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EPOXY VITRIMERS BASED ON DGEBA AND EPOXIDIZED PLANT OIL AS CANDIDATES FOR COMPOSITE MATRIX APPLICATIONS

The growing demands related to sustainable development and the need to reduce the environmental impact of the materials industry are leading to a search for alternatives to classic thermosetting resins. Vitrimers – polymers containing covalent adaptive networks, combine the good mechanical properties and thermal stability of cross-linked materials with the possibility of recycling and reprocessing.

This study presents epoxy compositions obtained from epoxidized vegetable oil, an acid and anhydride hardener, as well as a transesterification catalyst. The mechanical properties, thermal stability and recyclability of the vitrimers were evaluated, indicating their potential for use in composite materials in line with the rules of the circular economy.

Keywords: epoxy vitrimers, composite matrix, recycling

INTRODUCTION

The matrix in composite materials has a key structural and protective role. It is responsible for maintaining the layered structure of the composite, the shape of the element and the mutual arrangement of the reinforcing fibers [1–4]. It separates the stresses acting within the material volume, provides uniform load transfer to the fibers and, in the event of damage to some of them, takes over and transfers the stresses to the undamaged fibers, maintaining the integrity of the structure [1,3,4]. Epoxy resins are among the key thermosetting matrixes used in aviation, automotive and construction industries due to their high mechanical strength, chemical resistance and thermal stability [1,3]. The disadvantages of conventional epoxy thermosets are their severely restricted recyclability. The formation of a permanent covalent network during the curing process significantly hinders the efficient recovery of the material by mechanical or thermomechanical methods. This hindrance contradicts the fundamental principles of the circular economy [5,6]. The solution to this problem came in the form of vitrimers – materials based on covalent adaptive networks (CANs) that allow bond exchange without losing network integrity, thus enabling repair and recycling [7–9].

A widely studied family of epoxy vitrimers is obtained using carboxylic acids and anhydrides as hardeners in the presence of transesterification catalysts [10–14]. The use of zinc salt as a catalyst not only reduces the temperature and time of curing, but also promotes the dynamic exchange of ester bonds in the cross-linked structure, allowing self-repair and reprocessing [10–13,15–17]. In recent years, the importance of renewable raw materials in resin synthesis has also grown [18,19]. Epoxidized vegetable oils, such as epoxidized soybean oil, have been shown to reduce the formulation of viscosity and facilitate composite processing. They remain compatible with the dynamically cross-linked epoxy network, thereby ensuring the recyclability of vitrimers [20–22].

This paper presents a composition based on an epoxy resin, epoxidized vegetable oil and an acid-anhydride mixture in the presence of a zinc catalyst. Its mechanical properties, thermal stability and recyclability were evaluated, indicating that the developed resin systems are promising candidates for matrix materials in fiber-reinforced composites that comply with the principles of sustainable development.

MATERIALS AND METHODS

Materials

Diglycidyl ether bisphenol A (DGEBA, LEP=0.530, Epidian®6, Sarzyna Chemical, 99 %), succinic anhydride (SAN, Thermo Scientific, 99 %), succinic acid (SuA, Chempur®, 99.5 %), epoxidized soybean oil (ESO, LEP=0.405, Ergoplast® ES, Boryszew S.A.), zinc acetylacetonate ($Zn(AcAc)_2$, Sigma-Aldrich, 99.9 %), and propylene glycol (PG, Chempur®, chemically pure) were used to prepare the epoxy compositions and conduct a chemical recycling process..

Vitrimer preparation

Liquid epoxy resin with the addition of 20-50 wt% epoxidized soybean oil (relative to the total epoxy mixture) was introduced into a reactor equipped with a mechanical stirrer. Next, a zinc catalyst was added in an amount of up to 10 mol% relative to the total number of moles of hardener (succinic acid + succinic anhydride). The mixture was heated to 130°C with constant stirring, and after reaching the set temperature, stirring was continued until a homogeneous dispersion of the catalyst was obtained. At the temperature of 130°C, a mixture of hardeners was introduced. A molar ratio of anhydride acyl groups to epoxy groups in the epoxy mixture of 1:1 and a molar ratio of acid carboxyl groups to epoxy groups 1:1 was used (Table 1). After adding the hardeners, the mixture was stirred until a homogeneous composition without visible agglomerates was obtained. The resulting composition was poured into a prepared Teflon (PTFE) mold and then thermally cured at 150°C for 3 hours.

Table 1. Content of epoxidized soybean oil in composition.

SAMPLE	**Epoxy / Alkyl group ratio**	**CAN Catalyst**	**ESO content**
V/1	1:1	10 mol% vs. curing agent	50 wt%
V/2			35 wt%
V/3			20 wt%

Methods

Hardness

Hardness measurements were performed in accordance with the PN-EN ISO 868 [23] standard by means of a Shore TI-D Durometer Test Stand (*Sauter Controls, Germany*). The tests were conducted at ambient temperature. For each material series, the hardness was calculated as the average of five repetitions.

Impact strength

Impact strength tests were carried out according to the PN-EN ISO 180:2004 [24] standard using the Izod method without a notch, employing a HIT5.5P impact tester (*Zwick Roell, Germany*). Measurements were performed at ambient temperature on specimens measuring 80 × 10 × 4 mm. In accordance with the standard, the pendulum was adapted to the amount of energy absorbed. Therefore, for V/1 test, a pendulum with an energy of 5.5 J was utilized, and for V/2 and V/3 tests, an energy of 2.75 J was applied. The impact strength values were calculated as the average of five specimens for each type of material.

Tensile strength

The mechanical properties of the epoxy vitrimers, including the tensile strength and elongation at break were evaluated employing a tensile tester (*Instron 4466; Instron; Norwood, MA, USA*) with Bluehill2 software, equipped with an extensometer according to PN-EN ISO 527-2:2012 [25]. The tensile tests were conducted on cured resin samples measuring 75 × 5 × 3 mm, at a crosshead speed of 100 mm/min at ambient temperature. The final values were calculated as the average of six measurements. The sample thickness was measured at five points in accordance with ISO 16012:2015 [26], using a digital micrometer (*Mitutoyo Absolute Tester, Tokyo Sangyo Co. Ltd., Japan*) with a resolution of 0.001 mm.

Thermal analysis

The thermal properties of the epoxy vitrimers were investigated by means of thermoanalytical techniques, including thermogravimetry (TG) and differential scanning calorimetry (DSC). The TGA analysis was conducted with a thermobalance (*TGA 2; Mettler Toledo; Columbus, OH, USA*). Approximately 10 mg of the cured resin samples were placed in a 70 µL open platinum crucible and heated from 30°C to 800°C at a heating rate of 20°C/min. The measurements were performed under a dynamic atmosphere of either nitrogen (inert) or air (oxidizing) with a flow rate of 100 mL/min. From the TG curves, the degradation onset temperature (T_{onset}) and the peak degradation temperature (T_{peak}) were calculated. These parameters served as indicators of vitrimer thermal stability. The thermograms were analyzed employing STARe thermal analysis software. The glass transition temperature (T_g) of the cured resins was determined using a differential scanning calorimeter (*DSC 822e; Mettler Toledo; Columbus, OH, USA*). Approximately 10 mg of each sample was placed in a 40 µL aluminum crucible, which was then sealed with a perforated lid (1.0 mm). The crucible was heated twice in a dynamic nitrogen atmosphere (50 mL/min) from -20°C to 190°C at a heating rate of 10°C/min. The T_g values were determined from the second heating run.

Recycling

The hardened vitrimer material was subjected to chemical recycling. A 25 g sample was placed in a 250 mL flask, after which a solvent (e.g. propylene glycol) was added in a 4:1 weight ratio to the material. The mixture was heated to 180°C for 15 minutes with constant stirring. After the dissolution process was complete, the solvent was removed by a rotary vacuum evaporator (*Hei-VAP Value; Heidolph Instruments; Schwabach, Germany*).

RESULTS AND DISCUSSION

Mechanical properties

The hardness of the vitrimers was highly dependent on the amount of epoxidized soybean oil in the composition. ESO in the described tests acts as a plasticizer; consequently, the hardest sample was the one containing 20 wt% ESO (V/3), the hardness of which was 79.7. In contrast, increasing the oil content to 50 wt% (V/1) resulted in a decrease in hardness of over 30% (Table 2).

Table 2. Mechanical properties of epoxy vitrimers

Sample	**Hardness** [Shore D]	**Impact strength** [kJ/m²]
V/1	55.5	96.73P(N)
V/2	69.0	23.21C*
V/3	79.7	10.45C*

Symbols P(N) and C* denote, respectively, partial (non-hinge) and complete breaks according to PN-EN ISO 180.

The addition of ESO also influenced the impact strength of the investigated epoxy vitrimers (Table 2). The lowest value, 10.45 kJ/m^2, was determined for the vitrimer containing 20 wt% ESO (V/3); this sample broke completely. With increasing ESO content, the impact strength of the epoxy vitrimer grew, a trend attributable to the lower network density, which provides greater mobility of the epoxy network, thus enabling the material to absorb more impact energy instead of undergoing brittle fracture. Confirming this, the impact strength for the vitrimer containing 50 wt% ESO (V/1) was 96.73 kJ/m^2 and the sample only partially fractured.

By comparing the obtained values of strength properties, a significant effect of the ESO content on the tensile strength and elongation at break was also observed. All the values of tensile strength were in the range of 20–56.7 MPa (Figure 1), with the highest value obtained for sample V/3, i.e. having the lowest ESO content. As the presented results demonstrate, increasing the ESO content led to a decline in the tensile strength. ESO introduces additional, more flexible segments into the epoxy network structure, thereby reducing the number of cross-links. This causes a decrease in the cross-link density, thereby reducing the strength of the cured composition but increasing its flexibility [27]. This was confirmed by the growth in elongation at break. For the sample containing 50 wt% ESO (V/1), the elongation at break was 40%, while reducing the ESO content to 35 and 20 wt% resulted in a drop in elongation at break to 4.0 and 2.2%, respectively.

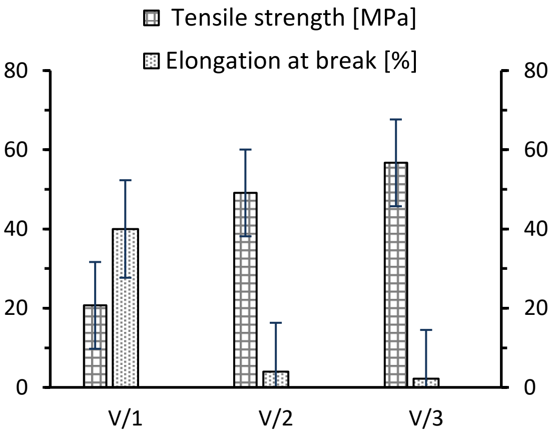

Figure 1. Tensile strength and elongation at break of vitrimers.

Thermal analysis

Thermogravimetric analysis in air revealed that all the vitrimer formulations exhibited high thermal stability (Table 3). The degradation onset temperature at 5% weight loss (T_{onset}) ranged from 339.6 to 359.6°C, with the highest value observed for V/3 containing 20 wt% ESO. The principal degradation step occurred at a temperature ranging from approximately 380 to 450°C, with the temperature corresponding to the maximum rate of weight loss (T_{peak}) falling within the range of 410 to 419°C. The slight increase in T_{onset} with decreasing ESO content suggests that the more rigid DGEBA-rich networks are somewhat more resistant to thermo-oxidative degradation than the ESO-rich ones, although the differences remain insignificant.

Table 3. Thermal stability in oxidizing atmosphere and glass transition temperature of epoxy vitrimers

SAMPLE	T_{onset} [°C]	T_{peak} [°C]	T_g [°C]
V/1	339.6	410.3	24.8
V/2	340.7	419.0	50.9
V/3	359.6	415.7	63.3

Differential scanning calorimetry (DSC) revealed a significant effect of the ESO content on the glass transition temperature (T_g). T_g increased from 24.8°C for V/1 (50 wt% ESO) to 50.9°C for V/2 (35 wt% ESO) and 63.3°C for V/3 (20 wt% ESO). These findings are consistent with the anticipated decline in cross-link density and the incorporation of flexible aliphatic segments that accompanies increasing ESO content. It is noteworthy that the T_g of V/1 is close to room temperature, which suggests that this formulation behaves as a rubbery material under ambient conditions and is more suitable for tough, flexible components rather than rigid structural parts. In contrast, V/3 combines a higher T_g with superior tensile strength, making it a more suitable candidate for load-bearing composite matrix applications at moderate temperatures.

Recycling

The performed chemical recycling procedure allowed complete dissolution of the cured material and the production of a liquid recyclate. After removing the excess solvent, the recovered recyclate was mixed with a fresh, liquid vitrimer composition at 15 wt%, 20 wt%, and 30 wt% relative to the total fresh composition, and then the prepared mixture was cured at T=150°C for 6 hours. For the obtained epoxy polymers containing recyclate, the tensile strength, elongation and glass transition temperature were determined (Table 4).

Table 4. Mechanical properties and glass transition of epoxy vitrimers with recyclate.

SAMPLE	**Tensile strength** [MPa]	**Elongation at break** [%]	**T_g** [°C]
V/3 + 15 wt% recyclate	42.3	4.9	34.1
V/3 + 20 wt% recyclate	36.9	12.0	37.2
V/3 + 30 wt% recyclate	14.9	66.0	29.9

As the recyclate content in the material increases from 15 to 30% by weight, the tensile strength dwindles from 42.3 to 14.9 MPa, while the elongation at break rises from 4.9 to 66% (Table 4, Figure 2). This indicates a progressive decrease in cross-link density and an increase in network heterogeneity. The moderate T_g values (29.9–37.2°C) of the materials containing recyclate confirm this trend. From the point of view of the industrial application of composite materials, those containing up to 15–20% by weight of recyclate still show a reasonable balance between strength and flexibility, while higher recyclate contents primarily result in highly stretchable, soft materials that can be used for manufacturing flexible components.

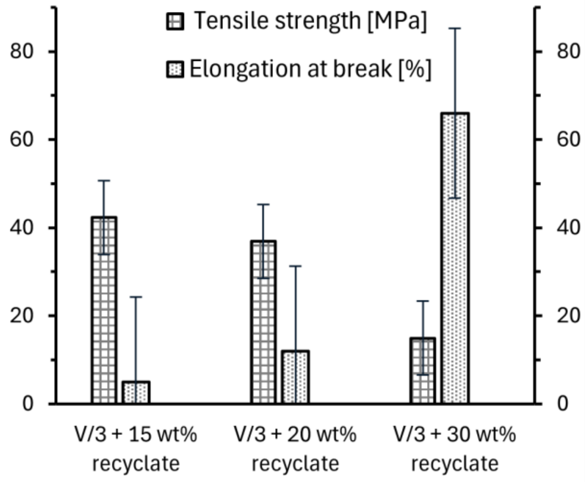

Figure 2. Tensile strength and elongation at break of vitrimers with recyclate.

CONCLUSIONS

The present study addresses the challenge of developing epoxy vitrimers based on diglycidyl ether of bisphenol A (DGEBA) and epoxidized soybean oil (ESO). The objective was to synthesize a matrix material that combines the robust performance of conventional epoxy resins with the recyclability required by the circular economy, achieved through the formation of dynamic covalent adaptive networks (CANs) via a zinc-catalyzed transesterification mechanism. The results demonstrate that ESO effectively tunes the thermomechanical properties of the polymers. A clear trade-off between rigidity and flexibility was observed: the formulations with the lower ESO content (20 wt%) exhibited a higher tensile strength (56.7 MPa) and a glass transition temperature (T_g) of 63.3°C, rendering them suitable for structural applications. In contrast, higher ESO loading (50 wt%) acted as an effective plasticizer, significantly raising the impact strength (96.73 kJ/m²) and elongation at break while decreasing the hardness and thermal resistance. These trends are consistent with reports on bio-based epoxies and ESO-modified vitrimer systems, in which increasing the fraction of flexible aliphatic segments lowers the cross-link density and T_g, while enhancing the toughness, impact resistance, elongation and processability [20–22].

Although the Zn^{2+} catalyzed transesterification observed here is consistent with vitrimer mechanisms described in earlier research [11–13,15–17], the present formulation differs from those systems in several respects. In contrast to polyester- or rosin-based networks reported in the literature, this vitrimer employs a combination of DGEBA with ESO and a mixed succinic acid/anhydride curing system, with $Zn(AcAc)_2$ serving as the catalyst. Furthermore, complete dissolution was achieved within 15 minutes at 180°C in propylene glycol, with successful reincorporation of 15–20 wt% recyclate, resulting in only a moderate reduction in strength. By comparison, most cited studies discuss recyclability qualitatively and do not provide equivalent processing parameters.

As reported in the literature [14,21] comparable recycling efficiency and property retention are primarily concerned with the ability of vitrimers to retain reprocessability and structural integrity after recycling. Nevertheless, it should be noted that these works generally do not provide numerical post-recycling mechanical or thermal data. In contrast, the present system provides explicit performance metrics following recycling, including tensile strength values of 42.3 MPa, 36.9 MPa, 14.9 MPa and T_g values of 37.2ºC, 34.1ºC, 29.9ºC for samples containing 15, 20 and 30 wt% recyclate, respectively. These results offer a more detailed characterization of vitrimer recyclability. The combined success of chemical recycling in propylene glycol and the reintegration of up to 20 wt% recycled material without substantial performance loss further confirms the viability of this system for closed-loop life cycles.

Overall, these findings carry significant implications for the composites industry. The developed vitrimers present a practical, recyclable matrix platform that balances performance and processability, addressing the long-standing challenge of thermoset waste without compromising environmental responsibility.

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