determined by the relative proportion of palmitic (saturated), stearic (saturated), oleic (monounsaturated), linoleic (diunsaturated), and linolenic (triunsaturated) fatty acids in the composition of the corresponding VOs (Table 1). Moreover, considering the rising demand for vegetable oils, notably due to the population growth, a careful selection of vegetable oil feedstocks has been carried out to avoid food competition.

For the first time in a preliminary work, we showed the recycling properties of epoxidized linseed oil (ELO)-based thermosets.^{19–21} In the present work, we developed a new series of vegetable-based thermosetting resins, by the copolymerization of 12 newly synthesized EVOs with 2,2'-dithiodibenzoic acid (DTBA). Through this study, the 12 new EVOs were synthesized with the objective to cover the larger domain of the epoxy content, i.e., from 2.77 to 6.77 mequiv·g⁻¹. In this manner, we will gain knowledge on the potential of EVOs to generate thermosets when reacted with DTBA and on their properties. To our knowledge, this is the first study proposing the cross-linking of EVO series with DTBA. If the literature is rich in reporting studies dedicated to EVO cross-linking with anhydrides or aliphatic diacids, there are no much studies on EVO curing using aromatic diacids, and with aromatic diacids containing disulfide linkage are not at all present. Indeed, these S–S linkages allow the incorporation of dynamic cross-links to form covalent adaptable networks (CANs)²² that conduct to thermosets with reprocessable, recyclable, and reshaping abilities. Disulfide dynamic bonds have attracted much attention in the design of a series of CANs, as displayed using 4-aminophenyl disulfide (AFD) as the cross-linker for DGEBA by Odriozola et al.²³ or for the castor oil (CO)-derived polyurethane by Chen et al.²⁴ To our knowledge, this paper investigates for the first time how the epoxy content characterizing the new EVOs impact on the copolymerization reactivity with the DCAs and, therefore, on the performances of the corresponding epoxy/acid vitrimer-like thermosets.

The reactivity study was achieved by differential scanning calorimetry analysis (DSC). The structural evolution of the thermosetting resins was studied by attenuated total reflection-

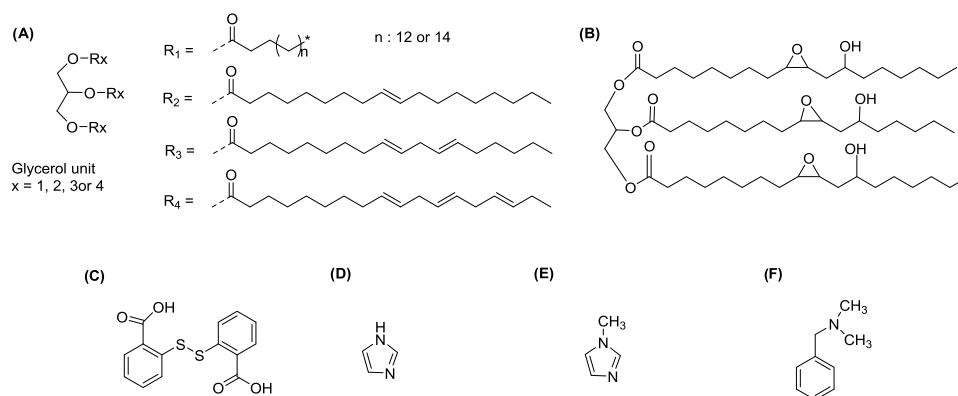


Figure 1. Structures of selected reagents.

Fourier transform infrared spectroscopy (ATR-FTIR). Thereafter, the thermomechanical properties of the thermosets were analyzed by DSC, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and tensile testing. Finally, their solvent stability and network degradability were investigated as a possible option of recycling mechanism. Therefore, this work gives an overview, a complete study, from thermoset synthesis to a detailed investigation of their properties, for a large series of newly epoxidized vegetable oils cross-linked with an aromatic diacid hardener.

MATERIALS AND METHODS

Materials. The chemical structures of the reagents used in this study are shown in Figure 1. The new biorenewable epoxidized monomers are classified based on the epoxy content as tabulated in Table 1. Figure 1A exhibits the general structure of the EVOs and that of the epoxidized castor oil (ECO) in Figure 1B.

ELO and epoxidized soybean oil (ESO) were generously provided by Valtris Chemicals (England), while the new EVOs (SP-3S-30-005 and SP-3S-30-006) by SPECIFIC POLYMERS (France). Their chemical characteristics are reported in Table S1.

The hardener and the initiators are commercially available and were purchased from Sigma-Aldrich and used as received without further purification: 2,2'-dithiodibenzoic acid (DTBA, 95%) (C), imidazole (IM, 99%) (D), 1-methylimidazole (1-MI, 99%) (E), and *N,N*-dimethylbenzylamine (DMBA, 99%) (F).

Sample Preparation. The thermosetting formulations were carried out by mixing the EVO monomer with the DTBA at a 1:1 molar ratio between the epoxy and acid groups, according to the method by Dusek et al.^{21,25} The selected initiator was added at 1 wt % and mixed at 80 °C with the previous mixture. The curing and postcuring protocols for the preparation of the EVO thermosets were determined based on the DSC study of reactivity presented in Figure S2 and Table S3. The DSC analysis allowed one to determine for each formulation the optimal temperatures of curing and postcuring, i.e., those temperatures conducting to a complete reaction (no residual enthalpy in the second scan during heating from 25 to 250 °C at 10 °C·min⁻¹) and to the highest T_g values of the obtained thermosets.

Characterization Techniques. *Differential Scanning Calorimetry (DSC).* The copolymerization reactions were carried out on a Mettler Toledo DSC 3 instrument equipped with STAR software from 25 to 220 °C. The samples (about 10–15 mg) were placed in 100 μ L aluminum crucibles. The temperature rate for all scanning runs was at 10 °C·min⁻¹. The DSC technique was also used to determine the thermosets' glass transition using the same heating rate, over a temperature range from -80 to 180 °C.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR analyses were performed using a Thermo Scientific Nicolet iS50 FTIR spectrometer with a deuterated *L*-aniline-doped triglycine sulfate (DLATGS) detector in an attenuated total reflectance (ATR) mode. The absorption bands were recorded in the range of 4000–525 cm⁻¹

at 4 cm⁻¹ resolution and 32 scans. The data were analyzed using OMNIC software. The percentage of the functional group conversion is defined using eq 1

$$\% = \frac{\left(\frac{A_{823}}{A_{1586}}\right)_0 - \left(\frac{A_{823}}{A_{1586}}\right)_t}{\left(\frac{A_{823}}{A_{1586}}\right)_0} \times 100 \quad (1)$$

where area absorbance peaks were calculated at the initial time (A_0) and at the end of the curing protocol (A_t). The peak at 823 cm⁻¹ corresponds to oxirane C–O groups and that at 1586 cm⁻¹ is the reference band, which belongs to the δ_{C-C} of the aromatic signal.

Thermogravimetric Analysis (TGA). TGA measurements were carried out on a Mettler Toledo TGA 2. The microbalance has a precision of ± 0.1 μ g. The samples of about 10 mg were placed in 70 μ L 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.

The statistic heat-resistant index temperature (T_s) is a characteristic of the thermal stability and was calculated according to eq 2

$$T_s = 0.49 \times [T_{5\%} + 0.6 \times (T_{30\%} - T_{5\%})] \quad (2)$$

where $T_{5\%}$ and $T_{30\%}$ are the temperatures at, respectively, 5 and 30% weight loss.

Dynamic Mechanical Analysis (DMA). DMA analyses were carried out on a Mettler Toledo DMA 1 instrument, equipped with STAR[®] software for curve analysis. The analyzed samples were prepared according to the curing protocol given in Table S3 and had rectangular dimensions of 30 \times 7 \times 2 mm³ (length \times width \times thickness). Elastic modulus values (E') and damping factors ($\tan \delta$) were collected at 3 °C·min⁻¹ heating rate from -50 to 170 °C and 1.0 Hz frequency. The DMA was operated using the tension method. The glass transition was assigned at the maximum of the damping factor ($\tan \delta = E''/E'$). The cross-linking density of EVO thermosets was calculated using eq 3, according to Flory theory of the rubber elasticity²⁶

$$\nu = \frac{E'}{3RT} \quad (3)$$

where E' is the storage modulus in the rubbery plateau region at $T_g + 50$ °C, R is the gas constant, and T is the absolute temperature in Kelvin.

Tensile Testing. The tensile tests were performed on a mechanical universal testing machine Instron, model 3365, controlled by BlueHill Lite software developed by Instron (Norwood, MA), according to standard ISO 527-141 and ASTM D638-0842.

To produce specimens for tensile tests, the reactive mixture was stirred at 80 °C for 10 min, placed into a silicone mold, and cured in an oven, according to Table S3 that summarizes the curing and postcuring protocols. These protocols were previously determined, based on DSC studies of reactivity for each formulation. The tensile bars were produced using silicon molds allowing one to obtain

Table 2. Reaction Enthalpy, Interval, and Temperature of the Reaction Peak (T_{peak}) of EVOs/DTBA/IM Systems during the Copolymerization Reaction

VOs feedstock	EVOs in copolymerization systems	epoxy content (mequiv·g ⁻¹)	ΔH (J·g ⁻¹)	T_{peak} (°C)	reaction interval
karanja oil	EKRNO	2.77	84 ± 3	164 ± 1	145–186
castor oil	ECO	2.85	109 ± 3	147 ± 1	130–170
St John's wort oil	ESJWO	2.97	108 ± 3	168 ± 1	154–186
peanut oil	EPO	3.35	112 ± 3	171 ± 1	151–192
rapeseed oil	ERPO	3.99	138 ± 3	164 ± 1	147–184
soybean oil	ESO	4.20	149 ± 3	159 ± 1	142–182
rosehip seed oil	ERHO	4.7	155 ± 3	161 ± 1	140–189
safflower oil	ESFO	4.93	172 ± 3	158 ± 1	142–180
grapeseed oil	EGRO	4.94	175 ± 3	162 ± 1	139–182
camelina oil	ECMO	5.29	188 ± 3	153 ± 1	136–176
linseed oil	ELO	5.61	197 ± 3	151 ± 1	131–180
hemp oil	EHO	6.09	194 ± 3	160 ± 1	135–190
perilla oil	EPLO	6.77	207 ± 3	152 ± 1	126–187

samples of dimensions 75 × 10 × 2 mm³ (length × width × thickness).

The analyses were performed using a crosshead speed of 10 mm·min⁻¹. For each formulation, five samples were tested to evaluate the average calculations of tensile properties (Young's modulus, tensile strength, and elongation at break).

Density Calculation. Density was calculated by measuring the volume of each sample and its weight using a Mettler Toledo ML 3002T precision balance (±0.0001 g).

Solvent Stability. The stability of thermosets in solvents was studied in methanol, ethanol, acetone, toluene, 1 N NaOH, and 1 N HCl for 72 h at room temperature to confirm the complete cross-linking and to evaluate the sample resistance in these solvents. Toluene was chosen as a good solvent for the swelling test, the swelling factor (Q_m) being calculated according to eq 6. The materials' cross-link density was determined using Flory–Rehner theory^{26,27} according to eq 4

$$\nu = \frac{\ln(1 - \nu_{2,s}) + \nu_{2,s} + X_1 \nu_{2,s}^2}{\nu_1 \left(\frac{\nu_{2,s}}{2} - 1/\sqrt[3]{\nu_{2,s}} \right)} \quad (4)$$

where ν_1 is the molar volume of the solvent (for toluene $\nu_1 = 106.27$ cm³·mol⁻¹, calculated as the ratio between the molar mass and the density), X_1 is the Flory Huggins polymer–solvent interaction parameter that for toluene is ~0.391,²⁸ and $\nu_{2,s}$ is calculated using eq 5

$$\nu_{2,s} = \frac{1}{\frac{\rho_{\text{polymer}}}{Q_m} + \frac{1}{\rho_{\text{solvent}}}} \quad (5)$$

where ρ_{polymer} and ρ_{solvent} are the densities of the polymer and of the solvent, respectively. The swelling factor Q_m is calculated using the following equation

$$Q_m = \frac{w_s - w_d}{w_s} \quad (6)$$

where w_s and w_d are the swelled mass and the swelled dry mass at the equilibrium, respectively.

The test was performed at room temperature, keeping the rectangular specimens in toluene for 2 days. The complete dissolution of the thermosets was tested in the dimethylformamide (DMF) solution of 5 wt % of 1–4 dithiothreitol for 24 h at 50 °C. All of the solvent tests were conducted on small rectangular 10 × 10 × 2 mm³ specimens.

RESULTS AND DISCUSSION

The copolymerization reactions of the EVOs with the DTBA hardener were studied using three different initiators, i.e.,

imidazole (IM), 1-methylimidazole (1-MI), and *N,N*-dimethylbenzylamine (DMBA) (respectively, D, E, and F in Figure 1). The correlation of EVO's structure and their epoxy index vs thermoset properties is part of the aim of this study. As references, the epoxidized linseed oil (ELO) and the epoxidized soybean oil (ESO) were chosen because (i) these two EVOs have epoxy indexes in the middle point of the variation range of the newly synthesized and herein studied EVOs and (ii) because both ELO and ESO are commercially available, produced, and applied at the industrial scale. Moreover, numerous studies highlighted the reactivity of these two epoxidized monomers with anhydride or acid hardeners.^{29–34} The evolution of the thermoset's properties in the function of the EVO structure will be analyzed considering EVO's monomers with comparable structures as the ELO and ESO references (i.e., same natures of fatty acids) but will also be compared with epoxidized castor oil (ECO) to gain knowledge on the influence of the additional hydroxyl groups present in its structure on the thermoset material performances. For all aforementioned systems, we will discuss further the properties of the final thermoset materials as a function of their epoxy content.

Copolymerization Reaction Investigation by DSC and FTIR Studies. The copolymerization reactions of the EVOs with DTBA catalyzed by IM, 1-MI, and DMBA were investigated by DSC to analyze if the EVOs show comparable reactivity in function of the initiators, as the reference system ELO/DTBA/initiator.

The dynamic DSC analyses were performed without the initiator and also with three selected initiators: IM, 1-MI, and DMBA. The DSC results are displayed in Figure S1. First, we can highlight the very good reactivity between the EVO's monomer and the DTBA hardener. Indeed, all of the studied systems are characterized by high values of reaction enthalpies, even in the systems without initiators. Moreover, the uncatalyzed systems react with a higher reaction enthalpy than the systems with initiators (Table S2). This result could be attributed to the occurrence of concomitant main and secondary reactions, such as homopolymerization or etherification. In comparison, the initiators introduce a selectivity through the EVOs/DTBA copolymerization; therefore, it decreases the starting temperature and the enthalpy of the reaction is given mainly by the main reaction. According to these results, it appears clearly that IM, as demonstrated for ELO,^{19,20} allows higher conversions during copolymerization,

together with a lower interval of the reaction for all of the EVOs/DTBA systems.

According to our previous results,^{19,20} the ELO/DTBA reaction in the presence of 1-MI is characterized by a low reaction enthalpy and low onset temperatures, T_{on} , compared with those of the system initiated by IM (Table S2). Thus, 1-MI activates the conversion of epoxides at lower temperatures but with a lower selectivity of the copolymerization reaction. Thereafter, when DMBA is used as the catalyst, an efficient activation of the copolymerization reaction is produced, with the high reaction enthalpy for epoxidized karanja oil (EKRNO), ECO, epoxidized rapeseed oil (ERPO), and epoxidized hemp oil (EHO) monomers, but the reaction temperature range is shifted to higher temperatures. This result, combined with the low copolymerization conversions obtained for the ELO reference, made us to discard also this initiator from the subsequent studies.

An exception to this trend is the ECO/DTBA formulation, which has a particular behavior, that is, a higher reactivity and a lower reaction temperature was obtained without using a catalyst. This result can be attributed to the effect of the hydroxyl groups present in the ECO's structure.

In conclusion, IM was selected as the optimal initiator for the EVOs/DTBA copolymerization studies.

The copolymerization and reactivity of the ELO/DTBA/IM system were then considered as the reference and, therefore, the reactivities of the new EVOs were compared with this formulation. In Table 2 and Figure S2, the comparison of the DSC thermograms of EVOs/DTBA/IM copolymerization reactions is reported. The DSC results display that the enthalpy of the copolymerization reaction increases with the EVO's epoxy content (Table 2 and Figure 2). The EVOs with

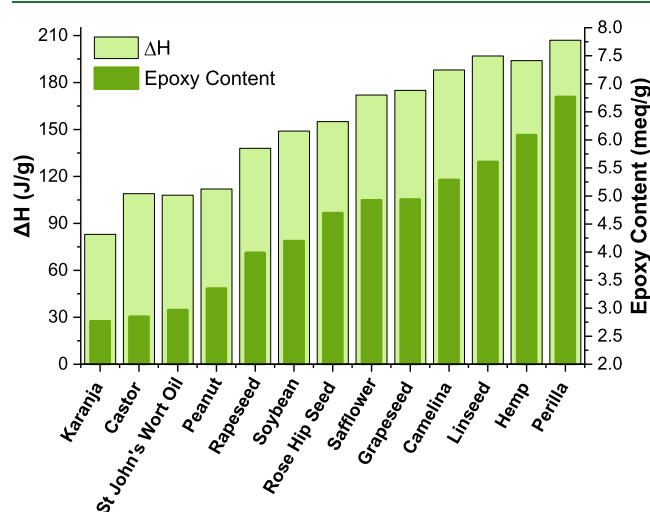


Figure 2. Correlation of the EVOs/DTBA/IM copolymerization enthalpy and monomers' epoxy content.

low epoxy content, such as EKRNO or epoxidized St John's wort oil (ESJWO) with 2.77 and 2.97 mequiv·g⁻¹, exhibit lower copolymerization enthalpy (84 and 108 J·g⁻¹) compared with epoxidized perilla oil (EPLO) characterized by the highest epoxy content and, thus, the highest enthalpy of copolymerization (207 J·g⁻¹). With the increase of the EVO's epoxy content, we can notice an increase of the temperature interval of the reaction. As we can observe in Figure S2, the copolymerization exothermic peaks have comparable T_{endset}

but the T_{onset} values appear at lower temperatures for the EVOs with higher epoxy content.

FTIR analyses of the samples before and after curing provide the direct experimental indication of the involved copolymerization reactions, following the characteristic epoxy and carboxylic acid reactive groups. As example, Figure 3 illustrates

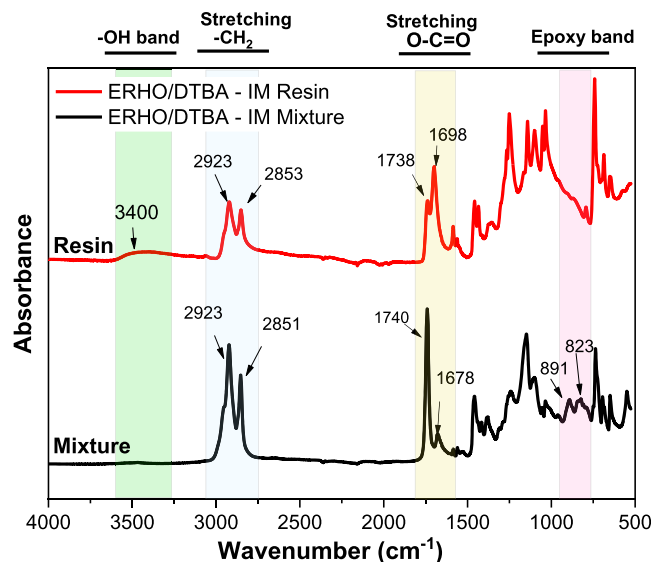


Figure 3. FTIR spectra comparison of the ERHO/DTBA/IM uncured mixture and of the thermoset resin.

the structural evolution and the comparison between the FTIR spectra of the epoxidized rosehip seed oil (ERHO)/DTBA/IM reactive mixture and the thermoset resin. In the FTIR spectrum of the uncured mixture, we can notice the oxirane characteristic bands at 823 and 891 cm⁻¹ that completely disappear in the spectrum of the cured material. In the thermoset's spectrum, we can notice that the increased -OH peak at 1678 cm⁻¹ in the mixture disappears after curing, being ~3400 cm⁻¹. Moreover, the formation of the new ester peak, with the stretching of the carbonyl (C=O_{ester}), appears in the resin spectrum at 1738 cm⁻¹.

In compliance with the DSC analysis, the ECO system gave different FTIR results for the epoxy monomers and for the thermosets, due to the presence of alcohol groups in their structure. The FTIR spectrum of the ECO monomer (Figure 4) shows the presence of the typical bands of -OH, -CH₂, and O-C=O at, respectively, ~3400, 2925, 2855, and 1737 cm⁻¹, while the absorption band of the characteristic epoxide ring vibration appears at 844 cm⁻¹. In the spectrum of the thermoset material, a new ester peak appears but we should notice the presence of few residual epoxy peaks at 865 cm⁻¹. The presence of these residual groups can be explained by the fact that the DTBA can also react with the -OH functions from the ECO structure. Therefore, the DTBA is in defect regarding the main copolymerization stoichiometry.

The copolymerization conversions for the EVO thermosets were calculated by applying eq 1. The results are summarized in Figure 5 and Table S4. EKRNO and ESJWO-based thermosets display the highest conversion (97%) in the series of EVOs, except for the reference, ELO^{19,21} (99%). Conversions superior to 90% were also obtained for epoxidized peanut oil (EPO) (95%), ERPO (94%), ECO (92%), and epoxidized grapeseed oil (EGRO) (92%).

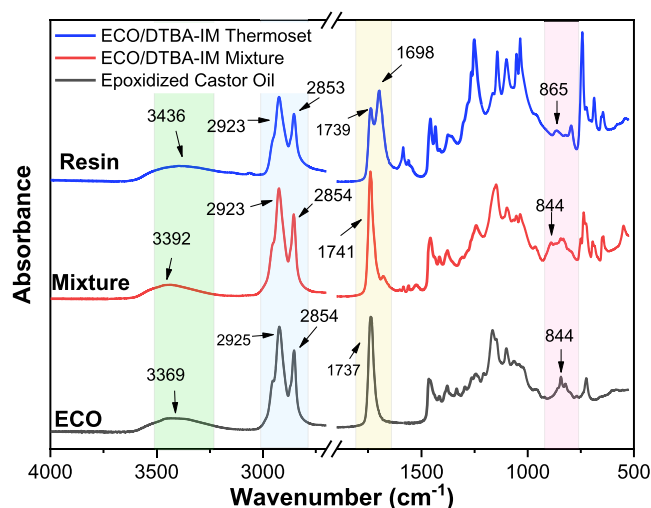


Figure 4. FTIR results and comparison between the ECO monomer, the ECO/DTBA/IM mixture, and the final thermoset.

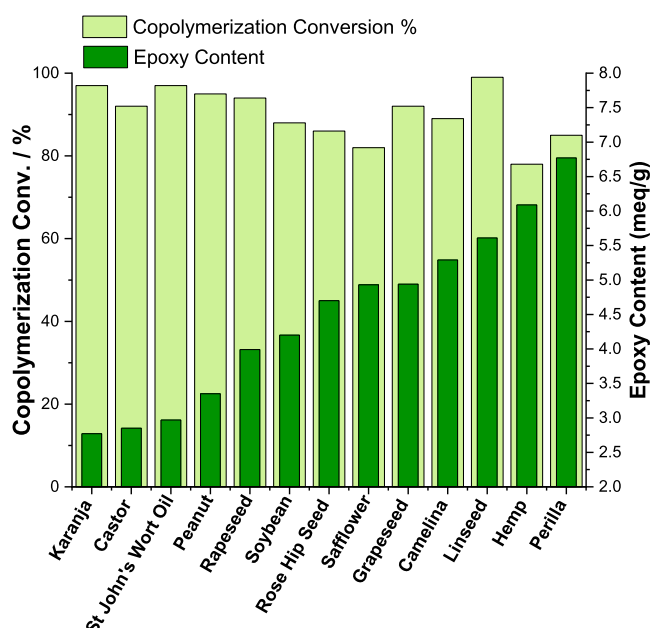


Figure 5. Conversion of epoxy functions for the EVO thermosets correlated with the epoxy content.

EHO shows the lowest conversion compared to EVOs having similar structures. This result has to be correlated to the larger copolymerization reaction range and predicts a lower T_g value for this thermoset. The same trend was observed for epoxidized safflower oil (ESFO)-based thermoset.

Thermomechanical Properties of EVOs/DTBA/IM Thermosets. Figure 6 shows the results of DMA analysis, i.e., the temperature dependence of loss factor ($\tan \delta$) (Figure 6A) and of the storage modulus (E') (Figure 6B) for the prepared thermosets. The values of DMA data are listed in Table 3. We can notice that all of the thermosets reveal a single $\tan \delta$ peak, as in the case of T_g measurements performed by DSC, highlighting the existence of homogeneous networks. As shown in Figure 6 and Table 3, we can observe an increase of the $\tan \delta$ values with the epoxy content in the copolymer's formulation. The $\tan \delta$ value varies from 33 °C, for thermosets made with EVOs with low epoxy content, to 111 °C, for EPLO

having the highest epoxy content (6.77 mequiv·g⁻¹). To compare the viscoelastic results, both the evolution of T_g , determined by DSC, and that of $\tan \delta$, measured by DMA, are plotted in Figure 7, showing that the data fit with a linear trend in function of the epoxide content.

In line with these results, the evolution of storage modulus with the temperature (Figure 6B) shows high E' values for the thermosets based on EVOs having high epoxy content. The calculation made using eq 3 allows one to evaluate the cross-link density of the prepared network. Once again, the results show that increasing the epoxy content leads to an increase in the thermoset cross-link density from 0.025 (EKRNO thermoset) to 3.0 mmol·cm⁻³ (EPLO thermoset). We can notice that EPLO and the reference ELO thermosets are the resins with the highest cross-linking (Table 3), while thermosets with low epoxy content exhibit the lowest cross-linking density (Figure 11).

ECO-based thermoset material shows the α transition at 52 °C and the lowest modulus in the rubbery plateau. Besides its low epoxy content, this low value of E' could be correlated with the lower reactivity with the DTBA hardener. However, considering all aforementioned outcomes obtained for this system, the main hypothesis explaining these results is the presence of the hydroxyl groups in the ECO structure and its possible reaction with DTBA leading to imbalanced stoichiometry and, thus, to incomplete epoxy/DTBA curing reactions. Moreover, secondary reactions as esterification or etherification implying the -OH reactions with -COOH or with epoxy functions could occur the copolymerization reaction, according to Hernandez et al.³⁵ A large range of T_g values was obtained in the series of prepared thermosets, from 17 °C for EKRNO-based thermoset to 91 °C for EPLO-based resin. Figure 7A shows the evolution of this transition in function of the EVO epoxy content. These results are also presented in function of $\tan \delta$ values correlated with the epoxy content, as shown in Figure 7B.

Likewise, in the study of copolymerization reactivity, we can highlight that the increase of the epoxy content leads to an increase of the corresponding T_g values of thermosets. In the case of ECO thermosets, higher values of T_g were measured, ~27 °C, again probably due to the presence of alcohol moieties in the structures participating in the cross-linking reactions, or in the hydrogen bonding, compared to the EVOs with the similar epoxy content as ESJWO, $T_g \sim 17$ °C. These results are consistent with those reported by Gerbase et al.³⁶ in which the lower T_g of ESO thermosets compared with that of ELO-based resins were correlated with the ESO lower epoxy index.

The low values of T_g obtained for EVOs with low epoxy content are also in agreement with the polymers derived from EVOs with the low iodine content, as presented in the literature for ECO cured with citric acid.³⁴ Generally, the aliphatic and flexible structures usually lead to low T_g values, compared with aromatic thermosets. For instance, Williams et al.⁷ prepared DGEBA/DCAs epoxy vitrimers with T_g values ranging from 50 to 70 °C. Wang et al.³⁷ reported the synthesis of ESO/methylhexahydrophthalic anhydride (MHHPA) resins with $T_g \sim 40$ °C, while an increase of mechanical properties was obtained by adding DGEBA in the blends. Kodam et al.⁴ investigated the epoxidized karanja oil cured with citric and tartaric acid and measured higher T_g values (~112 °C) attributed to high acid functionalities of the hardeners and to the hydroxyl groups of the starting building blocks producing

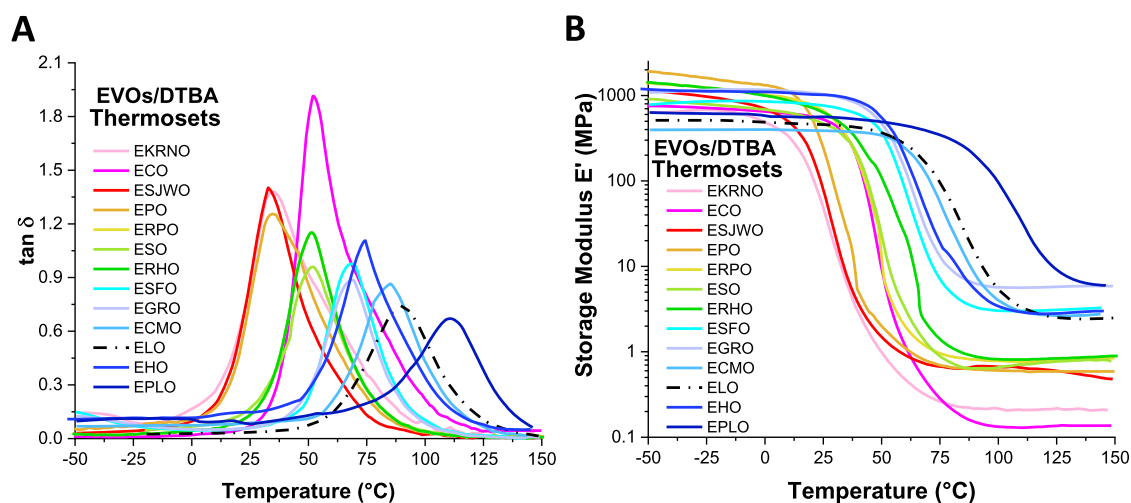


Figure 6. DMA results: $\tan \delta$ (A) and storage modulus E' (B) vs temperature for the EVOs/DTBA/IM thermosets.

Table 3. Summarized DSC and DMA Data of EVOs/DTBA/IM Thermosets

EVOs/DTBA/IM thermosets	T_g (°C)	$\tan \delta$ (°C)	($\tan \delta$) max	$E'_{\text{glassy plateau}}$ (MPa)	$E'_{\text{rubbery plateau}}$ (MPa)	cross-link density ($\text{mmol} \cdot \text{cm}^{-3}$)	ρ ($\text{g} \cdot \text{cm}^{-3}$)
EKRNO	17	34	1.40	630	0.21	0.025	1.11
ECO	27	52	1.91	850	0.14	0.02	0.93
ESJWO	17	33	1.40	1145	0.48	0.072	1.06
EPO	24	35	1.36	1900	0.59	0.07	1.33
ERPO	40	51	1.11	1400	0.82	0.09	1.35
ESO	45	52	0.96	900	0.82	0.08	0.95
ERHO	53	60	0.86	1430	0.92	0.11	1.13
ESFO	48	68	0.99	780	3.13	0.31	1.12
EGRO	50	67	0.90	1090	5.84	0.58	1.11
ECMO	64	85	0.86	400	2.78	0.77	0.98
ELO	76	91	0.75	500	2.63	1.25	1.02
EHO	62	76	1.11	1200	3.03	0.75	1.15
EPLO	91	111	0.68	630	5.98	3.00	0.98

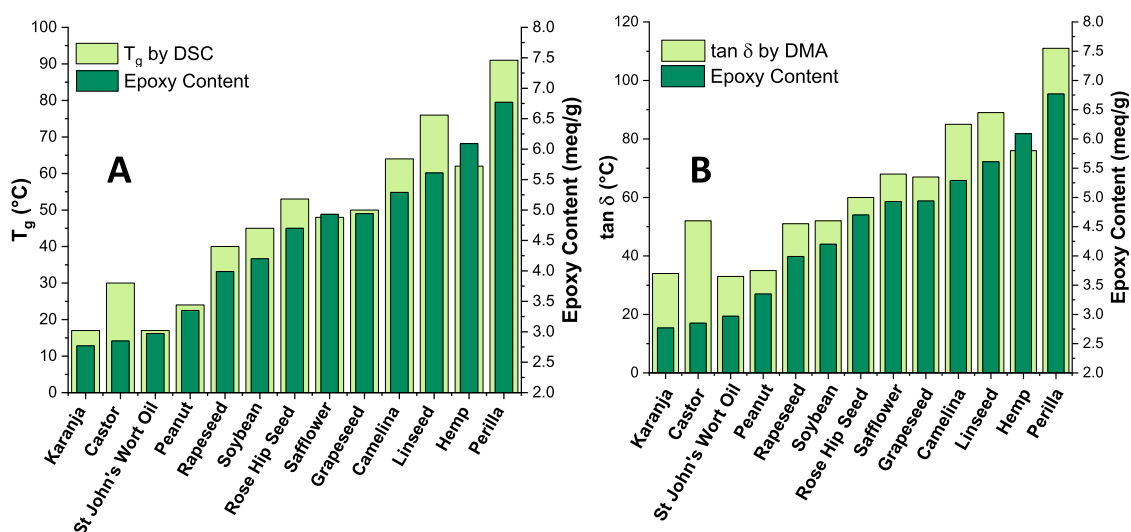


Figure 7. Glass transition evaluated by dynamic DSC analysis (A) and $\tan \delta$ (B) measured by DMA analysis in function of the EVO's epoxy content.

higher cross-linking density. Similarly, high T_g values were obtained by curing ELO with methylhexahydrophthalic anhydride (MHHPA) obtaining thermosets with α -transition of 134 °C, whereas ELO cured with 3,3,4,4-benzophenone-tetracarboxylic dianhydride (BTDA) lead to cross-linked resins

with $\tan \delta$ around 245 °C.³² In contrast, Zeng et al.²⁹ obtained materials with T_g values from −16 to −21 °C for ESO/aliphatic diacid cross-linkers.

Therefore, the T_g values are strongly dependent not only on the EVO structure but also on the nature and structure of the

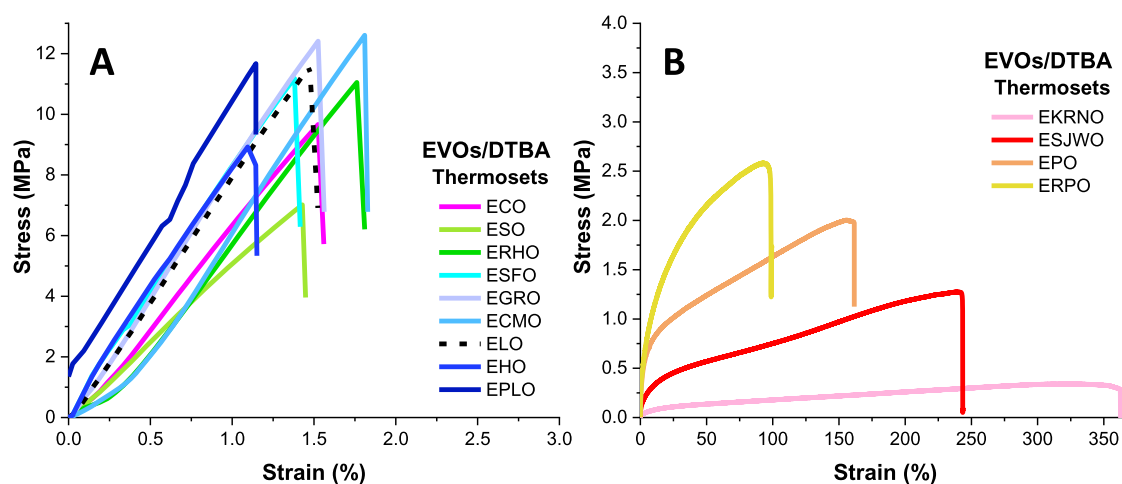


Figure 8. Stress–strain curves of EVOs/DTBA-based thermosets (A) stiff and (B) ductile EVO-based thermosets.

hardener. A proper selection of the hardener contributes to the achievement of high performances even if the EVOs have aliphatic structures. Here, without changing the hardener structure, we succeeded to reach a high T_g value, of 91 °C, by copolymerization of epoxidized perilla oil with DTBA.

The static mechanical properties of the samples were studied by tensile testing. Figure 8 shows the stress–strain curves of EVOs/DTBA thermosets, and Table 4 summarizes the main

Table 4. Tensile Results (Averaged) for the EVOs/DTBA Thermosetting Resins

EVOs/DTBA/IM thermosets	Young modulus (MPa)	stress at break, σ (MPa)	elongation at break, ϵ (%)
EKRNO	0.73 \pm 0.08	0.39 \pm 0.07	347.2 \pm 54.7
ECO	731.6 \pm 59.2	7.96 \pm 1.85	1.21 \pm 0.36
ESJWO	2.42 \pm 0.77	1.21 \pm 0.09	247.5 \pm 11.0
EPO	21.1 \pm 8.2	2.03 \pm 0.21	167.4 \pm 25.5
ERPO	476.2 \pm 74.9	2.73 \pm 0.42	117.4 \pm 0.82
ESO	752.2 \pm 20.2	10.3 \pm 3.03	1.70 \pm 0.15
ERHO	771.3 \pm 39.2	10.1 \pm 4.38	2.04 \pm 0.55
ESFO	804.0 \pm 32.54	11.5 \pm 1.47	1.42 \pm 0.20
EGRO	825.5 \pm 31.93	12.7 \pm 2.75	1.62 \pm 0.38
ECMO	830.6 \pm 37.3	12.1 \pm 1.95	2.04 \pm 0.29
ELO	811.0 \pm 36.05	10.9 \pm 1.10	1.36 \pm 0.13
EHO	822.1 \pm 96.6	9.82 \pm 0.67	1.21 \pm 0.18
EPLO	815.3 \pm 10.1	11.5 \pm 4.55	1.23 \pm 0.68

tensile results. From Figure 8, we can notice that two kinds of stress–strain results were obtained, separating the synthesized thermosets into hard and brittle (Figure 8A) and soft and plastic (Figure 8B). The EVOs with, in general, low epoxy content and, therefore, low cross-linked networks behave as soft and flexible, which is well consistent with the trend of their T_g . From Figure 8B, we can notice that these EVOs, based on ERPO, EPO, ESJWO, and EKRNO, have low to very low Young's modulus and tensile strength and the stress at break values ranging from 2.73 to 0.39 MPa. These resins exhibited high elongation at the break, from 117 to 347%. These results are in good agreement with the results reported by Imbernon et al.³⁸ for elastomers synthesized from epoxidized natural rubber and dithiodibutyric acid cross-linker.

In contrast, the thermosets obtained from EVOs with an epoxy content >4.20 mequiv·g^{−1} reveal higher tensile strength and Young's modulus values. These thermosets have strength

at the break at around 10–12 MPa, while the elongation values are very low, $<2\%$, characteristics for hard and brittle thermosets.

A peculiar trend shows the ECO-based thermoset that has a tensile behavior close to that of thermosets based on EVOs with high epoxy content, despite the fact that ECO is from the category of EVOs with low content, ~ 2.85 mequiv·g^{−1}. This result can be again explained by the contribution of the hydroxyl functions present in its structure to increase the network chemical connectivity, confirmed by its T_g and $\tan \delta$ values, superior to those of thermosets from EVOs with a comparable epoxy content.

All of the EVO thermosets exhibit better mechanical properties than some other EVO-based polymer networks, which were cured by carboxylic acids^{4,29,33,39} or the EVOs/disulfide cross-linker⁴⁰ that showed lower σ and ϵ . These results open the window for industrial applications.

The literature shows that starting from vegetable oils, a large diversity of derivatives can be synthesized with very good properties. For example, Webster and Pan developed high-performance thermosets by preparing epoxidized sucrose esters of fatty acids (ESEFAs) (soybean, linseed, safflower) cross-linked with 4-methylhexahydrophthalic anhydride (MHHPA) using two ratios of epoxy/anhydride of 1:0.5 and 1:0.75.⁴¹ The modulus and tensile strength of ESS (epoxidized sucrose soyate) were higher than those of the ESO control thermoset by factors of 7.6 and 2, respectively, while the properties of the ESL (epoxidized sucrose linseedate) thermoset were even higher with a modulus 21 times superior and a tensile strength 4.5 times greater than that of the ESO thermoset. The same authors reported increased properties,⁴² replacing ESO cross-linked with dodecenylsuccinic anhydride (DDSA), dipentaerythritol (DPE), tripentaerythritol (TPE), or sucrose esters of soybean oil, synthesized using transesterification from soybean methyl ester and the corresponding polyols. The increased values in T_g and moduli were correlated to the presence of the available hydroxyl groups, which can facilitate the formation of polyester networks through the rapid reaction between the hydroxyl and anhydride.

Wang et al.⁴³ reported very good properties of epoxy polymer derivatives of soybean oil, synthesized by amidation of soybean oil with three amino alcohols (1-amino-2-propanol, 3-amino-1-propanol, and 1,3-diamino-2-propanol), followed by (meth)acrylation, then by the free radical polymerization of

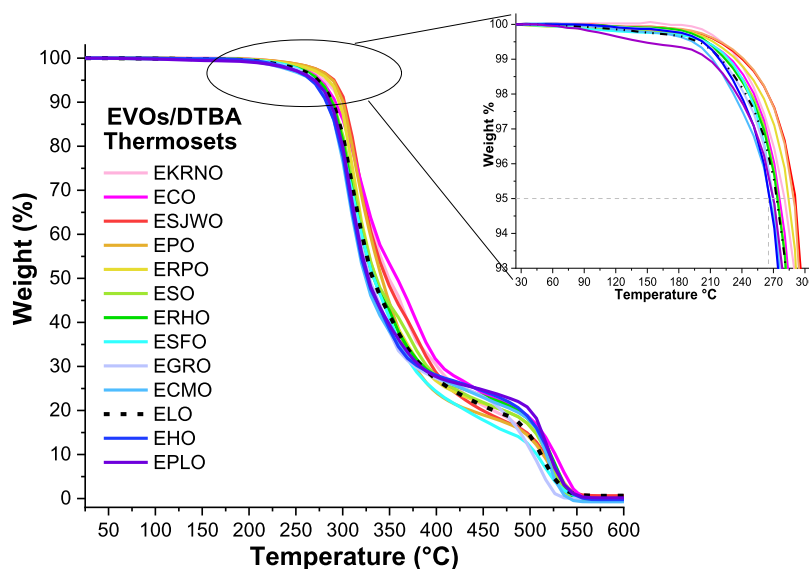


Figure 9. TGA thermograms during heating the EVO thermosets at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in air; zoom in the region 25–320 $^{\circ}\text{C}$.

unsaturated fatty side chains, and finally, the epoxidation of unsaturations. The authors obtained an increased tensile strength and modulus replacing ESO/4-methyl-1,2-cyclohexanedicarboxylic anhydride with these soybean oil epoxy polymers, obtaining values from 1.4 MPa (control, ESO-based thermoset) to 37 MPa for the tensile strength and from 2.4 MPa (ESO-based thermoset) to 561 MPa Young's modulus.

Zhou et al.⁴⁴ observed that the mechanical strength, Young's modulus, and toughness improved with the increase of the epoxy group density for sunflower oil-based epoxy copolymers EP(SFMA-co-VM) synthesized by the sunflower oil-based monomer (SFMA) and vanillin-derived methacrylate (VM).

The thermal stability profiles of the obtained thermosets are displayed in Figures 9 and S3 and Tables 5 and S5. All of the

bonds provokes a decrease of thermoset's thermal stability due to their lower dissociation energy compared with that of C–C bonds. Moreover, higher the oxirane ring content, more ester and hydroxyl groups are created through the curing. These functions can also promote the thermal scissions of the networks.

The thermal stability of the EVO thermosets are similar to those of epoxy resins containing disulfide dynamic bonds,⁴⁶ but lower if we compare it with ELO/adipic acid or glutaric anhydride systems³³ or with ESO/dicarboxylic acid (DCA) thermosets with different carbon chain-lengths.²⁹ Figure S3 displays the derivative thermogravimetric analysis (DTG) curves highlighting the main degradation steps.

The statistic heat-resistant index temperature values (T_s) (Table 5) have a trend similar to the $T_{5\%}$ values. For the thermosets based on EVOs with low epoxy content, ESJWO and EKRNO thermosets, the T_s values are higher compared to the reported values for epoxidized sucrose soyate cured with citric or malic acids⁴⁷ (148–154 $^{\circ}\text{C}$). Supanchaiyamat et al.⁴⁸ correlated the first thermal degradation stage with the breaking of the ester linkages, while the second one with the cleavage of the products formed during the first degradative step.

Solvent Stabilities and Chemical Degradability Behavior. To evaluate the solvent stability of the EVO thermosets, weighed and measured samples were immersed for 72 h in methanol, ethanol, acetone, toluene, 1 N NaOH, and 1 N HCl. Three thermosets were selected to analyze how the low or high epoxy content impact on solvent stability: ESJWO, ECO, and EPLO thermosets. Their behavior after immersion in the mentioned solvents was compared (Figure 10A–C). After 72 h, these resins were generally stable in all solvents and no changes were observed in 1 N HCl solution.

ECO resin (Figure 10C) shows similar behavior as ESJWO and EPLO resins. Gerbase et al.³⁶ reported higher chemical resistance for ESO cured with cyclic anhydrides in polar organic solvents (acetone, ethanol) than in toluene where an interaction of polymer–solvent by network's swelling was observed. For DGEBA cured with 4-aminophenyl disulfide, Ruiz de Luzuriaga et al.⁴⁹ showed that the materials were not affected after immersion at room temperature for 72 h in 1 N NaOH and HCl, THF, toluene, acetone, and ethanol.

Table 5. $T_{5\%}$ and T_s Values Determined by TGA Analysis

EVOs/DTBA/IM thermosets	$T_{5\%}$ ($^{\circ}\text{C}$)	T_s ($^{\circ}\text{C}$)
EKRNO	285	171
ECO	275	169
ESJWO	290	170
EPO	285	164
ERPO	285	172
ESO	271	167
ERHO	275	165
ESFO	271	162
EGRO	265	161
ECMO	265	162
ELO	275	167
EHO	265	164
EPLO	265	159

EVO thermosets show similar degradation behavior in air, with good thermal stability, in the same range of ELO thermoset reference. The $T_{5\%}$ values are ranging from 265 $^{\circ}\text{C}$ for EPLO thermosets to 290 $^{\circ}\text{C}$ for ESJWO. Resins of EVOs with low epoxy content exhibit higher thermal stability, whereas increasing the epoxy content decreases the thermal stability. The reason for this behavior could be connected to the amount of DTBA in the network, and consequently to the S–S bonds in the resins. Ma et al.⁴⁵ reported that the presence of S–S

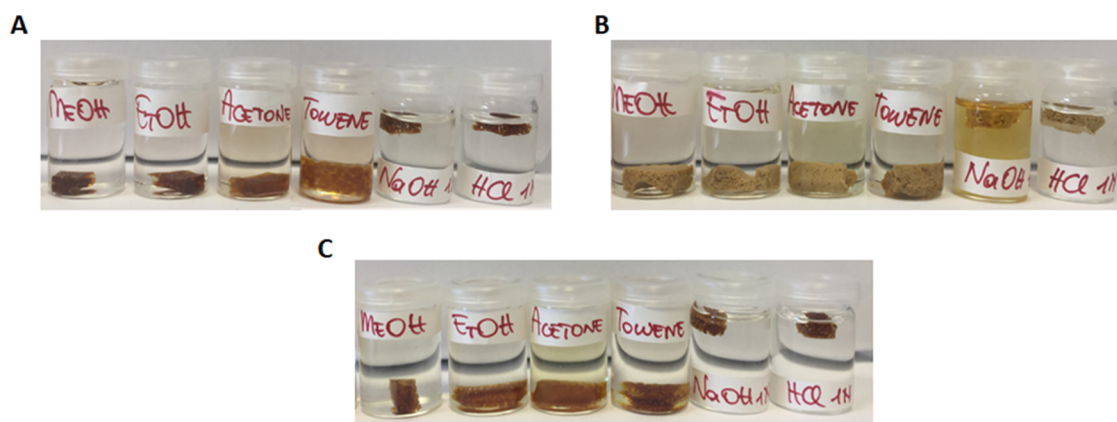


Figure 10. Solvent stability study for selected thermosets: ESJWO (A), EPLO (B), and ECO (C) after 72 h in methanol, ethanol, acetone, toluene, 1 N NaOH, and 1 N HCl.

We already proved the ELO/DTBA thermoset disintegration in 1 N NaOH at 80 °C or at room temperature after 3 days.²⁰ This behavior could be attributed to a synergic effect: the disulfide metathesis^{50,51} and also the cleavage of the ester bonds. As example, Ma et al.⁴⁵ reported that the isosorbide-derived epoxy cross-linked with 4-aminophenyl disulfide exhibits a complete degradation after 3 h in alkaline solution, attributing this result to S–S cleavage and to the water-soluble nature of isosorbide.

From Figure 10B, we can observe that EPLO resin presents a faster autodegradation in alkaline solution compared to ESJWO thermoset due to its higher epoxy content and, consequently, due to a higher content on ester connections formed during cross-linking.

Regarding the swelling tests, toluene was selected as a solvent for this test for 24 h at room temperature. The results are traced and plotted in Figure 11. Vitrimers are known for

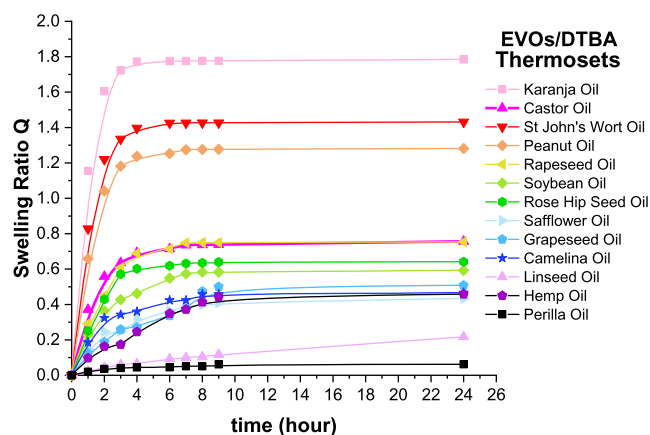


Figure 11. Swelling tests performed in toluene for 24 h.

“swell, but do not dissolve, in good solvents” as reported by Leibler et al.,⁵² and the swelling equilibrium of the thermosets in given solvents is an indicator of the cross-linking.⁵³ The degree of swelling is known to be dependent on the cross-link density of thermoset networks. The higher the cross-link density, the lower is the degree of swelling: EPLO has the lowest swelling ability. EKRNO and ESJWO thermosets show the highest swelling, confirming the lowest network cross-link density. The swelling ratio of the EVOs is lower than that of

acrylated epoxidized soybean oil (AESBO)/maleic anhydride thermosets⁴⁸ or of other bio-based thermosets.⁵⁴

The swelling test results were used further to determine the cross-link density of the networks, as described by Flory–Rehner theory.^{26,27} Applying this method, the network density values were evaluated by measuring their swelling in toluene at room temperature for 48 h. Previously, we determined by DMA data (Figure 12) that the cross-linking significantly

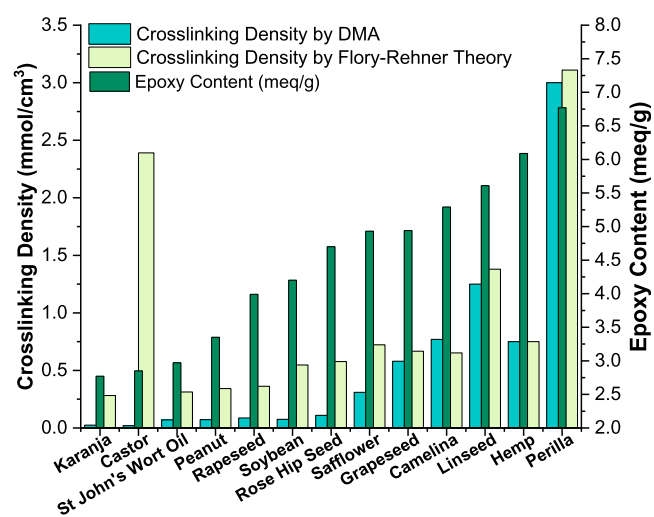


Figure 12. Cross-linking density is determined by the rubber elasticity and by Flory–Rehner theories, in function of the EVO epoxy content.

increased with the epoxy content, as confirmed by the rubbery-elasticity theory. The results are reported and compared in Table S6. The corroborated data by the two analyses demonstrate the same trend but with higher values for the results extracted by the swelling tests. For the thermosets based on EVOs with high epoxy content, the results are close, especially for EPLO and EHO materials. A contradictory result has been observed for ECO thermoset with one of the highest cross-linking densities measured by Flory–Rehner theory.

Finally, the reduction of the disulfide bonds to thiols was performed using a DMF solution with 5 wt % of dithiothreitol, according to Zhou et al.,⁴⁶ at 50 °C for 24 h. Similar results were obtained by Ruiz de Luzuriaga et al.,⁴⁹ who showed a complete dissolution of DGEBA/4-aminophenyl disulfide

thermosets in 2-mercaptoethanol in DMF solution immersed at room temperature for 24 h.

Figure 13 displays this reduction for ERHO thermoset resin. The thiol groups present in the solvent solution react with the

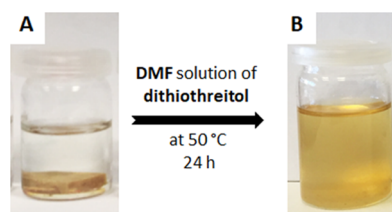


Figure 13. ERHO thermoset (A) before and (B) after immersion in DMF solution with dithiothreitol.

cross-linked dynamic disulfide networks, producing a complete debonding of the S–S connections. This complete thermosets' dissolution opens important windows to chemical recyclability for thermoset materials.

Bio-Based Content. Finally, the bio-based content of the EVOs/DTBA/IM thermosets was evaluated as “the amount of bio-based carbon in the material or product as a percent of the weight (mass) of the total organic carbon in the product”.⁵⁵

All of the starting EVO monomers were obtained from renewable materials, as seeds of vegetables, while the hardener and the initiator are not bio-based products. Considering ELO thermoset formulation, the carbon content in the starting materials is: in ELO ~ 70.5%, in DTBA ~ 47%, and in IM ~ 53%, respectively. Therefore, for the ratio EVO/hardener = 1/1: 2.5 g of ELO reacts with 2.149 g of DTBA and 0.046 g of IM, consequently the bio-based content according to Pan et al.⁴¹ is

$$\begin{aligned} \text{bio-based content \%} &= \frac{(2.5 \text{ g} \times 70.5\%)}{(2.5 \text{ g} \times 70.5\%) + (2.149 \text{ g} \times 47\%) + (0.046 \text{ g} \times 53\%)} \\ &= 63.0\% \end{aligned}$$

$$\begin{aligned} \text{carbon bio-based content \%} &= \frac{\text{bio-based carbon}}{\text{bio-based carbon} + \text{petro-based carbon}} \end{aligned}$$

$$\begin{aligned} \text{carbon bio-based content \%} &= \frac{57 \times 0.532}{57 \times 0.532 + 14 \times 0.458 + 3 \times 0.01} \\ &= 82.5\% \end{aligned}$$

The bio-based content determined for all of the thermosets (Table S7) is in the range from 79% for EKRNO to 58% for EPLO, while the carbon bio-content varies from 91% for EKRNO to 80% for EPLO. Increasing the epoxy content, the bio-based content and the carbon bio-content decrease due to a higher amount of needed hardener in the formulation.

CONCLUSIONS

A series of novel bio-based epoxy thermosets were developed using a broad range of epoxidized vegetable oils. These EVO monomers were copolymerized with a disulfide aromatic dicarboxylic acid (DCA) and, therefore, the reactivity of these systems was compared. The new EVOs allow one to obtain materials with a wide range of thermomechanical properties,

thanks to their variation in chemical structures and concomitant reactivities with the acid hardener. By an appropriate choice of epoxy content in the EVO structure, the final properties could be predicted. Indeed, the copolymerization of EVOs with DTBA produced materials, exhibiting either high $T_g \sim 91^\circ\text{C}$, $\tan \delta$ values of 111°C , and cross-link density of $3 \text{ mmol}\cdot\text{cm}^{-3}$ as in the case of EPLO or low T_g values ($\sim 17^\circ\text{C}$) as in the case of EKRNO-based thermoset, characterized by a low epoxy content. The large range of tensile properties, from soft and plastic (for thermosets based on EVOs with an epoxy content $< 4 \text{ mequiv}\cdot\text{g}^{-1}$) to hard and rigid could be used to develop novel sustainable thermosetting materials with modulated properties and, thus, of interest for very different application fields. The obtained materials, with a high bio-based carbon content $> 80\%$ can find applications in protective coatings, structural matrix, and composites.

The chemical recyclability results are opening windows for a future work that will be dedicated to the investigation of 3R ability (recyclability, repairability, and reshapability) of these new EVO thermosets.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.biomac.0c01059>.

Characteristics of the selected reagents; thermocuring studies of the reaction of the EVOs/DTBA with and without initiators by DSC analysis; curing and postcuring conditions for the EVOs/DTBA/IM; thermoset material characterization by TGA, DMA, ATR-FTIR, and bio-based content and carbon bio-content % for EVOs/DTBA/IM (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

VO, vegetable oil; EVO, epoxidized vegetable oil; ELO, epoxidized linseed oil; EKRNO, epoxidized karanja oil; ECO, epoxidized castor oil; ESJWO, epoxidized St John's wort oil; EPO, epoxidized peanut oil; ERPO, epoxidized rapeseed oil; ESO, epoxidized soybean oil; ERHO, epoxidized rosehip seed oil; ESFO, epoxidized safflower oil; EGRO, epoxidized grapeseed oil; ECMO, epoxidized camelina oil; EHO, epoxidized hemp oil; EPLO, epoxidized perilla oil; IM, imidazole; 1-MI, 1-methyl imidazole; DMBA, *N,N'*-dimethyl benzamine; DTBA, 2,2'-dithiodibenzoic acid; DGEBA, diglycidyl ether of bisphenol A; DCA, dicarboxylic acids; FTIR, Fourier transform infrared spectroscopy; DSC, differential scanning calorimetry; DMA, dynamic mechanical analysis; TGA, thermogravimetric analysis; DTG, derivative thermogravimetric analysis; DMF, dimethylformamide; AESBO, acrylated epoxidized soybean oil; MHHPA, methylhexahydrophthalic anhydride

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