

Article

Kinetical Study, Thermo-Mechanical Characteristics and Recyclability of Epoxidized Camelina Oil Cured with Antagonist Structure (Aliphatic/Aromatic) or Functionality (Acid/Amine) Hardeners

Chiara Di Mauro ¹, Aratz Genua ²  and Alice Mija ^{1,*} 

¹ Institut de Chimie de Nice, UMR CNRS 7272, Université Côte d'Azur, 06108 Nice, France; chiara.di-mauro@univ-cotedazur.fr

² CIDETEC, Basque Research and Technology Alliance (BRTA), Paseo Miramon 196, 20014 Donostia-San Sebastian, Spain; agenua@cidetec.es

* Correspondence: alice.mija@univ-cotedazur.fr

Abstract: In an attempt to prepare sustainable epoxy thermosets, this study introduces for the first time the idea to use antagonist structures (aromatic/aliphatic) or functionalities (acid/amine) as hardeners to produce reprocessable resins based on epoxidized camelina oil (ECMO). Two kinds of mixtures were tested: one combines aromatic/aliphatic dicarboxylic acids: 2,2'-dithiodibenzoic acid (DTBA) and 3,3'-dithiodipropionic acid (DTDA); another is the combination of two aromatic structures with acid/amine functionality: DTBA and 4-aminophenyl disulfide (4-AFD). DSC and FT-IR analyses were used as methods to analyze the curing reaction of ECMO with the hardeners. It was found that the thermosets obtained with the dual crosslinked mechanism needed reduced curing temperatures and reprocessing protocols compared to the individual crosslinked thermosets. Thanks to the contribution of disulfide bonds in the network topology, the obtained thermosets showed recycling ability. The final thermomechanical properties of the virgin and mechanical reprocessed materials were analyzed by DMA and TGA. The obtained thermosets range from elastomeric to rigid materials. As an example, the ECMO/DTBA₇₀4-AFD₃₀ virgin or reprocessed thermosets have $\tan \delta$ values reaching 82–83 °C. The study also investigates the chemical recycling and the solvent resistance of these vitrimer-like materials.

Keywords: dual-crosslinked networks; dual-dynamic hardeners; recyclability; epoxidized camelina oil; mechanical recycling; chemical recycling



Citation: Di Mauro, C.; Genua, A.; Mija, A. Kinetical Study, Thermo-Mechanical Characteristics and Recyclability of Epoxidized Camelina Oil Cured with Antagonist Structure (Aliphatic/Aromatic) or Functionality (Acid/Amine) Hardeners. *Polymers* **2021**, *13*, 2503. <https://doi.org/10.3390/polym13152503>

Academic Editor: Angels Serra

Received: 21 June 2021

Accepted: 27 July 2021

Published: 29 July 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The interest in and development of dynamic covalent chemistry (DCvD) [1] and reactions that use dynamic covalent bonds have grown exponentially in recent years. The introduction of interchangeable and reversible bonds in polymer networks, due to the sensitivity to external stimuli, is playing a fundamental role in the emerging technologies of self-repairing or recycling systems. The opportunity of reconnecting chemical bonds allows the reduction in waste in landfills and prolonging the life cycle of products according to the circular economy and global warming.

The transesterification reaction, in which an ester and an alcohol are in equilibrium with a different ester/alcohol pair, is an example of a direct exchange reaction. This reaction has long been described by Leibler et al. [2,3], preparing vitrimers starting from DGEBA and a mix of di- and tricarboxylic acids, for which the exchange reactions are thermally activated.

There are several potentially dynamic covalent functions, including acetals, borazaromatic anhydrides, borate esters, disulfides, hydrazones, imines and olefins [1,4,5]. Among the first reactions used in DCvC, the disulfide exchange reaction was one of the

foremost studied reactions. The metathesis of aromatic disulfides and the exchange capacity are known to occur at room temperature [6,7]. Rekondo et al. [8] synthesized a polyurethane elastomer using an aromatic diamine disulfide crosslinker, 4-aminophenyl disulfide (4-AFD), and showed that self-healing occurred at room temperature with a repairing efficiency of more than 95%. Zeng et al. [9] obtained a reprocessable castor oil-based polyurethane by incorporating 4-AFD and reported [10–14] that the mechanical properties were completely recovered after reprocessing. For the first time, our team produced reprocessable, repairable and recyclable epoxidized vegetable oil (EVO) thermosets by using 2,2'-dithiodibenzoic acid (DTBA) as a crosslinker. The synthesized networks showed reprocessable and repairable abilities for up to 10 cycles. However, diamine hardeners have also been used in the literature to produce epoxy thermosets starting from bio-based monomers [15–17].

Recently, Chen et al. [18] synthesized a poly (esteramide) vitrimer from castor oil via melt condensation with sebacic acid, polyamide 1010 monomer salt and 4-AFD, obtaining a reprocessable material, several times, without the erosion of network structures or of mechanical properties. Liu et al. [19] reported a catalyst-free epoxy vitrimer based on epoxidized soybean oil (ESO)/4-AFD that showed comparable mechanical properties, gel fraction and chemical structure after repeatedly cutting and compression molding it several times.

The combination of epoxy matrices has long been used, specifically EVOs with DGEBA, with the advantage of being transparent and better for the environment than 100% petroleum-based epoxy resins [20–22]. However, very few studies have been published regarding the mix of hardeners. Ding et al. [23] prepared bio-based thermosets by curing ELO with adipic acid/glutaric anhydride catalyzed by N, N'-4-dimethylaminopyridine (DMAP), with the properties being modulated depending on the ratio of the two hardeners. Williams et al. [24] synthesized vitrimers from DGEBA with citric acid (CA)/sebacic acid (SA) by adding a small amount of n-alkylamine. The authors highlighted that the presence of tertiary amines catalyzes the transesterification reaction by increasing the physical crosslinks and promoting the associations of alkyl chains.

In this regard, our team developed reversible double-crosslinking networks by curing epoxidized linseed oil (ELO) with different amounts of two diacid disulfide hardeners: DTBA/3,3'-dithiodipropionic acid (DTDA) initiated by imidazole, with the disulfide exchange mechanism being proven by high-performance liquid chromatography coupled with mass spectroscopy [25].

In this study, we obtained a series of thermosets by curing epoxidized camelina oil (ECMO) with different ratios of aromatic/aliphatic diacids $DTBA_xDTDA_y$ and in parallel with an acid/amine $DTBA_x$ 4-AFD $_y$ mixture of hardeners, to modulate the properties of the final epoxy resins (Figure 1). The aim of this work was to analyze the structure–property correlation, i.e., the effect of the chemical structure of the disulfide hardener regarding its reactivity with the ECMO, but especially the networks' recyclability. For this reason, we designed two kinds of hardener systems: (i) one full aromatic ($DTBA_x$ 4-AFD $_y$) where we compared acid vs. amine dynamic hardeners, i.e., the electron-withdrawing group vs. electron-donating one and (ii) one where the aliphatic vs. aromatic structures were analyzed regarding their impact on thermosets' properties and, again, especially their recycling. Matxain et al. [26] reported theoretical calculations for a series of aliphatic and aromatic disulfide compounds and so evaluated the electronic conditions related to the radical-mediated mechanism of self-healing. The authors showed that bond dissociation energy (BDE) values for dialkyl disulfides are around 65 kcal/mol and only 50 kcal/mol in diaryl disulfides. Moreover, they showed that phenyl rings substituted with nucleophiles such as NH_2 have reduced BDE by delocalization of the electron of the generated sulfonyl radical into the aromatic ring. Therefore, starting with these theoretical computations, we aimed here to investigate how the substitutions of the disulfide hardeners affect not only the crosslinking kinetics but also the thermosets' overall properties, especially their recycling. To the best of our knowledge, this study introduces for the first time the idea to

use antagonist structures (aromatic/aliphatic) or functionalities (acid/amine) as hardeners to produce reprocessable EVO resins. Modulating the percentages of one or the other hardener in the preparation of thermosetting will guarantee targeted properties according to the specific application required. The reactivity study of these new formulations was carried out using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). The thermo-mechanical properties of virgin and recycled materials were analyzed by thermogravimetric (TGA) and dynamic mechanical analyses (DMA). Finally, the solvent stability vs. recycling ability were evaluated to predict a potential recyclability scenario from a chemical point of view.

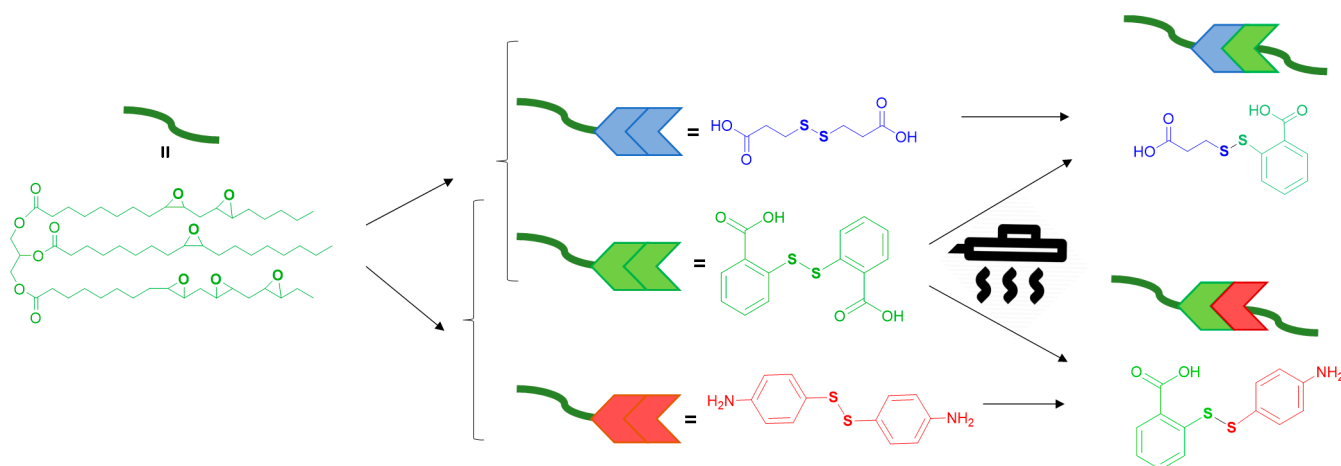


Figure 1. Schematized connectivity structures between ECMO with aliphatic–aromatic diacids or diacid–diamine crosslinkers.

2. Materials and Methods

2.1. Materials

Epoxidized camelina oil (ECMO) was purchased from Specific Polymers. The chemical structure and characteristics are reported in Table S1. The hardeners and the initiator are commercially available and were purchased from Sigma-Aldrich (Merck): 2,2'-dithiodibenzoic acid (DTBA), 95%, 4-aminophenyl disulphide (4-AFD), 98%, 3,3'-dithiodipropionic acid (DTDA), 99%, and imidazole (IM), 99%. All reagents were used without further purification.

2.2. Preparation of Crosslinked Networks

The epoxy thermosets were prepared using a stoichiometric ratio R 1:1 for epoxy/acid (e/a) and epoxy/amine functionalities, with the epoxy group considered monofunctional during the reaction with an acid [27] and bifunctional with an amine [28].

A total of five epoxy/DTBA_xDTDA_y formulations were prepared, in which the origin of dicarboxylic acid groups was: 100% DTBA (ECMO/DTBA₁₀₀), 70% DTBA–30% DTDA (ECMO/DTBA₇₀DTDA₃₀), 50% DTBA–50% DTDA (ECMO/DTBA₅₀DTDA₅₀), 30% DTBA–70% DTDA (ECMO/DTBA₃₀DTDA₇₀) and 100% DTDA (ECMO/DTDA₁₀₀). A second series of five epoxy/acid/amino formulations was also prepared: 70% DTBA–30% 4-AFD (ECMO/DTBA₇₀4-AFD₃₀), 50% DTBA–50% 4-AFD (ECMO/DTBA₅₀4-AFD₅₀), 30% DTBA–70% 4-AFD (ECMO/DTBA₃₀4-AFD₇₀) and 100% 4-AFD (ECMO/4-AFD₁₀₀).

The composition of the formulations and their acronyms are given in Table S2.

The preparation of resins based on ECMO with DTBA₁₀₀, DTDA₁₀₀ and DTBA_xDTDA_y was carried out according with a procedure described elsewhere. The ECMO formulations with the DTBA_x4AFD_y mixture were prepared by melting the aromatic diamine in the epoxy monomer and consequently added DTBA and the initiator.

For the DMA analysis, the specimens were prepared in special rectangular molds. The analyzed cured resins and recycled samples had rectangular dimensions of 30 × 7 × 2 mm³ (length × width × thickness).

2.3. Mechanical Reprocessing Procedure

For the mechanical reprocessing, a piece of crosslinked thermoset was ground, and the obtained small pieces were compressed between two Kapton films in a CARVER heating press. The applied reprocessing conditions (temperature, time and pressure) are reported in Table S5.

2.4. Chemical Recycling Procedure

The complete dissolution of the thermosets was tested in a solution of 5 wt.% of 1–4 dithiothreitol in DMF, for 24 h at 50 °C. A greener recycling of thermosets was performed by immersing the samples in 1N NaOH for 72 h at 80 °C. The tests were conducted on rectangular 10 × 10 × 2 mm³ specimens.

2.5. Methods

Differential scanning calorimetry (DSC) experiments were carried out on a Mettler-Toledo DSC 3 apparatus controlled by STAR Software developed by Mettler-Toledo. Freshly prepared mixtures of about 5–7 mg were placed into 40 µL aluminum crucibles, and the copolymerization reactions were thermally conducted by heating the crucibles at 10 °C/min in the range 25–250 °C. DSC was used also to evaluate the T_g of the cured thermosets by applying two cycles of heating–cooling (at 10 °C·min^{−1}) in the range from −60 °C to 180 °C.

The FT-IR analyses were recorded using a Thermo Scientific Nicolet iS50 FT-IR spectrometer with a deuterated L-alanine-doped triglycine sulfate (DLATGS) detector in attenuated total reflectance (ATR) mode. The absorption bands were recorded in the range of 4000–525 cm^{−1} by applying 32 scans and a resolution of 4 cm^{−1}. The data were analyzed using OMNIC software.

Thermogravimetric analysis (TGA) measurements were carried out on a Mettler-Toledo TGA 2. Samples of about 10 mg were placed into 70 µL alumina pans. The cured networks were heated at 10 °C·min^{−1} from 25 to 1000 °C under 50 mL·min^{−1} air.

Dynamic mechanical analyses (DMAs) were performed by using a Mettler-Toledo DMA 1 instrument, equipped with STAR software. The analyzed samples had rectangular dimensions of 30 × 7 × 2 mm³ (length × width × thickness) and the analyses were carried out with the tension method. Elastic moduli (E') and damping factors ($\tan \delta$) were collected at a 3 °C·min^{−1} heating rate from −50 to 150 °C and 1.0 Hz frequency. Crosslinking density was calculated by Flory's expression, as shown by Equation (1):

$$\nu = \frac{E'}{3RT} \quad (1)$$

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

Solvent resistance experiments were carried out by immersing the samples for 72 h at room temperature in ethanol, acetone, THF and 1 N NaOH solution. The tests were conducted on rectangular 10 × 10 × 2 mm³ specimens.

3. Results and Discussion

3.1. Reactivity Studies on the Function of the Dual-Dynamic Crosslinker Combination

The reactivity of ECMO/DTBA_xDTDA_y formulations was studied by dynamic DSC and the obtained results are displayed in Figure S1 and the data are listed in Table S3. We can firstly notice that the systems epoxy/DTBA₁₀₀ and epoxy/DTDA₁₀₀ show a single exothermic peak, attributed to the epoxy–acid curing reactions (Figure S1A). In the thermograms of ECMO/DTBA_xDTDA_y, we can observe that when decreasing the DTBA percentage, the T_{on} of crosslinking reactions decreases from 137 to 126 °C for ECMO/DTBA₇₀DTDA₃₀ and, thereafter, it increases again, to 141 °C for ECMO/DTDA₁₀₀. The same effect can be observed for the T_{peak} that moves from 155 °C for the ECMO/DTBA₁₀₀ curing formulation to 143 °C for the ECMO/DTBA₃₀DTDA₇₀ system and increases again

to 147 °C for ECMO/DTDA₁₀₀. A reduction in the reaction enthalpy can be observed in the presence of the aliphatic hardener. A lower ΔH was measured for ECMO/DTBA₅₀DTDA₅₀ and in the meantime a higher secondary reaction was observed. Ding et al. [23], using ELO cured with different amounts of glutaric anhydride (GA) and adipic acid (AA), observed that with the increase in AA content, the ΔH increases, with the mixture GA₆₀AA₄₀ at $\sim 286 \text{ J}\cdot\text{g}^{-1}$ and being less reactive than the system 20:80 with an enthalpy of $\sim 302 \text{ J}\cdot\text{g}^{-1}$.

All the blends with a mixture of diacid crosslinkers showed a faster α conversion compared with the blends made with individual DTBA or DTDA (Figure S1B), and ECMO/DTBA₃₀DTDA₇₀ exhibits a faster conversion, in good correlation with the highest enthalpy of the system.

When the ECMO was reacted with 4-AFD diamine crosslinker (Figure 2A), the exotherm was shifted to high temperatures with a T_{peak} at $\sim 248 \text{ }^\circ\text{C}$. When the reaction occurred in the presence of an acid/amine mixture of crosslinkers, all the thermograms were shifted to lower temperatures. By adding the 4-AFD in the DTBA blends, a subsequent reduction in reaction enthalpy was observed, from $171 \text{ J}\cdot\text{g}^{-1}$ for the ECMO/DTBA₁₀₀ system to $106 \text{ J}\cdot\text{g}^{-1}$ for the blend ECMO/DTBA₃₀ 4-AFD₇₀. This result can be correlated with the hydrogen bonds in the networks containing the mixture of hardeners. However, by blending DTBA_x4-AFD_y, the shape of the thermograms became more complex with the appearance of a second broad exothermic peak at high temperatures around 215–230 °C. The second exothermic peak increases in the presence of diamine in the blends. This peak can be attributed to the epoxy homopolymerization which takes place because of the stoichiometric imbalance produced by the hindrance and the high functionality in both hardener acids as well as amine in the mixture. It should be noted that the enthalpy of ECMO/DTBA_x4-AFD_y reactions, given in Table 1, can correspond to several processes, such as epoxy–acid, epoxy–amine and acid–amine reactions.

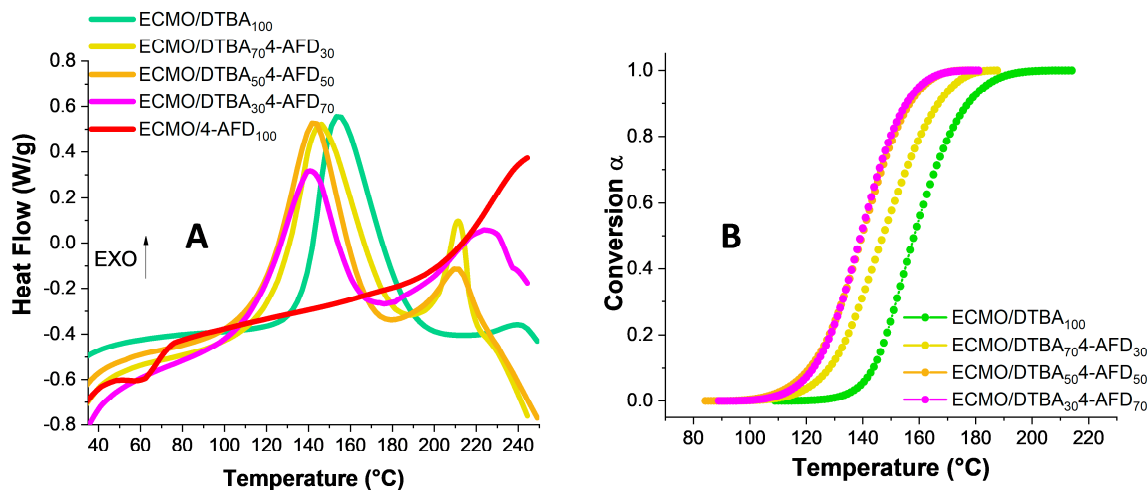


Figure 2. (A) DSC thermograms and (B) degree of conversion α for the ECMO/DTBA_x4-AFD_y hardeners.

Table 1. DSC results for the curing of ECMO/DTBA_x4-AFD_y systems.

Thermosets	$T_{\text{peak 1}}$ (°C)	Reaction Interval 1	ΔH_1 (J·g ⁻¹)	$T_{\text{peak 2}}$ (°C)	Reaction Interval 2	ΔH_2 (J·g ⁻¹)
ECMO/DTBA ₁₀₀	171	137–187	155	/	/	/
ECMO/DTBA ₇₀ 4-AFD ₃₀	145	125–175	155 ± 1	212	202–217	28 ± 1
ECMO/DTBA ₅₀ 4-AFD ₅₀	143	118–166	151 ± 1	211	197–221	14 ± 1
ECMO/DTBA ₃₀ 4-AFD ₇₀	141	115–160	106 ± 1	220	214–235	50 ± 1
ECMO/4-AFD ₁₀₀	248	155–/	/	/	/	/

Finally, the full conversion was reached faster when the diamine dynamic crosslinker was added, with comparable values for ECMO/DTBA₅₀4-AFD₅₀ and ECMO/DTBA₃₀4-AFD₇₀ systems (Figure 2B).

3.2. Structural Evolution by FT-IR Studies

The FT-IR spectral absorbances as a function of the formulations of the crosslinking ECMO/DTBA_xDTDA_y and ECMO/DTBA_x4-AFD_y mixtures are illustrated in Figure 3. Increasing the percentage of DTDA, the peak due to the C=O_{ester} is shifted from 1737 cm⁻¹ in ECMO/DTBA₁₀₀ to 1729 cm⁻¹ in ECMO/DTBA₃₀DTDA₇₀, up to the formation of a single band at 1728 cm⁻¹ in the fully DTDA blend (Figure S2).

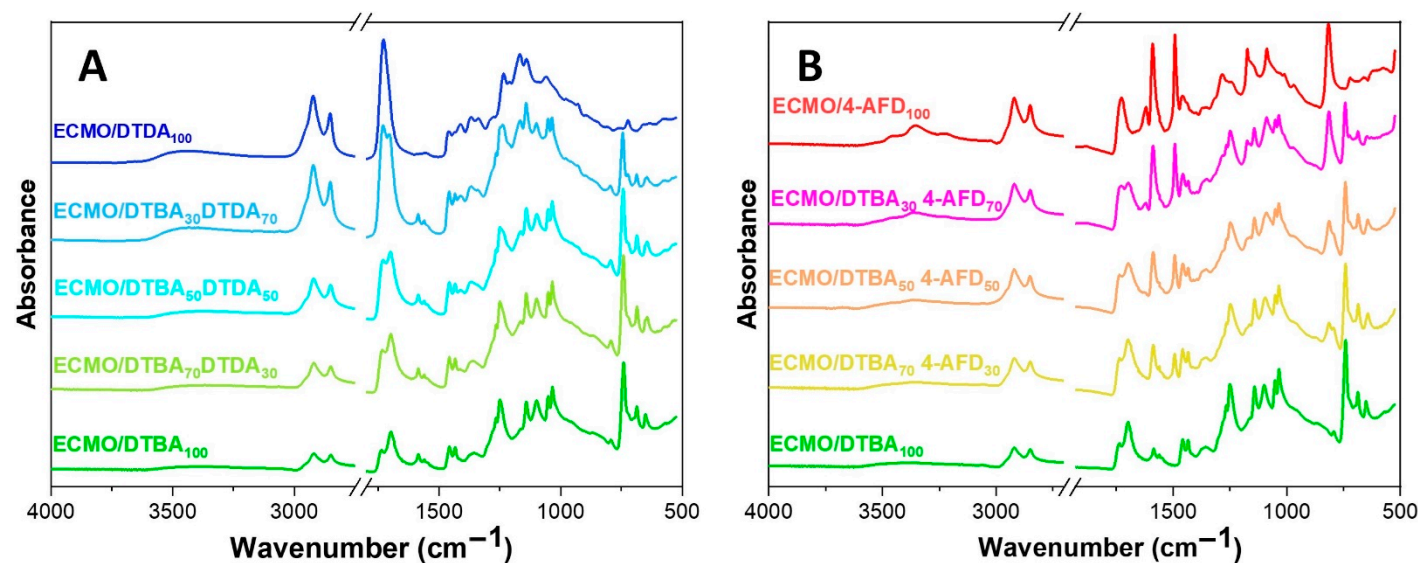


Figure 3. FT-IR spectra of the reactive groups in the uncured mixtures of ECMO/DTBA_xDTDA_y (A) and ECMO/DTBA_x4-AFD_y (B).

Similarly, Figures 3B and S3 show the characteristic bands for ECMO/DTBA_x4-AFD_y uncured mixtures. The comparison of FT-IR spectra of the uncured mixture and cured ECMO/4-AFD₁₀₀ resin is given in Figure S4; we can observe the stretching of the oxirane ring at 3030 cm⁻¹ (located from 3050 and 2990 cm⁻¹) and the disappearance of the epoxy groups (~1000 cm⁻¹) in the cured sample. The stretching of the primary amine in the uncured mixture is located at 3460 and 3364 cm⁻¹ with an additional combination band at ~3213 cm⁻¹ in the cured resin attributed to the stretching vibration of the formed amide groups. The end of the curing protocol was also confirmed by the formation of the secondary amine (in the region 3450–3300 cm⁻¹), the formation of stretching and the combination band of –N⁺–H at ~3000 cm⁻¹ and the absence of the epoxy group absorbance.

Figure 4 illustrates the FT-IR comparison of the reactive ECMO/DTBA₅₀ 4-AFD₅₀ mixture and of the final ECMO/4-AFD₅₀ and ECMO/DTBA₁₀₀ thermosets. Due to excessive overlapping of the 4-AFD signal with the epoxy peak in the region from 850 cm⁻¹ to 800 cm⁻¹, it was not possible to study its conversion over time for ECMO/DTBA_x4-AFD_y systems. However, the FT-IR spectra allowed us to follow the evolution of the most relevant reactive groups and the formation of crosslinked networks during the isothermal curing at 130 °C taking, as an example, the formulation ECMO/DTBA₅₀4-AFD₅₀.

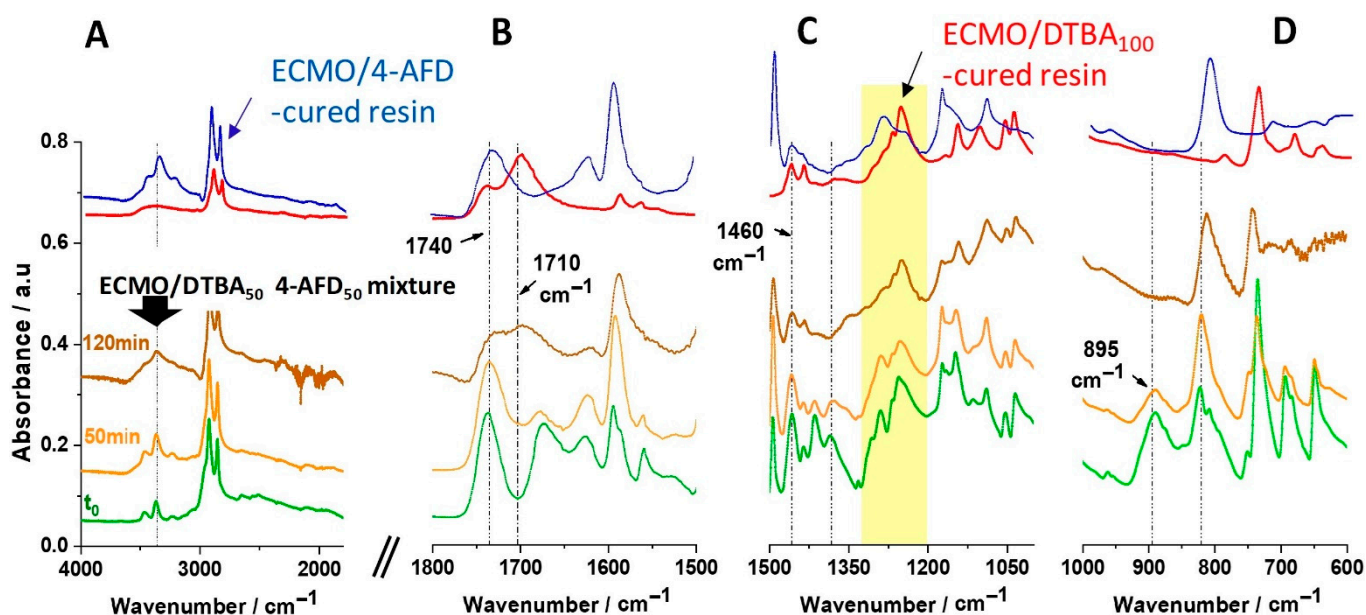


Figure 4. Evolution FT-IR spectra of the ECMO/DTBA₅₀ 4-AFD₅₀ mixture during curing at 130 °C for different curing times ($t = 0, 50, 90, 120$ min) in comparison with cured resin of ECMO/DTBA₁₀₀ and ECMO/4-AFD₁₀₀: (A) zoomed in view of the region from 4000–1800 cm⁻¹; (B) zoomed in view of the region from 1800–1500 cm⁻¹; (C) zoomed in view from 1500 to 1000 cm⁻¹ and (D) zoomed in view from 1000 to 600 cm⁻¹.

During the first hour of the reaction, the decrease in the broad peaks at 1678 cm⁻¹ and 895 cm⁻¹, assigned to free carboxylic groups, together with the simultaneous appearance of a new ester “C=O” absorption band at about ~1740 cm⁻¹ and 1710 cm⁻¹, are noticed. It indicates the occurrence of an esterification addition reaction between acid–epoxy, confirmed by the presence of the same peak in the cured ECMO/DTBA₁₀₀ resin (Figure 4).

Concerning the evolution of amine signals of 4-AFD, the quantification of primary and secondary amines in the epoxy/amine reactive system is limited because of their positions in the FT-IR spectra. The band of N-H stretching of primary amines is very close to the strong O-H as well as to the secondary amine absorption bands in the 3600–3300 cm⁻¹ region. However, regarding the FT-IR spectrum of the cured ECMO/4-AFD resin and comparing it with that of ECMO/DTBA₅₀ 4-AFD₅₀ after 2 h of curing at 130 °C, it seems that the epoxy–amine reaction also occurred. We can notice in these systems the presence of –OH stretching vibration at 3463 cm⁻¹ (Figure 4 and Figure S4) and a new peak also appearing at 3354 cm⁻¹, corresponding to –NH stretching vibration. These bands are proof of hydrogen non-covalent interactions in ECMO/DTBA_x 4-AFD_y systems.

3.3. Thermoset and Recycled Material Characterization

The combination of DTDA and 4-AFD with the DTBA allowed us to obtain hardeners that reacted with ECMO at lower temperatures compared with the individual hardeners. Therefore, these combinations permitted us to decrease the curing and post-curing temperatures. Once the curing process was optimized by the help of several DSC investigations to check the full completion of the crosslinking reaction, the thermoset samples were

characterized (their thermal and chemical stability, mechanical and dynamic mechanical properties). Table S4 displays the characteristics of the cured thermosets and the curing and post-curing protocol for the selected systems.

The presence of exchangeable S-S bonds combined with transesterification reactions gives the materials excellent reprocessing properties. The recycling conditions and characteristics of the reprocessed thermosets are displayed in Table S5. The synergy of the reversible mechanisms combined the hardeners association gave lower recyclable conditions than those of thermosets obtained with individual crosslinker.

3.3.1. Glass Transition Evaluation by DSC and DMA Analyses

The glass transitions of virgin and reprocessed thermosets were determined by DSC. The effects of the hardeners' combination and their proportions are shown in Figure 5. The ECMO/DTBA₁₀₀ thermoset presents a higher T_g (~65 °C) due to the aromatic contribution to the network's rigidity. Interestingly, the T_g of ECMO/4-AFD₁₀₀ is three times lower, ~22 °C, probably because the lower reactivity of this system produces a deficient crosslink density. Increasing the aliphatic contribution by DTDA percentage, the glass transitions values move to a lower value, reaching −3 °C for ECMO/DTDA₁₀₀, a sign of a very soft and elastic thermoset. A slow decrease in the T_g range was observed after the recycling process.

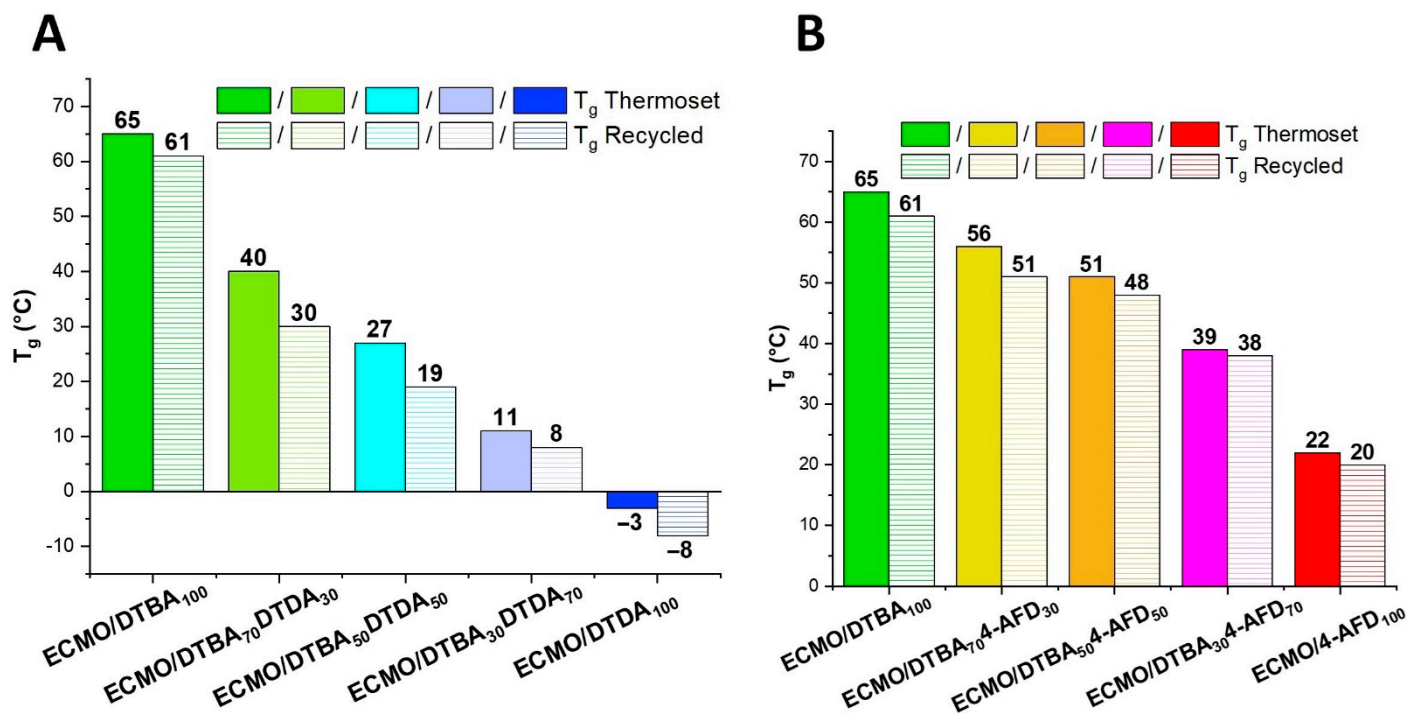


Figure 5. T_g for the virgin and recycled ECMO/DTBA_xDTDA_y (A) and ECMO/DTBA_x4-AFD_y (B) thermosets.

The dynamic mechanical properties of both ECMO/DTBA_xDTDA_y and ECMO/DTBA_x4-AFD_y virgin and reprocessed samples were studied by DMA. Figure 6 shows the variation in storage moduli (E') and $\tan \delta$ values as a function of the temperature. The corresponding data are summarized in Table 2. The loss moduli variations for the different compositions vs. temperature are displayed in Figure S5.

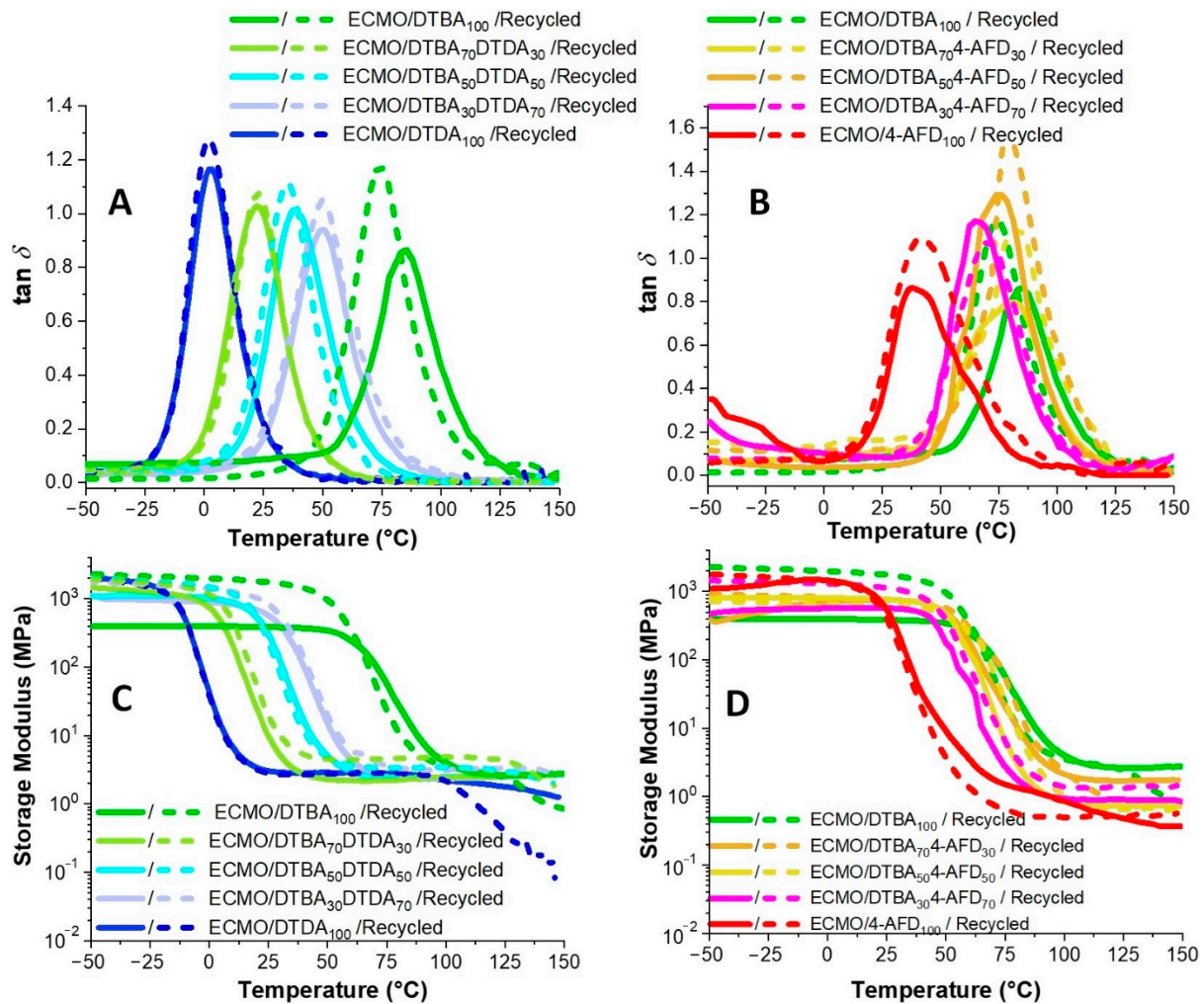


Figure 6. DMA curves of $\tan \delta$ and storage moduli vs. temperature for the virgin or recycled thermosets based on ECMO cured with: (A) and (C) $DTBA_xDTDA_y$; (B) and (D) $DTBA_x4-AFD_y$.

Table 2. Thermomechanical properties of the virgin and reprocessed resins.

Thermosets	Tan δ , Virgin/Recycled (°C)	Tan δ_{max} , Virgin/Recycled	E' glassy plateau/ Virgin/Recycled (MPa)	E' rubbery plateau/ Virgin/Recycled (MPa)	Crosslink Density, Virgin/Recycled (mmol/cm ³)
ECMO/DTBA ₁₀₀	85/75 ± 1	0.9/1.2	400/2290	2.78/0.83	0.71/0.24
ECMO/ DTBA ₇₀ DTDA ₃₀	50/50 ± 1	0.9/1.0	1000/1820	2.47/3.32	0.25/0.34
ECMO/ DTBA ₅₀ DTDA ₅₀	39/35 ± 1	1.0/1.1	1100/2030	2.60/3.10	0.27/0.38
ECMO/ DTBA ₃₀ DTDA ₇₀	22/22 ± 1	1.0/1.1	1500/1970	2.56/4.57	0.27/0.53
ECMO/DTDA ₁₀₀	3/2 ± 1	1.2/1.3	2280/2000	2.82/2.87	0.35/0.33
ECMO/DTBA ₇₀ 4-AFD ₃₀	82/83 ± 1	0.79/1.1	400/900	1.70/0.87	0.48/0.18
ECMO/DTBA ₅₀ 4-AFD ₅₀	74/81 ± 1	1.3/1.53	800/720	0.74/0.66	0.35/0.28
ECMO/DTBA ₃₀ 4-AFD ₇₀	65/70 ± 1	1.2/1.07	400/1460	0.91/1.35	0.23/0.25
ECMO/4-AFD ₁₀₀	36/41 ± 1	0.86/1.1	1110/1780	0.53/0.51	0.21/0.17

The maximum value of the $\tan \delta$ peak was taken as the α -transition temperature. As already observed in the DSC results, the $\tan \delta$ increases gradually with the DTBA content in the hardener mixtures due to the improved stiffness of the network structure: from 3 °C for ECMO/DTDA₁₀₀ to 85 °C for ECMO/DTBA₁₀₀, while the thermoset made with 4-AFD has a value of ~52 °C for ECMO/4-AFD₁₀₀.

Liu et al. [19] reported, for ESO/4-AFD thermosets, a damping factor from 26 to 34 °C as a function of the applied curing protocol, while the crosslink density varies from 0.095 to 0.190 mmol·cm⁻³.

The reprocessed ECMO/DTBA₅₀DTDA₅₀ thermosets exhibit a smaller decrease in $\tan \delta$ than that of recycled ECMO/DTBA₁₀₀; in contrast, an increase in the damping factor was observed for DTBA_x4-AFD_y.

Figure 6C,D show the variation in the storage moduli with the temperature for the systems with acid-type hardeners, DTBA_xDTDA_y (Figure 6C) or combined acid/amine ones, DTBA_x4-AFD_y (Figure 6D). In Figure 6C, there are four domains: the glassy region, the transition region, the rubbery plateau and the terminal or viscoelastic region. Therefore, reaching $T \gg T_g$, it is possible to observe the passage from the amorphous solid rubbery state to the viscous liquid state in some recycled ECMO/DTBA_xDTDA_y thermosets (Figure 6C), associated with an increased chain mobility. Especially in the recycled ECMO/DTDA₁₀₀ and ECMO/DTBA₁₀₀ thermosets, we can notice the presence of liquid–liquid transitions, with T_{ll} reported as being correlated with a disintegration, a “quasi-melting”, on heating, of long-lived and stable segments—segments associated with neighboring segments in amorphous polymers, depending on the thermal history and the formation of stable associations of the segments during material cooling [29]. The T_{ll} transition corresponds therefore to a short-range order–disorder transition, i.e., a loss of intramolecular ordering. We can hypothesize that in the ECMO/DTBA_xDTDA_y recycled systems, the dual-dynamic mechanism of transesterification and S-S cleavage activated by the heating at $T \gg T_g$ favors the occurrence of this T_{ll} transition. Moreover, this loss of order appears to be exacerbated in the recycled ECMO/DTDA₁₀₀ aliphatic thermoset, while for the recycled ECMO/DTBA₁₀₀ aliphatic–aromatic thermoset, the E' drop at this transition is lower. This behavior can be correlated with the fact that the aromatic disulfides metathesis is more efficient in terms of exchange of the disulfide bonds. In contrast, this T_{ll} transition is not present in the recycled ECMO/DTBA_x4-AFD_y thermosets (Figure 6D). We can attribute this result to the structural contribution of non-covalent interactions, such as the hydrogen bonds (highlighted by FT-IR spectra from Figure 4 and Figure S4) and π – π stacking (both DTBA and 4-AFD are aromatics), that keep the disulfide bonds closer and allow the constant reconstruction and rearrangement of the network during the heating. In these systems, the non-covalent interactions seem to favor the conformationally regular intramolecular regions.

From the E' plots (Figure 6C,D), it can be observed that the virgin or recycled DTBA_xDTDA_y and DTBA_x4-AFD_y thermosets show higher storage moduli in the glassy state than that of the virgin ECMO/DTBA₁₀₀ and that the recycled thermosets have higher E' values in the glassy region. As can be seen, the epoxy resins cured by DTBA_xDTDA_y show higher storage moduli in the glassy region or in the rubbery plateau, compared with the resins cured by DTBA_x4-AFD_y. Moreover, in these latter systems, the recycled samples show increased values of $\tan \delta$.

3.3.2. Materials' Thermal Stabilities

Thermogravimetric analyses of ECMO/DTBA_xDTDA_y thermosets show a 5% weight loss ($T_{5\%}$) range from 245 °C for ECMO/DTDA₁₀₀ to 270 °C for ECMO/DTBA₁₀₀ (Figure 7, and Table 3). The reduced thermal stability of thermosets with a higher ratio of aliphatic crosslinkers can be attributed to the ease of breaking the aliphatic chains with respect to aromatic DTBA and could also be associated with the lower crosslinking density of the network based on DTDA crosslinkers, as shown in Table 2. No significant thermal stability

reduction was observed after the recycling protocol, the $T_{5\%}$ decreasing with $\sim 5\text{--}10\text{ }^{\circ}\text{C}$, excepting the recycled ECMO/DTDA100 resin, with a higher decrease of $T_{5\%}$ with $\sim 20\text{ }^{\circ}\text{C}$.

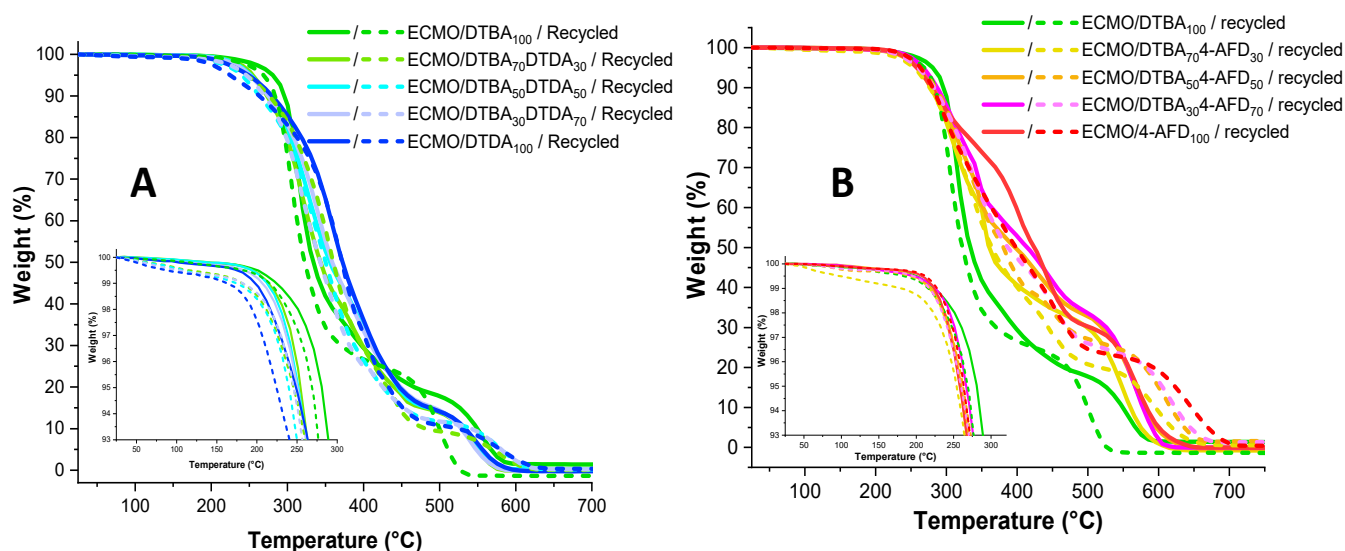


Figure 7. TGA and zoomed-in view of the $T_{5\%}$ area (from $25\text{--}300\text{ }^{\circ}\text{C}$) for the virgin and recycled ECMO thermosets: DTBA and DTDA combination (A) and DTBA and 4-AFD and mixtures (B).

Table 3. $T_{5\%}$ for virgin and recycled thermosets.

Thermosets	$T_{5\%}$ Virgin/Recycled ($^{\circ}\text{C}$)	Thermosets	$T_{5\%}$ Virgin/Recycled ($^{\circ}\text{C}$)
ECMO/DTBA ₁₀₀	270/265 \pm 1	ECMO/DTBA ₇₀ 4-AFD ₃₀	260/255 \pm 1
ECMO/DTBA ₇₀ DTDA ₃₀	255/245 \pm 1	ECMO/DTBA ₅₀ 4-AFD ₅₀	260/260 \pm 1
ECMO/DTBA ₅₀ DTDA ₅₀	250/240 \pm 1	ECMO/DTBA ₃₀ 4-AFD ₇₀	265/260 \pm 1
ECMO/DTBA ₃₀ DTDA ₇₀	250/245 \pm 1	ECMO/4-AFD ₁₀₀	260/260 \pm 1
ECMO/DTDA ₁₀₀	245/225 \pm 1		

The ECMO/DTBA_x4-AFD_y thermosets exhibit closer values of $T_{5\%}$ (Figure 7), centered at $260\text{ }^{\circ}\text{C}$, whatever the ratio of the hardeners, showing a strong influence of the diamine crosslinker as obtained for other thermoset resins made with 4-AFD [30,31]. Comparable results were reported by Liu et al. [19] for epoxidized soybean oil cured with 4-AFD; the authors observed excellent thermal stability with an onset decomposition temperature of around $270\text{ }^{\circ}\text{C}$. Zhou et al. [30] for a vitrimer based on bis (4-glycidylphenoxy) disulfide cured with 4-AFD obtained 5% weight loss at $275\text{ }^{\circ}\text{C}$.

Two well-separated decomposition processes can be observed in the TGA and DTG curves (Figure S6) for the thermosets obtained with DTBA_xDTDA_y. The first degradation stage involves pyrolysis with the breakdown of the ester–methylene linkages and of hydroxyls, and the second involves the thermo-oxidative degradation of the products formed in the first step. Concerning the DTBA_x4-AFD_y thermosets, complex DTG thermograms with three-step degradations can be observed in Figure 7. Similar results were found and reported by Liu et al. [19], who attributed the first stage to the thermal decomposition of disulfide bonds, the second to the ESO moieties and the last to the thermo-oxidation of the benzene rings and $\pi\text{--}\pi$ conjugations.

3.4. Solvent Resistance and Chemical Recyclability

The epoxy resins based on disulfide bonds can be recycled in DMF solution of dithiothreitol [14,28,30]. Figure 8A and Figure S8A present the full degradation and chemical recycling ability after 24 h at $50\text{ }^{\circ}\text{C}$ of the thermosets based on ECMO/DTBA_xDTDA_y and ECMO/DTBA_x 4-AFD_y.

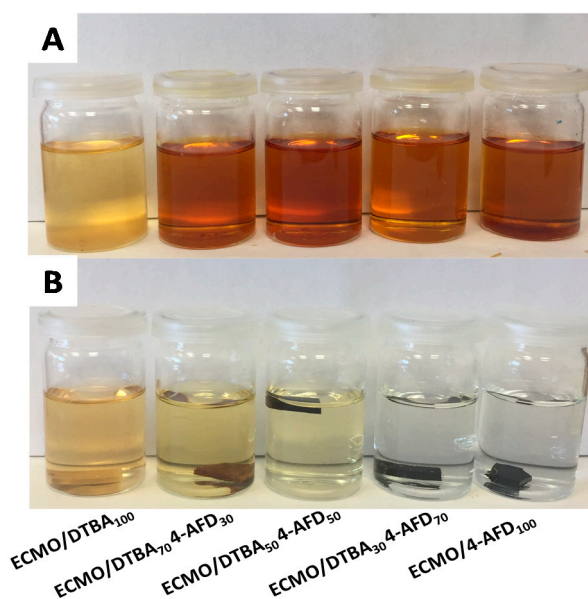


Figure 8. (A) Chemical recycling in DMF solution of dithiothreitol for ECMO/DTBA_x 4-AFD_x after 24 h at 50 °C and (B) solvent resistance in 1N NaOH solution after 3 days at room temperature.

The solvent resistance of the thermosetting resins was tested in ethanol, acetone, THF and 1N NaOH for 72 h at room temperature. Figure S8 displays the good resistance of the ECMO/DTBA_x 4-AFD_y thermosets in ethanol and acetone. However, the solvent resistances of ECMO/DTBA_xDTDA_y resins in 1 N NaOH (Figure S7B) show differences, exhibiting higher solubility than those based on DTBA_x4-AFD_y (Figure 8B) and with an increased ratio of the diamine crosslinker, the thermosets became completely insoluble. Odriozola et al. [32] showed comparable results in 1 N NaOH solution for fiber-reinforced polymer composites based on DGEBA/4-AFD epoxy resin. The same team reported that epoxy composites were insoluble in different chemicals, such as THF, toluene, acetone, ethanol and 1 N HCl. As for ELO/DTBA₁₀₀ thermosets, all the ECMO/DTBA_xDTDA_y resins show full and sustainable recyclability after 3 days at 80 °C (Figure S7B).

Finally, in contrast with the degradation behavior of the reprocessable resins based on ELO and ESO with DTBA, Figure S9 displays the progressive resistance of ECMO/DTBA_x4-AFD_y resins in THF. As vitrimers, these thermosets swell without degradation in “a good solvent” [3,32–34].

4. Conclusions

This study reveals the proof of concept of mixing hardeners with opposite properties, aliphatic–aromatic and acid–amine, and the use of these combinations to cure epoxidized camelina oil, a bio-based epoxy monomer with 5.24 meq/g. All the molecules used as hardeners contain dynamic disulfide bonds, to engender reprocessability and recyclability in the thermosets. Moreover, the mixture of crosslinkers causes a reduction in the temperatures of the reaction, as shown in the DSC thermograms, so there are less drastic conditions for curing and reprocessing, compared with the systems with an individual crosslinker. The addition of DTBA, as an aromatic diacid, in ECMO/DTDA and ECMO/4-AFD matrices, produces an increase in the glass transition, the thermal stability and the crosslink density.

On the one hand, the thermosets exhibited strong solvent resistance while, on the other hand, thanks to the nature of the disulfide bonds in the network structure, full chemical recycling was obtained.

We can use these outcomes to create a series of thermosetting materials by modulating the ratios between the hardeners to obtain a variety of properties, ensuring, at the same time, recycling ability.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/polym13152503/s1>. Figure S1. DSC thermograms for the ELO bio-epoxy monomers combined with the diacid aromatic/aliphatic hardeners (a) and the dynamic diacid–diamine aromatic crosslinkers (b) in R 1:1 and 1 wt% of IM; Figure S2. DSC thermograms and degree of conversion α (B) for the ECMO bio-epoxy monomers combined with the diacid aromatic/aliphatic hardeners in R 1:1 and 1 wt% of IM; Figure S3. FT-IR zoomed-in view of the ECMO/DTBA_xDTDA_y blends in the region from 1800 to 1150 cm⁻¹; Figure S4. Evolution of FT-IR spectra of the cured ECMO/DTBA_x4-AFD_y blends: (A) zoomed-in view of the region of 4000–2600 cm⁻¹ and (B) 1850–1550 cm⁻¹; Figure S5. FT-IR evolution of the reactive groups of the ELO/4-AFD₁₀₀ in presence of 1 wt.% IM mixture and after the curing protocol; Figure S6. Loss modulus vs. temperature for the virgin and recycled (A) ECMO/DTBA_xDTDA_y and (B) ECMO/DTBA_x4-AFD_y thermosetting resins; Figure S7. DTG for the neat ECMO/DTBA_xDTDA_y and combination of the diacid crosslinkers (A) and neat ECMO/DTBA_x4-AFD_y and mixture of diacid/diamine (B); Figure S8. (A) Chemical recycling in DMF solution of dithiothreitol for ECMO/DTBA_xDTDA_x after 24 h at 50 °C and (B) solvent resistance in 1N NaOH solution after 3 days at room temperature; Figure S9. Solvent resistance tests in (A) ethanol and (B) acetone after 72 h at room temperature for the ECMO/DTBA_x4-AFD_y resins; Figure S10. Solvent test in THF for ECMO/DTBA_x4-AFD_y resins after 72 h at room temperature; Table S1. Structures and characteristics of the selected reagents; Table S2. Material designation and composition of ECMO/DTBA_xDTDA_y–DTBA_x4-AFD_y blends; Table S3. DSC results for the ELO/DTBA_xDTDA_y and ELO/DTBA_x4-AFD_y systems; Table S4. DSC results for the ECMO/DTBA_xDTDA_y systems; Table S5. Curing and post-curing protocol for the ECMO/DTBA_xDTDA_y and ECMO/DTBA_x4-AFD_y blends; Table S6. Recycling conditions and aspects of the reprocessed ECMO/DTBA_xDTDA_y and ECMO/DTBA_x4-AFD_y blends.

Author Contributions: Conceptualization, A.G. and A.M.; data curation, C.D.M.; investigation, C.D.M.; validation, A.G. and A.M.; writing—original draft preparation, C.D.M. and A.M.; writing—review and editing, C.D.M. A.G. and A.M.; project administration, A.G. and A.M.; supervision, A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the ECOXY project funded by the Bio Based Industries Joint Undertaking under the European Union Horizon 2020 research and innovation program (grant agreement n° 744311).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

EVO: Epoxidized vegetable oil; ECMO: Epoxidized camelina oil, DCA: Dicarboxylic acids; DTBA: 2,2'-dithiodibenzoic acid; DTDA: 3,3'-dithiodipropionic acid; 4-AFD: 4-aminophenyl disulfide; IM: Imidazole; FT-IR: Fourier transform infrared spectroscopy; DSC: Differential scanning calorimetry; DMA: Dynamic mechanical analysis; TGA: Thermogravimetric analysis; DTG: Derivative thermogravimetry; vs.: Versus.

References

1. Jin, Y.; Yu, C.; Denman, R.J.; Zhang, W. Recent advances in dynamic covalent chemistry. *Chem. Soc. Rev.* **2013**, *42*, 6634–6654. [[CrossRef](#)] [[PubMed](#)]
2. Capelot, M.; Unterlass, M.M.; Tournilhac, F.; Leibler, L. Catalytic Control of the Vitremer Glass Transition. *ACS Macro Lett.* **2012**, *1*, 789–792. [[CrossRef](#)]
3. Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **2011**, *334*, 965. [[CrossRef](#)] [[PubMed](#)]
4. Lehn, J.-M. Dynamic Combinatorial Chemistry and Virtual Combinatorial Libraries. *Chem. Eur. J.* **1999**, *5*, 2455–2463. [[CrossRef](#)]
5. Rowan, S.J.; Cantrill, S.J.; Cousins, G.R.L.; Sanders, J.K.M.; Stoddart, J.F. Dynamic Covalent Chemistry. *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952. [[CrossRef](#)]
6. Elenguer, A.M.; Friščić, T.; Day, G.M.; Sanders, J.K.M. Solid-state dynamic combinatorial chemistry: Reversibility and thermodynamic product selection in covalent mechanosynthesis. *Chem. Sci.* **2011**, *2*, 696–700. [[CrossRef](#)]
7. Lei, Z.Q.; Xiang, H.P.; Yuan, Y.J.; Rong, M.Z.; Zhang, M.Q. Room-Temperature Self-Healable and Remoldable Cross-linked Polymer Based on the Dynamic Exchange of Disulfide Bonds. *Chem. Mater.* **2014**, *26*, 2038–2046. [[CrossRef](#)]

8. Rekondo, A.; Martin, R.; Ruiz de Luzuriaga, A.; Cabañero, G.; Grande, H.J.; Odriozola, I. Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. *Mater. Horiz.* **2014**, *1*, 237–240. [[CrossRef](#)]
9. Chen, J.-H.; Hu, D.-D.; Li, Y.-D.; Meng, F.; Zhu, J.; Zeng, J.-B. Castor oil derived poly(urethane urea) networks with reprocessability and enhanced mechanical properties. *Polymer* **2018**, *143*, 79–86. [[CrossRef](#)]
10. Di Mauro, C.; Tran, T.-N.; Graillot, A.; Mija, A. Enhancing the Recyclability of a Vegetable Oil-Based Epoxy Thermoset through Initiator Influence. *ACS Sustain. Chem. Eng.* **2020**, *8*, 7690–7700. [[CrossRef](#)]
11. Tran, T.-N.; Di Mauro, C.; Graillot, A.; Mija, A. Chemical Reactivity and the Influence of Initiators on the Epoxidized Vegetable Oil/Dicarboxylic Acid System. *Macromolecules* **2020**, *53*, 2526–2538. [[CrossRef](#)]
12. Di Mauro, C.; Genua, A.; Mija, A. Building thermally and chemically reversible covalent bonds in vegetable oils based epoxy thermosets. Influence of epoxy-hardener ratio to promote recyclability. *Mater. Adv.* **2020**, *1*, 1788–1798. [[CrossRef](#)]
13. Tran, T.-N.; Di Mauro, C.; Graillot, A.; Mija, A. Monitoring the structure–reactivity relationship in epoxidized perilla and safflower oil thermosetting resins. *Polym. Chem.* **2020**, *11*, 5088–5097. [[CrossRef](#)]
14. Di Mauro, C.; Malburet, S.; Genua, A.; Graillot, A.; Mija, A. Sustainable series of new epoxidized vegetable oils-based thermosets with chemical recycling properties. *Biomacromolecules* **2020**, *21*, 3923–3935. [[CrossRef](#)] [[PubMed](#)]
15. Fache, M.; Montéremal, C.; Boutevin, B.; Caillol, S. Amine hardeners and epoxy cross-linker from aromatic renewable resources. *Eur. Polym. J.* **2015**, *73*, 344–362. [[CrossRef](#)]
16. Frias, C.F.; Serra, A.C.; Ramalho, A.; Coelho, J.F.J.; Fonseca, A.C. Preparation of fully biobased epoxy resins from soybean oil based amine hardeners. *Ind. Crops Prod.* **2017**, *109*, 434–444. [[CrossRef](#)]
17. Stemmelen, M.; Lapinte, V.; Habas, J.-P.; Robin, J.-J. Plant oil-based epoxy resins from fatty diamines and epoxidized vegetable oil. *Eur. Polym. J.* **2015**, *68*, 536–545. [[CrossRef](#)]
18. Chen, J.-H.; Yuan, W.-Q.; Li, Y.-D.; Weng, Y.-X.; Zeng, J.-B. Malleable and Sustainable Poly(ester amide) Networks Synthesized via Melt Condensation Polymerization. *ACS Sustain. Chem. Eng.* **2019**, *7*, 15147–15153. [[CrossRef](#)]
19. Liu, Y.-Y.; He, J.; Li, Y.-D.; Zhao, X.-L.; Zeng, J.-B. Biobased, reprocessable and weldable epoxy vitrimers from epoxidized soybean oil. *Ind. Crops Prod.* **2020**, *153*, 112576. [[CrossRef](#)]
20. Kumar, S.; Samal, S.K.; Mohanty, S.; Nayak, S.K. Study of curing kinetics of anhydride cured petroleum-based (DGEBA) epoxy resin and renewable resource based epoxidized soybean oil (ESO) systems catalyzed by 2-methylimidazole. *Thermochim. Acta* **2017**, *654*, 112–120. [[CrossRef](#)]
21. Karger-Kocsis, J.; Grishchuk, S.; Sorochynska, L.; Rong, M.Z. Curing, gelling, thermomechanical, and thermal decomposition behaviors of anhydride-cured epoxy (DGEBA)/epoxidized soybean oil compositions. *Polym. Eng. Sci.* **2014**, *54*, 747–755. [[CrossRef](#)]
22. Altuna, F.I.; Espósito, L.H.; Ruseckaite, R.A.; Stefani, P.M. Thermal and mechanical properties of anhydride-cured epoxy resins with different contents of biobased epoxidized soybean oil. *J. Appl. Polym. Sci.* **2011**, *120*, 789–798. [[CrossRef](#)]
23. Ding, C.; Tian, G.; Matharu, A. Adipic acid—Glutaric anhydride—Epoxidized linseed oil biobased thermosets with tunable properties. *Mater. Today Commun.* **2016**, *7*, 51–58. [[CrossRef](#)]
24. Altuna, F.I.; Casado, U.; dell’Erba, I.E.; Luna, L.; Hoppe, C.E.; Williams, R.J.J. Epoxy vitrimers incorporating physical crosslinks produced by self-association of alkyl chains. *Polym. Chem.* **2020**, *11*, 1337–1347. [[CrossRef](#)]
25. Tran, T.-N.; Di Mauro, C.; Malburet, S.; Graillot, A.; Mija, A. Dual Cross-linking of Epoxidized Linseed Oil with Combined Aliphatic/Aromatic Diacids Containing Dynamic S–S Bonds Generating Recyclable Thermosets. *ACS Appl. Bio Mater.* **2020**, *3*, 7550–7561. [[CrossRef](#)]
26. Matxain, J.M.; Asua, J.M.; Ruipérez, F. Design of new disulfide-based organic compounds for the improvement of self-healing materials. *Phys. Chem. Chem. Phys.* **2016**, *18*, 1758–1770. [[CrossRef](#)]
27. Matějka, L.; Pokorný, S.; Dušek, K. Acid curing of epoxy resins. A comparison between the polymerization of diepoxide-diacid and monoepoxide-cyclic anhydride systems. *Makromol. Chem. Macromol. Chem. Phys.* **1985**, *186*, 2025–2036. [[CrossRef](#)]
28. Kaufman, H.S. Handbook of epoxy resins. Henry Lee and Kris Neville. *J. Appl. Polym. Sci.* **1970**, *14*, 253. [[CrossRef](#)]
29. Bershtein, V.A.; Egorov, V.M.; Egorova, L.M.; Ryzhov, V.A. The role of thermal analysis in revealing the common molecular nature of transitions in polymers. *Thermochim. Acta* **1994**, *238*, 41–73. [[CrossRef](#)]
30. Zhou, F.; Guo, Z.; Wang, W.; Lei, X.; Zhang, B.; Zhang, H.; Zhang, Q. Preparation of self-healing, recyclable epoxy resins and low-electrical resistance composites based on double-disulfide bond exchange. *Compos. Sci. Technol.* **2018**, *167*, 79–85. [[CrossRef](#)]
31. Ma, Z.; Wang, Y.; Zhu, J.; Yu, J.; Hu, Z. Bio-based epoxy vitrimers: Reprocessability, controllable shape memory, and degradability. *J. Polym. Sci. Part A Polym. Chem.* **2017**, *55*, 1790–1799. [[CrossRef](#)]
32. Ruiz de Luzuriaga, A.; Martin, R.; Markaide, N.; Rekondo, A.; Cabañero, G.; Rodríguez, J.; Odriozola, I. Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. *Mater. Horiz.* **2016**, *3*, 241–247. [[CrossRef](#)]
33. Imbernon, L.; Oikonomou, E.K.; Norvez, S.; Leibler, L. Chemically crosslinked yet reprocessable epoxidized natural rubber via thermo-activated disulfide rearrangements. *Polym. Chem.* **2015**, *6*, 4271–4278. [[CrossRef](#)]
34. Zhou, L.; Chen, M.; Zhao, X. Rapid degradation of disulfide-based thermosets through thiol-disulfide exchange reaction. *Polymer* **2017**, *120*, 1–8. [[CrossRef](#)]