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# Biobased Vitrimeric Epoxy Networks

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The scientific strategies reported in the literature for developing biobased epoxy vitrimers are summarized. Biomass resources such as lignin, cellulose, or different vegetable oils can be exploited as biobased building blocks for epoxy thermosets as an alternative to the bisphenol-A-based ones. Biorenewable resources have been synthesized introducing dynamic covalent bonds in the cross-linked networks. This combination allows to achieve cross-linked biobased epoxy networks with thermoset-like properties at a temperature of use, but showing (re)processability, recyclability, and self-healing properties above a well-defined temperature named topology freezing transition temperature ( $T_v$ ).

## 1. Introduction

The global environmental pollution related to polymeric materials urges the scientific community to propose sustainable solutions. In the last decades, we have witnessed an exponential increase in the production of polymer resins and plastic (see **Figure 1**).<sup>[1]</sup> By 2050, plastic production is expected to account for 20% of worldwide fossil fuel consumption. The plastic waste generated in coastal regions is most at risk of entering the oceans, and in 2020, coastal plastic waste amounted to 99.5 million tonnes.<sup>[2]</sup> We consume more resources than the planet can generate, and growing rates of pollution and waste only exacerbate the problem. The concerns connected to the petroleum-based origin of polymeric materials and the problems related to the accumulation of plastic waste in the environment need an urgent solution.

One possible strategy to address this dramatic situation is exploiting of biobased resources as precursors for polymers. Human activity produces 998 million tonnes of agricultural waste,

and similar amount of food waste is produced. The valorization of these wastes could be of paramount importance but complex simultaneously. Finding a way to convert waste into added value products is the actual concern of most of the researchers to become greener and more sustainable.<sup>[3]</sup> The first problem in handling the residues is the variety of the biosources. Raw materials' different chemophysical attributes increase the difficulties of obtaining homogeneous and pure products. However, the structural components of the different plant biomasses can be divided into lignin, hemicellulose, and

cellulose.<sup>[4]</sup> From these biopolymers, interesting chemical products can also be achieved via derivatization and depolymerization processes.<sup>[5]</sup> Using bioderived polymers can represent a green alternative since they are based on renewable resources and possess low CO<sub>2</sub> emissions.

Thermoplastics dominate the current biobased polymer market, while the market of thermosetting polymers is still limited. Traditional thermosets are network polymers that cannot be thermally reprocessed; hence recycling is difficult if not impossible. Taking into consideration the large diffusion of polymeric thermosets in sectors such as automotive, boat industry, composites, and constructions, the development of biobased (re)processable and/or recyclable thermosets still represents a great challenge for sustainability. The issue is particularly urgent in the case of epoxy polymeric networks.

In fact, epoxy resins are widely used in different important industrial applications such as coatings, adhesives, matrices in composites, and electronic applications. They possess good mechanical properties, high thermal resistance, and excellent adhesion to substrates. However, most of them are petroleum-derived, leading to environmental and feedstock depletion issues. Furthermore, the most used epoxy resin is diglycidyl ether of bisphenol-A-based. The intensive use of bisphenol-A (BPA) is an important issue since the product is classified as carcinogen, mutagen, and reprotoxic.<sup>[6]</sup> It negatively impacts wildlife and can disrupt the human endocrine system by mimicking the human body hormones.<sup>[7]</sup> For this reason, several studies have been conducted to find alternative aromatic compounds to produce epoxy thermosets BPA-free.<sup>[8]</sup> and big efforts are made in the direction of finding biobased epoxy resin which can be used as precursor to achieve cured epoxy materials with comparable properties of the bisphenol-A-based one.

One promising strategy to achieve sustainable and recyclable epoxy thermosets is coupling biobased resources to synthesize the polymeric material with the introduction of dynamicity in cross-linked polymeric materials.<sup>[9]</sup> The dynamicity property can be imparted into the polymeric networks by the presence of

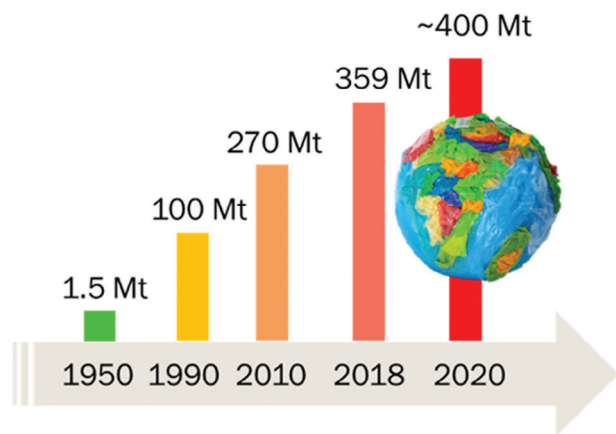
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**Figure 1.** Worldwide annual production of plastics from 1950 to 2020.<sup>[1]</sup>

labile dynamic bonds capable of undergoing reversible formation and cleavage, giving to the corresponding materials innovative recyclability properties.<sup>[10–14]</sup>

Within this frame, this review aims to summarize how scientists face the complex challenge of producing sustainable and recyclable polymeric epoxy thermosets. The proposed target has been reached by exploiting the peculiar properties of vitrimers, which allows direct recyclability or reprocessability of the polymeric networks and uses biobased polymeric precursors for the development of sustainable epoxy networks. Therefore, integrating vitrimeric properties with biobased materials appears a great combination of choice to achieve the expected aim, by combining together recyclability and sustainability. The topic is very interesting, as witnessed by the high number of literature reviews, and in this paper we have tried to summarize all the scientific reports where biobased epoxy networks were coupled with vitrimeric properties.<sup>[14–25]</sup>

## 2. Dynamic Polymer Networks

Dynamic polymer networks were introduced in 1990 by Lehn and co-workers, followed by the research work by Wudl and co-workers in 2002, when the word DYNAMERs was coined.<sup>[26–31]</sup> Subsequently, Bowman and co-workers designed specifically cross-linked polymer networks exhibiting reversible bonds and the name Covalent Adaptive Networks (CANs) was introduced.<sup>[32]</sup>

CANs can be classified as either dissociative or associative. In the dissociative CANs, cross-links are broken and afterward reformed. It is possible to reach an almost complete depolymerization, and eventually, it is possible to recover the starting monomers. In the case of associative CANs, a new bond is formed before an old one is broken. Thus, on average, the cross-link density remains more or less constant, allowing a topology network modification. The formation and the breaking of bonds are usually activated by temperature.<sup>[14]</sup> Therefore, in this case, the constant number of covalent bonds allows the thermoset to remain insoluble but with the possibility of recyclability and reshapeability.<sup>[33,34]</sup> Many review papers already reported in literature show different dynamic covalent chemistries to obtain CANs.<sup>[35–38]</sup>

Leibler and co-workers further investigated the concept of associative CANs in 2011, which exploited transesterification reaction to promote the dynamic covalent bond. Their research work showed that some covalent bonds in thermosets could be rendered reversible by the presence of a catalyst. They coined the term vitrimer for these materials.<sup>[33]</sup>

Finally, we can say that vitrimers are a special class of polymeric network materials showing dynamic covalent bond behavior. Differently from what happens in dissociative dynamic covalent bond, the bond exchange in vitrimers (showing associative dynamic covalent bond) occurs without distinct separated steps of bond dissociation and reassociation. Consequently, the network connectivity is never lost during the bond exchange process.<sup>[31,39]</sup> Vitrimers can be considered a new class of materials which are characterized by properties in between typical properties of thermoplastic or thermoset concerning their workability.<sup>[40,41]</sup> As a matter of fact, vitrimers are cross-linked polymer networks that can exhibit a gradual decrease of viscosity upon heating, giving them unique properties compared to classical thermosets, such as self-healing, (re)processability, and network rearrangement without loss of integrity.<sup>[42–45]</sup> Finally, we can describe vitrimers as cross-linked polymeric networks containing dynamic bonds that can be exploited to change network's topology via exchange reaction while keeping constant the number of chemical bonds and, therefore, cross-linking density. This peculiar property makes them particularly attractive in the vision of sustainability production of recyclable thermosets.

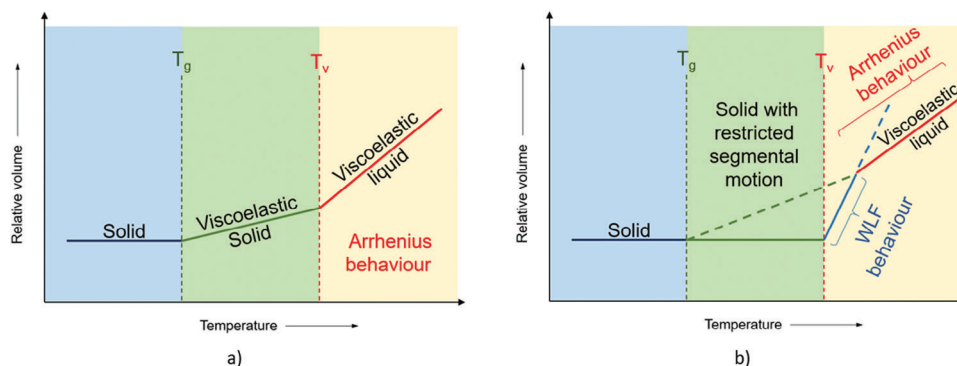
The associative dynamic covalent bond is activated at a certain temperature, named topology freezing transition temperature ( $T_v$ ), which, along with glass transition temperature ( $T_g$ ) is introduced to identify the viscoelastic phase transition in vitrimers. When dealing with amorphous thermoplastics, it is well-known that viscosity drops sharply above the  $T_g$ , following the William–Landel–Ferry model between  $T_g$  and 100 °C above  $T_g$ , and following Arrhenius-type behavior at higher temperatures.<sup>[46,47]</sup> In the case of semicrystalline thermoplastics, the viscosity drops at  $T_m$  and follows Arrhenius temperature dependence if  $T_m$  is  $\approx 100$  °C higher than its  $T_g$ .

When dealing with vitrimers, where viscosity is controlled by chemical exchange reaction, materials follow Arrhenius-type behavior when significantly heated above  $T_g$ , and thus, allows their processing without loss in network integrity. There could be two pathways (Figure 2), either  $T_g$  of the polymeric thermosets is found below or above  $T_v$ . In both cases, bond exchange could occur only at temperatures above  $T_g$ . Therefore, in the second scenario ( $T_g > T_v$ ), the  $T_v$  is purely theoretical.<sup>[48]</sup>

If the  $T_v$  is located above the  $T_g$ , the vitrimer behaves like a classical thermoset until reaching  $T_g$ , where a transition from glassy to rubbery state is observed. Subsequently, above  $T_v$ , the exchange reactions are fast enough to change the network topology, and the polymer flows like a viscoelastic liquid following and Arrhenius temperature dependence.

When  $T_v$  is located below the  $T_g$ , by heating the material above  $T_g$ , the bond exchange is already fast and there is a rapid change of state from glassy solid to viscoelastic liquid. The bond exchange may occur for a period of time via William–Landel–Ferry behavior and then following Arrhenius kinetics.<sup>[49]</sup>

At sufficiently high temperatures (above  $T_v$ ), vitrimers exhibit great stress relaxation through bond exchanging, notwithstand-



**Figure 2.** Temperature-dependent phase transitions of vitrimers. a)  $T_g$  below  $T_v$  and b)  $T_g$  above  $T_v$ .

ing the permanent network connectivity. Above  $T_v$ , the bond-exchange timescale is shorter than the observation time, which results in a transition to the viscous flow. Below  $T_v$ , the kinetic of exchange reaction is so slow that the network topology appears frozen, and the polymeric material behaves as the classic viscoelastic solid. By convention, the  $T_v$  is chosen as the temperature at which the viscosity reaches  $10^{12}$  Pa s.<sup>[33]</sup>

This theory comes from the original Leibler's investigation (where the effective viscosity crosses a value of  $10^{12}$  Pa s).<sup>[33]</sup> More recently, Winter and co-workers defined the  $T_v$  point based on power-law relaxation of the modulus.<sup>[50]</sup> Even if other techniques are also used to identify  $T_v$ , stress relaxation is the most accurate technique.<sup>[51,52]</sup>

The normalized stress-relaxation modulus decrease can be ascribed by an exponential behavior

$$\frac{G(T)}{G_0} = e^{-\frac{t}{\tau}} \quad (1)$$

where  $\tau$  represents the experimentally measured relaxation time at which  $(G(T)/G_0)$  equals  $1/e$  (the value described by Liebler of  $10^{12}$  Pa s). To evidence the Arrhenius relationship, and therefore a vitrimeric associative exchange mechanism, the plot of  $\ln\tau$  as a function of  $1/T$  should be a straight line.

### 3. Biobased Epoxy Vitrimers

Different authors reported the synthesis of biobased epoxy vitrimers as an alternative to the bisphenol-A-based epoxy resins.<sup>[13,14]</sup> In this section, we have focused, to the best of our knowledge, on pure biobased epoxy vitrimer, without the expectation to be comprehensive. The main focus of this review is the coupling of biobased epoxy monomers obtained from renewable resources with the introduction of dynamicity in the cross-linked polymeric materials to achieve sustainable and recyclable epoxy thermosets.

#### 3.1. Vegetable-Oil-Based Epoxy Vitrimers

Various vegetable oils have been proposed in the literature as important candidates to produce biobased epoxy vitrimers. Soybean oil is an interesting biobased precursor since it is an important

vegetable oil, composed of oleic and linoleic acid, whose unsaturated C=C bonds can be oxidized to obtain the epoxidized soybean oil (ESO). The generalized reactive process is schematized in **Figure 3**.

Liu et al. exploited dynamic cross-linker, such as disulfide-containing diamine, to cross-link ESO.<sup>[53]</sup> In **Figure 4**, the cross-linking reaction of ESO (reaction a) and the network topology rearrangement (reaction b) is schematized. The cross-linked epoxy network showed a  $T_g$  around 30 °C and good thermal stability. The epoxy thermoset can be thermally reprocessed or recycled due to the presence of disulfide bonds, which enabled the network to rearrange its topology under appropriate conditions.

Yang et al. reported the curing reaction of ESO in the presence of a rosin derivative fumaropimaric acid (FPA).<sup>[54]</sup> The schematized reaction is reported in **Figure 5**.

A novel and fully biobased vitrimer with a  $T_g$  of 65 °C and tensile strength of 16 MPa was synthesized, exhibiting excellent self-healing, shape memory, and reprocessability. The ESO-FPA polymer networks can undergo rearrangement through transesterification owing to the dynamic covalent bonds in the structure, as directly confirmed through stress relaxation. ESO-FPA also exhibited good self-healing above the  $T_v$  and excellent shape memory properties.

Di Mauro et al. investigated different epoxidized vegetable oils to achieve epoxy vitrimers, using the dynamic cross-linker containing the disulfide diamine. All the achieved vitrimers showed recycling temperatures between 120 and 170 °C.<sup>[55]</sup>

More recently, Bergoglio et al. investigated epoxidized castor oil, containing both epoxy groups and -OH groups to be exploited, respectively, for curing reaction and in the transesterification reaction, which imparts dynamic properties to the cross-linked network. The cross-linking reaction was UV-induced, in the presence of a sulfonium salt, and performed in the presence of dibutyl phosphate as a transesterification catalyst. The cross-linked network showed good thermomechanical properties. The stress-relaxation analysis showed that all the UV-cured formulations reached  $1/e$  relaxation modulus starting from 170 °C.<sup>[56]</sup>

Xu et al. reported the synthesis of epoxy-functionalized tung oil via a methyl esterification reaction, Diels-Alder reaction, and epoxidation reaction (reaction scheme reported in **Figure 6**).<sup>[57]</sup>

The obtained vegetable-oil-based epoxy resin was cured with citric acid (CA), achieving catalyst-free, self-healing, high mechanical strength fully biobased vitrimers. The terminal epoxy

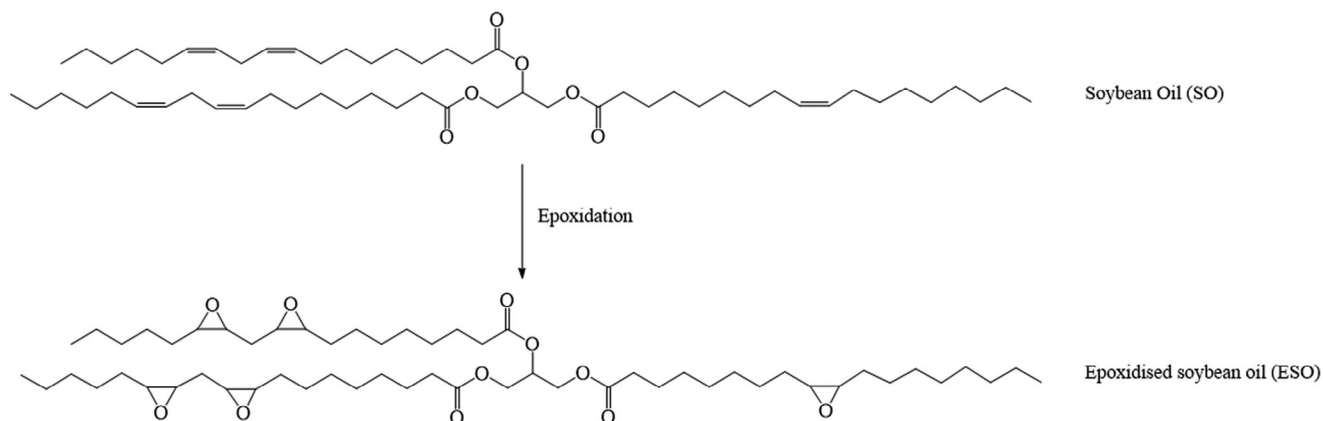


Figure 3. Soybean oil epoxidation general reaction.

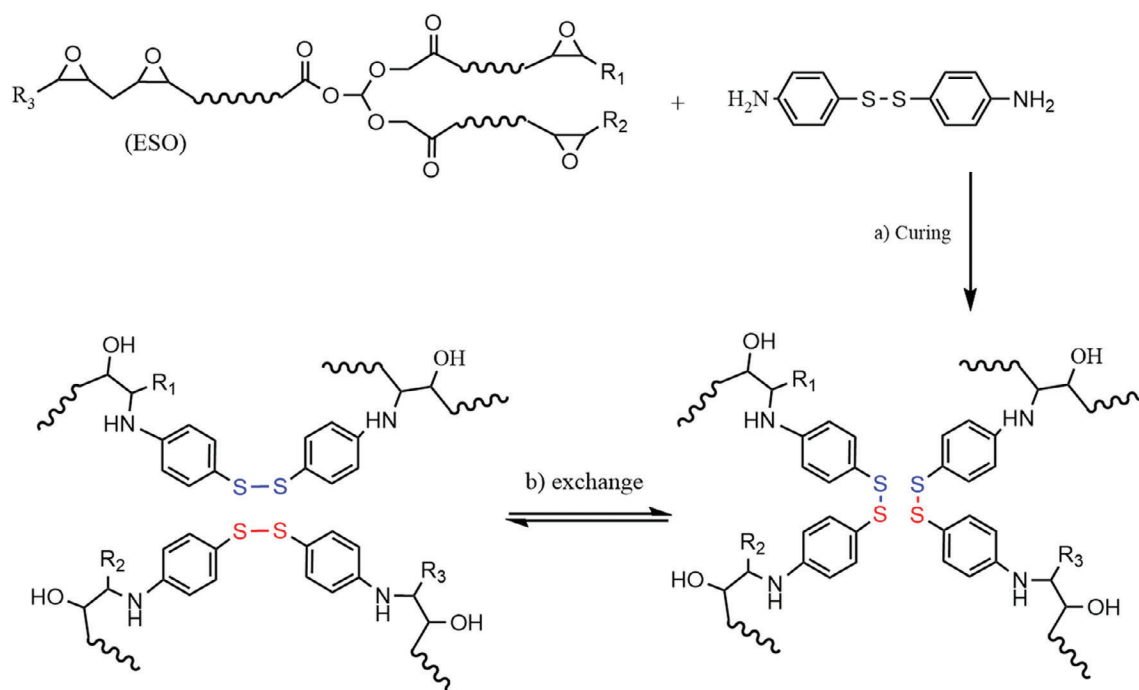


Figure 4. Cross-linking reaction of ESO (reaction a) and the network topology rearrangement (reaction b).

groups showed high reactivity toward cross-linking reaction, and the polymeric network possessed a high cross-link density, thus good thermal stability and mechanical properties. The use of the CA curing agent allowed introducing a large number of hydroxyl groups in the network structure which could act as a catalyst, allowing topological network rearrangement of the materials without any external catalyst. Due to their dynamic ester and H-bonds, the vitrimers exhibit good self-healing, recyclability, and shape memory properties, making them promising candidates for use as repairable and recyclable adhesives.

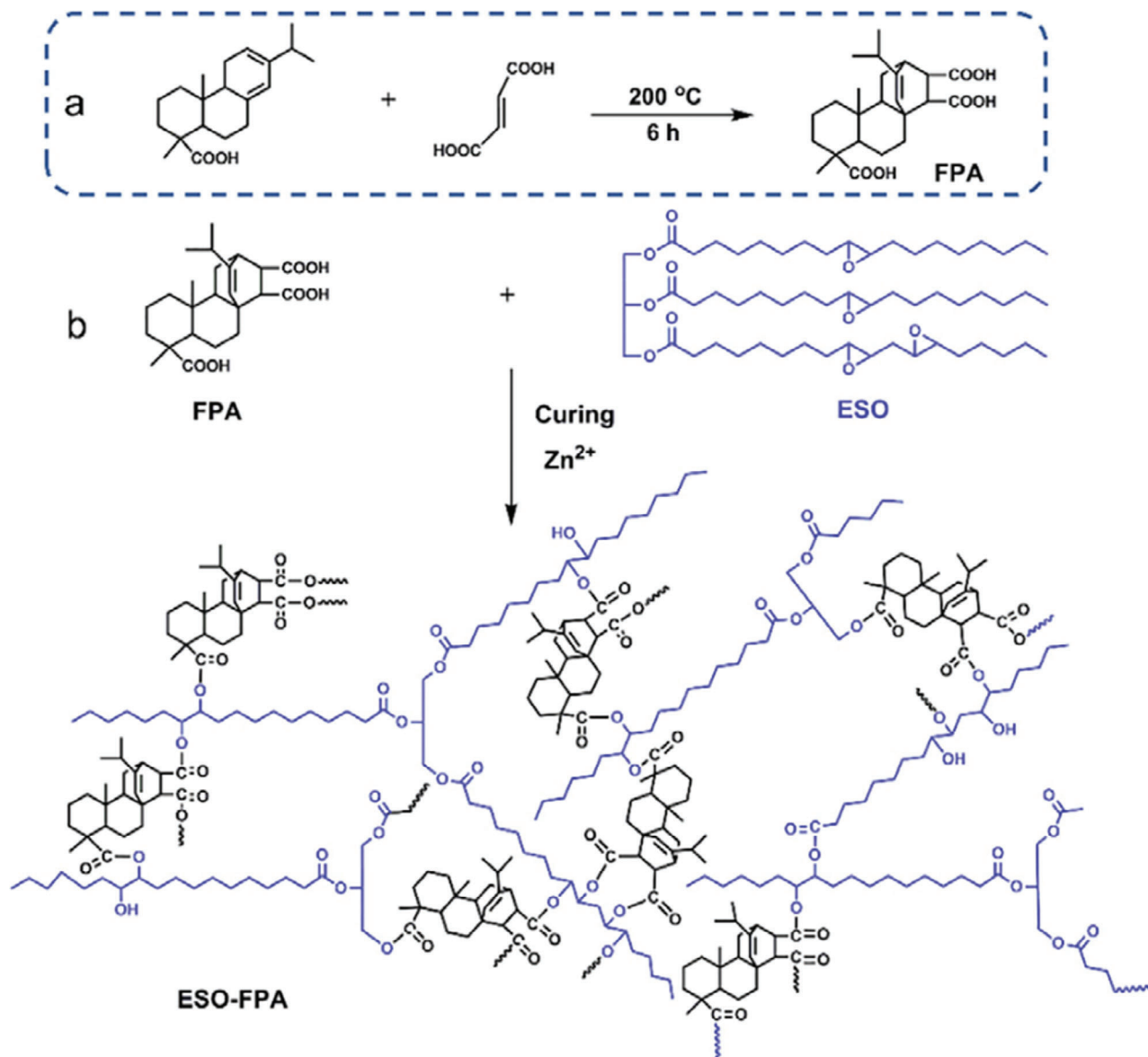
### 3.2. Eugenol-Based Epoxy Vitrimers

A different biobased epoxy precursor suggested by Liu et al. is eugenol, a biobased phenolic compound.<sup>[58]</sup> Eugenol epoxida-

tion (Eu-EP) was obtained via a dual-step reaction (see Figure 7) and cured with succinic anhydride (SA). The curing reaction of Eu-EP/SA results in the formation of ester bonds and hydroxyl groups, which could undergo dynamic exchange reactions. The epoxy network achieved in the presence of Eu-EP/SA in a 1:0.5 ratio showed a transesterification exchange reaction at a temperature above 150 °C, with a fast stress relaxation of the cross-linked polymer network. This was possible because of the high hydroxyl group content in the eugenol.

Ocando et al. started from eugenol to achieve a triepoxy monomer (see the proposed synthetic route in Figure 8).<sup>[59]</sup>

The starting biobased precursor was cross-linked by exploiting an aromatic amine containing a disulfide linkage, the 4-aminophenyl disulfide. It was possible to obtain a very high  $T_g$  cross-linked epoxy network containing the disulfide groups,



**Figure 5.** a) Synthetic route to FPA. b) Curing reaction of FPA and ESO. Reproduced with permission.<sup>[30]</sup> Copyright 2020, Materials & Design.

which can exchange upon heating, giving vitrimeric-like behavior to the cross-linked materials.

### 3.3. Vanillin-Based Epoxy Vitrimers

Vanillin is another aromatic building block investigated in the development of biobased epoxy network. The aldehyde group present in vanillin can be exploited to form dynamic imine linkages by condensation with amines. Liu et al. reported the condensation of vanillin with *p*-aminophenol to obtain a bisphenol structure with an internal imine linkage, which was used as a cross-linker of epoxidized soybean oil (see scheme in **Figure 9**).<sup>[60]</sup>

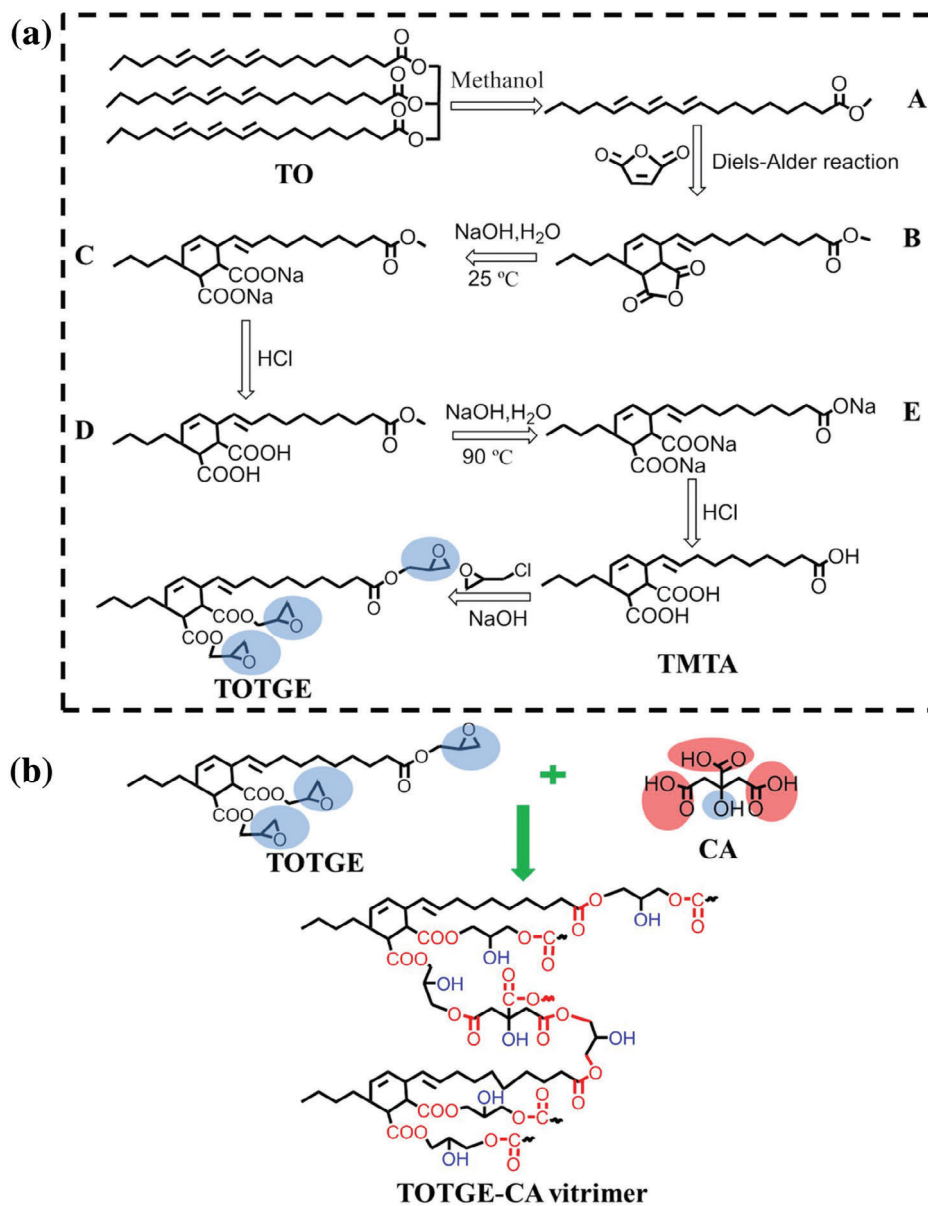
The achieved epoxy vitrimer was proposed as a matrix to fabricate carbon fiber fabric-reinforced composite with high tensile strength (145.4 MPa) and Young's modulus (1.18 GPa). The dy-

namic nature of Schiff base in the vitrimer enabled the composites to be easily recycled and reprocessed.

Similarly, Zhao et al. exploited a vanillin-based imine-containing bisphenol as a dynamic curing agent of ESPO, achieving vitrimeric materials with low activation energy.<sup>[61]</sup>

Vanillin was also modified with epichlorohydrin to obtain a difunctional monomer with epoxy and aldehyde group, which was cross-linked with a diamine to achieve a mixed epoxy-imine network, which showed stress relaxation activated by transamination or imine metathesis.<sup>[62]</sup> The composite materials obtained with this cross-linked matrix were either thermally reprocessed or degraded in an acidic environment.

Very recently, Guggari et al. reported the use of an aliphatic disulfide cystamine as a biobased dynamic cross-linker in the curing reaction of diepoxy modified vanillin. The exploitation of cystamine showed a competitive alternative to petroleum-based



**Figure 6.** a,b) Scheme of the epoxy functionalization and cross-linking reaction of tung oil. Reproduced with permission.<sup>[33]</sup> Copyright 2021, Industrial Crops and Products.

cross-linkers. The study highlights the promising prospects of using cystamine as a dynamic hardener to fine-tune exchange dynamics in fully biobased epoxy vitrimers.<sup>[63]</sup>

### 3.4. Itaconic-, Ferulic-, and Protocatecholic-Acid-Based Epoxy Vitrimers

Itaconic acid, derived from the fermentation of hydrocarbons, was epoxidized and exploited to prepare vitrimeric polymer network after cross-linking with maleic anhydride.<sup>[64]</sup> Since the curing process was performed in the presence of a large amount of glycerol, the obtained polymer network is an example of catalyst-free transesterification vitrimers, where the dynamic covalent

network was activated by multiple –OH groups brought by glycerol. The same system was investigated for preparing vitrimeric carbon-fiber-reinforced (CFR) epoxy matrix.<sup>[65]</sup> The CFRC prepared could be readily degraded under mild alkaline conditions at room temperature.

Yang et al. very recently reported the preparation of itaconic acid (IA)-based epoxy vitrimers by the insertion on the cross-linking network of dynamic  $\beta$ -hydroxy ester bonds and boronic ester bonds.<sup>[66]</sup> The obtained IA-based epoxy vitrimer possesses comparable thermal stability ( $T_5 = 255\text{ °C}$ ) and mechanical properties (tensile strength = 68.3 MPa, elongation at break = 16.8%, and toughness = 6.43 MJ m<sup>-3</sup>) to conventional epoxy resins due to the rigid network frameworks. Meanwhile, the IA-based epoxy vitrimer shows excellent self-healing, welding, physical repro-

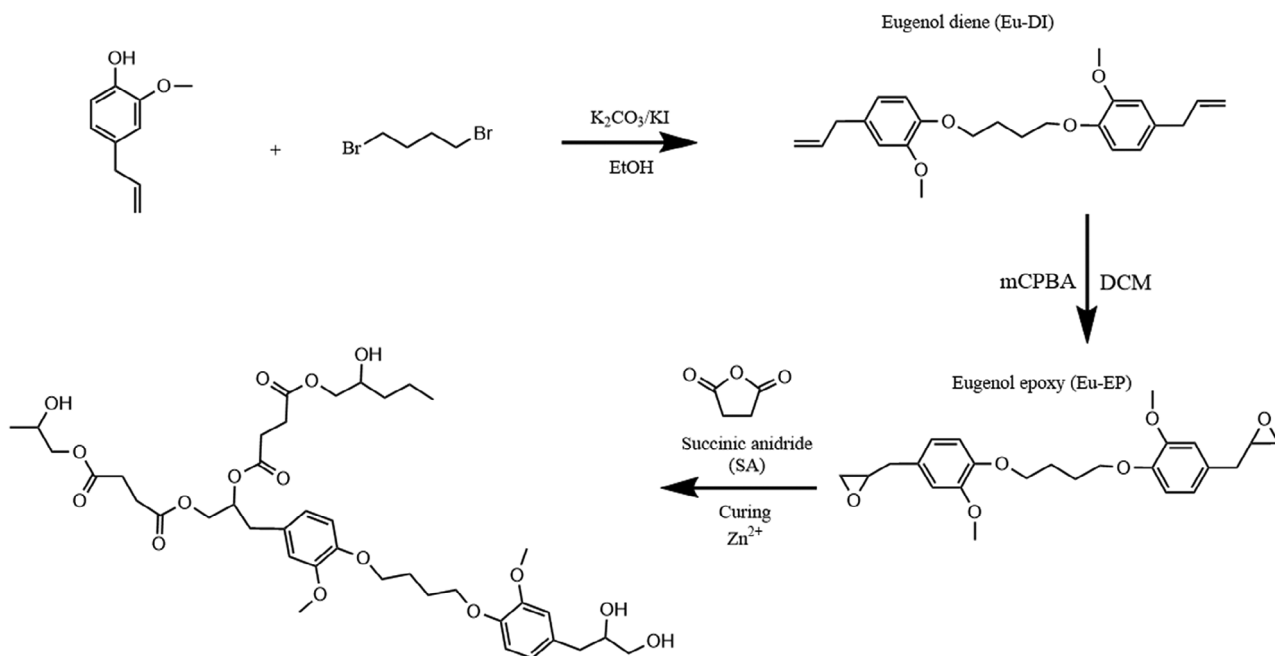


Figure 7. Synthetic route for eugenol epoxidation.

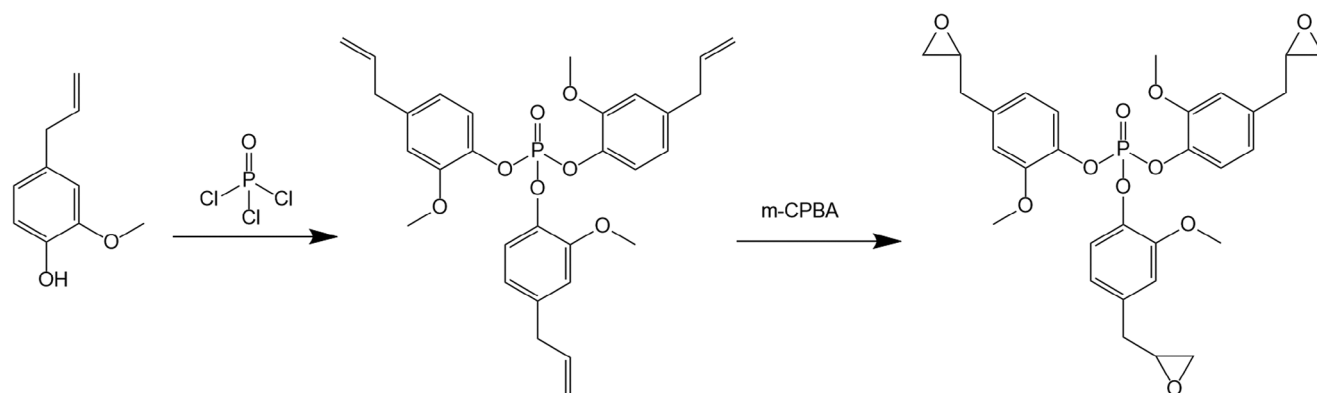


Figure 8. Synthetic route to achieve a triepoxy monomer from eugenol.

cessing, and chemical recycling due to the rearrangement of network typology by thermally induced dioxaborolane metathesis and transesterification.

Zhong et al. proposed the epoxidation of ferulic acid (FEP) and subsequent synthesis of ferulic-acid-based hyperbranched epoxy resin (FEHBP).<sup>[67]</sup> The epoxy resins FFEP and FEHBP were mixed in stoichiometric amounts and cross-linked in the presence of citric acid.

The hydroxyl groups and hyperbranched topological structure of FEHBP facilitated the dynamic transesterification exchanges and reversible cross-linking, and the obtained vitrimers exhibited excellent reprocessability. The epoxy vitrimers containing 10 phr FEHBP exhibited impressive properties, including high tensile stress (126.4 MPa), a  $T_g$  of 94 °C, fast stress relaxation (a relaxation time of 45 s at 140 °C), and retention of above 88% of tensile strength upon recycling.

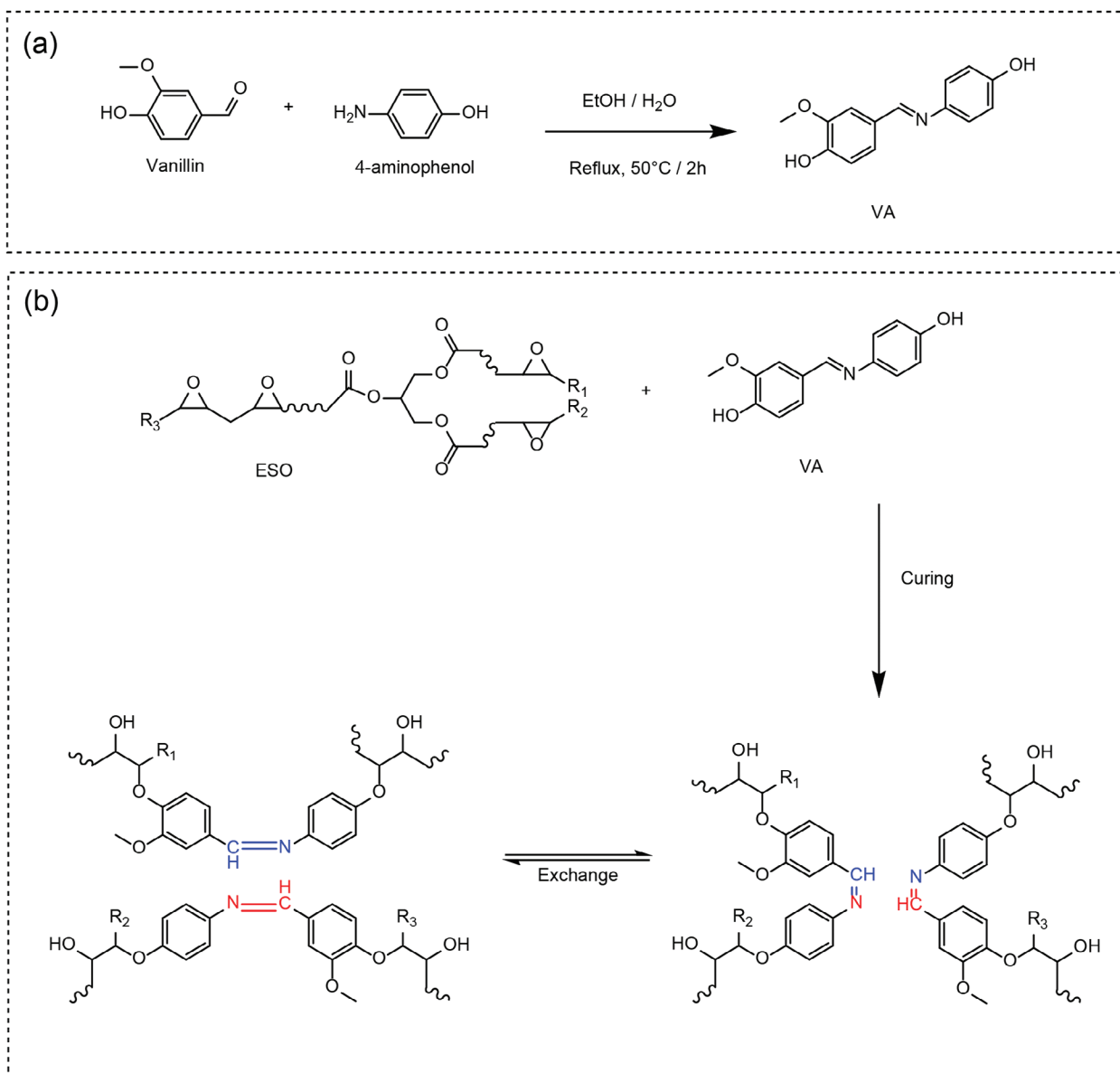
Tao et al. synthesized biobased epoxy monomer starting from protocatechuic acid.<sup>[68]</sup> The biobased precursor was cross-linked

with maleic anhydride, with different catalyst loadings and ratios of epoxy/anhydride, obtaining high performance epoxy vitrimers. The overall reaction scheme is reported in Figure 10.

The cross-linked epoxy resins showed better thermal and mechanical properties ( $T_g = 157$  °C, tensile strength = 65 MPa) than commercial BPA-based epoxy resins. Moreover, these biobased epoxy vitrimers showed reprocessability with extremely high efficiency and degradability in NaOH solution. The great properties of epoxy vitrimers derived from protocatechuic acid indicate that they can be used as renewable alternatives to BPA epoxy resins.

### 3.5. Lignin-Based Epoxy Vitrimers

Among the different biobased precursors, lignin appears to be a suitable starting product because it is one of the most important renewable resources of aromatic structures largely available. Lignin is strongly interconnected with cellulose and hemicellulose, and can be achieved via the Kraft process. Zhang et al.



**Figure 9.** a) Synthetic route of Vanillin Alcohol (VA), b) preparation and network topology rearrangement of ESO–VA.

and Hao et al. proposed two different strategies to enhance the carboxylic groups on Kraft lignin, either via ozonation (Figure 11, above) or reacting the –OH groups with cyclic anhydride to generate –COOH groups on the lignin surface (Figure 11, below).<sup>[69,70]</sup> The modified Kraft lignin was exploited as a polycarboxylic acid cross-linker of biobased aliphatic epoxy monomer, achieving transesterification vitrimers in the presence of a zinc catalyst.

It was possible to modulate the final properties of the cross-linked materials, achieving an enhancement of  $T_g$ , modulus, and tensile strength of the prepared lignin-based materials by increasing the lignin content. Because of the large amount of ester linkages and –OH groups derived by the presence of lignin, the transesterification reaction was easily activated at above 160 °C with a fast stress relaxation of the cross-linked networks.

The proposed epoxy cross-linked material was also suggested as a recoverable adhesive. When used for bonding aluminum sheets, the lignin-cross-linked epoxy adhesive exhibited a cohesive failure and showed a lap-shear strength of 6.3 MPa.<sup>[69]</sup> Nonetheless, at 190 °C, the two halves could be rebonded exploiting the transesterification reaction, and the rebonded adhesive still showed an adequate lap-shear strength.

### 3.6. Applications of Epoxy Vitrimers

Vitrimeric properties of cross-linked epoxy matrices were exploited in different interesting applications. As a first interesting property, reprocessability is an important advantage in producing sustainable thermosets.<sup>[44]</sup> The vitrimeric epoxy matrix

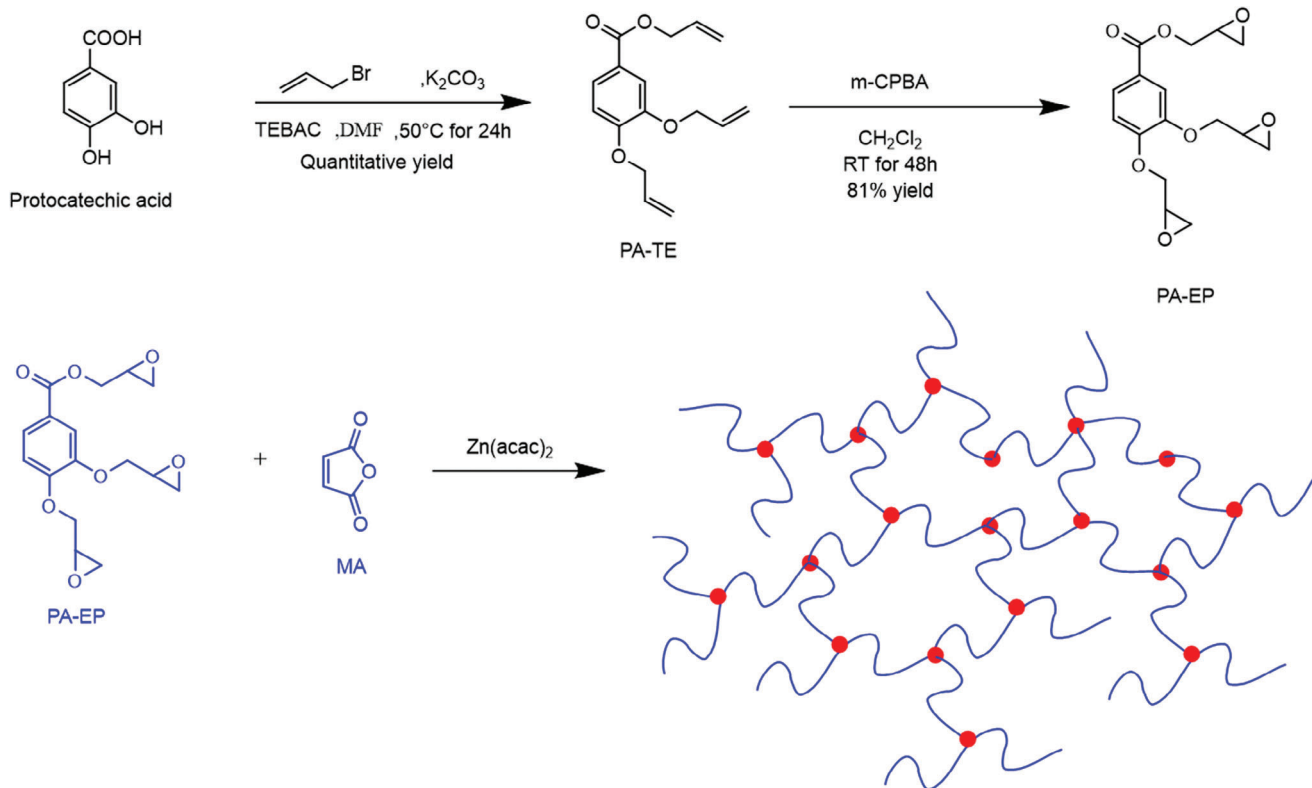


Figure 10. Scheme of the protocatecholic acid epoxidation and cross-linking reaction with maleic anhydride.

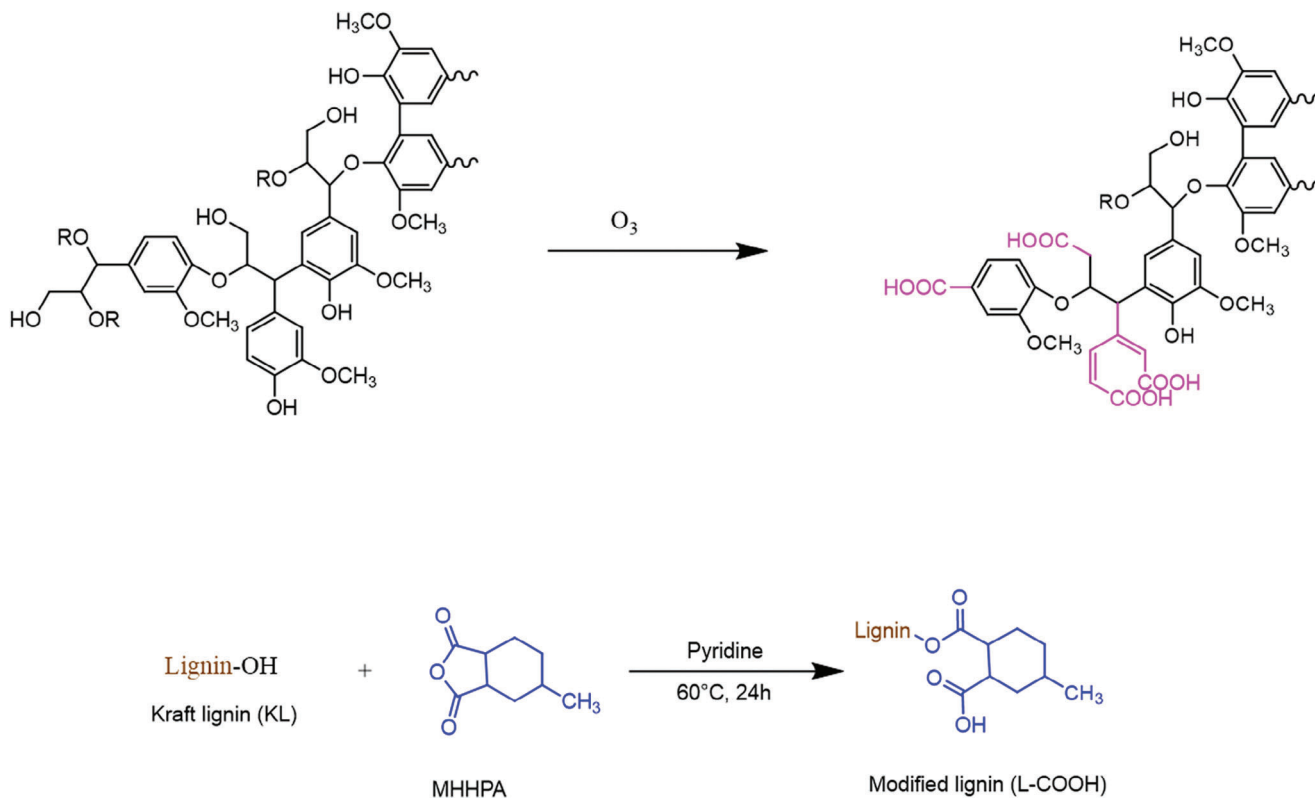


Figure 11. Reactive strategies to enhance the carboxylic groups on kraft lignin: via ozonation (reaction scheme above) or reacting the —OH groups of lignin with cyclic anhydride (reaction scheme below).

could be subjected to thermoforming reprocessability by applying heat and pressure to the damaged part.<sup>[71]</sup> The introduction of covalently bonded disulfide groups within a conventional epoxy-based network allowed cross-linked materials with good thermo-mechanical properties combined with mild healing temperatures (<100 °C). This behavior was exploited for self-healing coatings and composites. From an application point of view, it is very interesting to develop polymers and composites characterized by high modulus and low healing temperature. In this direction, self-healing glass-fiber reinforced epoxy matrices were developed based on disulfide epoxy thermosets. These composites showed multiple healings upon a short thermal treatment at 70 °C.<sup>[72]</sup>

Also, thermoset recyclability can be achieved by exploiting vitrimeric behavior, either using a solvent that can penetrate the network participating in the transesterification reaction, cleaving the chain in smaller fragments, and dissolving the matrix, or by grinding and reprocessing. The main issue for achieving good degradability performance is that good degradability needs low cross-linking density and flexible structures such as disulfide or acetals, resulting in low  $T_g$  and poor thermomechanical behavior. Wang et al. combined dynamic covalent boronic ester bonds and novolac resin, achieving fully recyclable carbon fiber composites with excellent mechanical properties and good recyclability.<sup>[73]</sup> While the most papers are related to fossil-based epoxy matrix, some of them report the use of biobased precursors.<sup>[74]</sup> Liu et al. synthesized a eugenol-based epoxy vitrimer which was completely degraded by exploiting the transesterification reaction with ethanol at 160 °C.<sup>[58]</sup>

Biobased epoxy networks were cross-linked via biobased anhydride to guarantee OH groups to be exploited for transesterification reactions. Different anhydrides, such as succinic anhydride, glutaric anhydride, and phthalic anhydride were used, achieving always good thermomechanical properties and high recyclability.<sup>[75–77]</sup>

In recent years, Hu et al. started from cardanol as a raw material to synthesize multifunctional biobased epoxy vitrimers, that were subsequently used as a matrix for CFRCs. The composite resulted in having fundamental properties for recycling. It showed a complete etching of the matrix in NaOH–ethanol solution, self-healing, welding, and mechanical reprocessing of the matrix, while maintaining satisfactory mechanical properties of the final composite.<sup>[21]</sup>

We can therefore assert that it is possible to extend the use of thermosetting polymers via self-healing and recycling, exploiting vitrimeric properties; this is very important in the frame of sustainability in sectors such as aerospace, automotive, electronics, and biomedical industries.

## 4. Conclusions

This review aimed to summarize all the scientific strategies reported in the literature for the development of biobased epoxy vitrimers. The concerns about plastic environmental pollution, together with fossil source depletion, are urging academia research to develop biobased epoxy polymer precursors. Biomass resources such as lignin, cellulose, or different vegetable oils can be exploited as biobased building blocks for epoxy thermosets alternative to the bisphenol-A-based ones.

Even if biobased epoxides can represent an important greener alternative, the thermosets cannot be reprocessed or recycled. For this reason, in this review, we focused on the strategies for achieving sustainable and recyclable epoxy thermosets, coupling biobased resources with the introduction of dynamic covalent bonds in the cross-linked networks. This combination allows to achieve cross-linked biobased epoxy networks with thermoset-like properties at a temperature of use, but showing (re)processability, recyclability, and self-healing properties above a well-defined temperature, named  $T_v$ .

We have shown how authors selected specific vegetable oils or other biobased molecules, such as eugenol, vanillin, itaconic acid, ferulic acid, or directly lignin, to achieve epoxy cross-linked thermosets with high thermomechanical performance and showing vitrimeric behavior showing relaxation modulus at a moderate temperature much below to the degradation temperature of the cross-linking materials.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

biobased epoxy network, epoxidized vegetable oils, vitrimers

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- [1] R. M. Cywar, N. A. Rorrer, C. B. Hoyt, G. T. Beckham, E. Y.-X. Chen, *Nat. Rev. Mater.* **2021**, *7*, 83.
- [2] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.
- [3] K. L. Law, N. Starr, T. R. Siegler, J. R. Jambeck, N. J. Mallos, G. H. Leonard, *Sci. Adv.* **2023**, *6*, eabd0288.
- [4] Z. Anwar, M. Gulfranz, M. Irshad, *J. Radiat. Res. Appl. Sci.* **2014**, *7*, 163.
- [5] L. Pezzana, E. Malmström, M. Johansson, M. Sangermano, *Polymers* **2021**, *13*, 1530.
- [6] P. Fenichel, N. Chevalier, F. Brucker-Davis, *Ann. Endocrinol.* **2013**, *74*, 211.
- [7] S. Ma, T. Li, X. Liu, J. Zhu, *Polym. Int.* **2016**, *65*, 164.
- [8] C. Noè, M. Hakkarainen, M. Sangermano, *Polymers* **2021**, *13*, 89.
- [9] W. Alabiso, S. Schlögl, *Polymers* **2020**, *12*, 1660.
- [10] T. Maeda, H. Otsuka, A. Takahara, *Prog. Polym. Sci.* **2009**, *34*, 581.
- [11] Y. Jin, Q. Wang, P. Taynton, W. Zhang, *Acc. Chem. Res.* **2014**, *47*, 1575.
- [12] C. J. Kloxin, C. N. Bowman, *Chem. Soc. Rev.* **2013**, *42*, 7161.
- [13] K. L. Chong, J. C. Lai, R. A. Rahman, N. Adrus, Z. H. Al-Saffar, A. Hassan, T. H. Lim, M. U. Wahit, *Ind. Crops Prod.* **2022**, *189*, 115857.
- [14] M. A. Lucherelli, A. Duval, L. Avérous, *Prog. Polym. Sci.* **2022**, *127*, 101515.
- [15] T. Vidil, A. Llevot, *Macromol. Chem. Phys.* **2022**, *223*, 2100494.
- [16] A. Kumar, L. A. Connal, *Macromol. Rapid Commun.* **2023**, *44*, 2200892.

- [17] Y. Yang, H. Liu, B. Lin, D. Tang, J. Xu, L. Dai, C. Si, *Ind. Crops Prod.* **2023**, *206*, 117690.
- [18] Y. Zhang, F. Ma, L. Shi, B. Lyu, J. Ma, *Curr. Opin. Green Sustainable Chem.* **2023**, *39*, 100726.
- [19] X. Yan, T. Liu, C. Hao, L. Shao, Y.-C. Chang, Z. Cai, S. Shang, Z. Song, J. Zhang, *Ind. Crops Prod.* **2023**, *202*, 116976.
- [20] A. Veloso-Fernández, L. Ruiz-Rubio, I. Yugueros, M. I. Moreno-Benítez, J. M. Laza, J. L. Vilas-Vilela, *Polymers* **2023**, *15*, 3737.
- [21] Y. Hu, S. Tong, Y. Sha, J. Yu, L. Hu, Q. Huang, P. Jia, Y. Zhou, *Chem. Eng. J.* **2023**, *471*, 144633.
- [22] P.-X. Tian, Y.-D. Li, Y. Weng, Z. Hu, J.-B. Zeng, *Eur. Polym. J.* **2023**, *193*, 112078.
- [23] M. A. Rashid, M. N. Hasan, M. A. Kafī, *Heliyon* **2023**, *9*, e16062.
- [24] M. A. Rashid, S. Zhu, L. Zhang, K. Jin, W. Liu, *Eur. Polym. J.* **2023**, *187*, 111878.
- [25] S. Nicolas, T. Richard, J. Dourdan, L. Lemiègre, J.-L. Audic, *J. Appl. Polym. Sci.* **2021**, *138*, 50904.
- [26] C. Fouquey, J.-M. Lehn, A.-M. Levelut, *Adv. Mater.* **1990**, *2*, 254.
- [27] L. Brunsveld, B. J. B. Bolmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071.
- [28] W. G. Skene, J.-M. P. Lehn, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 8270.
- [29] R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, *10*, 14.
- [30] N. Roy, B. Bruchmann, J.-M. Lehn, *Chem. Soc. Rev.* **2015**, *44*, 3786.
- [31] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698.
- [32] C. J. Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman, *Macromolecules* **2010**, *43*, 2643.
- [33] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965.
- [34] M. Capelot, D. Montarnal, F. Tournilhac, L. Leibler, *J. Am. Chem. Soc.* **2012**, *134*, 7664.
- [35] N. J. Van Zee, R. Nicolaj, *Prog. Polym. Sci.* **2020**, *104*, 101233.
- [36] G. M. Scheutz, J. J. Lessard, M. B. Sims, B. S. Sumerlin, *J. Am. Chem. Soc.* **2019**, *141*, 16181.
- [37] Z. P. Zhang, M. Z. Rong, M. Q. Zhang, *Prog. Polym. Sci.* **2018**, *80*, 39.
- [38] M. Podgórski, B. D. Fairbanks, B. E. Kirkpatrick, M. McBride, A. Martinez, A. Dobson, N. J. Bongiardina, C. N. Bowman, *Adv. Mater.* **2020**, *32*, 1906876.
- [39] H. Otsuka, *Polym. J.* **2013**, *45*, 879.
- [40] B. Krishnakumar, R. V. S. Prasanna Sanka, W. H. Binder, C. Park, J. Jung, V. Parthasarthy, S. Rana, G. J. Yun, *Composites, Part B* **2020**, *184*, 107647.
- [41] H. Sharma, S. Rana, P. Singh, M. Hayashi, W. H. Binder, E. Rossegger, A. Kumar, S. Schlögl, *RSC Adv.* **2022**, *12*, 32569.
- [42] Y. Zhu, J.-L. Gao, L.-J. Zhang, Y. Peng, H. Wang, F.-W. Ling, G.-S. Huang, J.-R. Wu, *Chin. J. Polym. Sci.* **2021**, *39*, 201.
- [43] M. Hayashi, *Polymers* **2020**, *12*, 1322.
- [44] J. Zheng, Z. M. Png, S. H. Ng, G. X. Tham, E. Ye, S. S. Goh, X. J. Loh, Z. Li, *Mater. Today* **2021**, *51*, 586.
- [45] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci.* **2016**, *7*, 30.
- [46] M. L. Williams, R. F. Landel, J. D. Ferry, *J. Am. Chem. Soc.* **1955**, *77*, 3701.
- [47] D. J. Lohse, S. T. Milner, L. J. Fetters, M. Xenidou, N. Hadjichristidis, R. A. Mendelson, C. A. García-Franco, M. K. Lyon, *Macromolecules* **2002**, *35*, 3066.
- [48] M. L. Martins, X. Zhao, Z. Demchuk, J. Luo, G. P. Carden, G. Toleutay, A. P. Sokolov, *Macromolecules* **2023**, *56*, 8688.
- [49] B. Krishnakumar, R. V. S. P. Sanka, W. H. Binder, V. Parthasarthy, S. Rana, N. Karak, *Chem. Eng. J.* **2020**, *385*, 123820.
- [50] H. Fang, W. Ye, Y. Ding, H. H. Winter, *Macromolecules* **2020**, *53*, 4855.
- [51] X. Shi, Q. Ge, H. Lu, K. Yu, *Soft Matter* **2021**, *17*, 2104.
- [52] L. Li, X. Chen, K. Jin, M. B. Rusayyis, J. M. Torkelson, *Macromolecules* **2021**, *54*, 1452.
- [53] Y.-Y. Liu, J. He, Y.-D. Li, X.-L. Zhao, J.-B. Zeng, *Ind. Crops Prod.* **2020**, *153*, 112576.
- [54] X. Yang, L. Guo, X. Xu, S. Shang, H. Liu, *Mater. Des.* **2020**, *186*, 108248.
- [55] C. Di Mauro, S. Malburet, A. Graillot, A. Mija, *ACS Appl. Bio Mater.* **2020**, *3*, 8094.
- [56] M. Bergoglio, D. Reisinger, S. Schlögl, T. Griesser, M. Sangermano, *Polymers* **2023**, *15*, 1024.
- [57] Y.-Z. Xu, P. Fu, S.-L. Dai, H.-B. Zhang, L.-W. Bi, J.-X. Jiang, Y.-X. Chen, *Ind. Crops Prod.* **2021**, *171*, 113978.
- [58] T. Liu, C. Hao, L. Wang, Y. Li, W. Liu, J. Xin, J. Zhang, *Macromolecules* **2017**, *50*, 8588.
- [59] C. Ocando, Y. Ecochard, M. Decostanzi, S. Caillol, L. Avérous, *Eur. Polym. J.* **2020**, *135*, 109860.
- [60] Y.-Y. Liu, J. He, Y.-D. Li, X.-L. Zhao, J.-B. Zeng, *Compos. Commun.* **2020**, *22*, 100445.
- [61] X.-L. Zhao, Y.-Y. Liu, Y. Weng, Y.-D. Li, J.-B. Zeng, *ACS Sustainable Chem. Eng.* **2020**, *8*, 15020.
- [62] S. Wang, S. Ma, Q. Li, X. Xu, B. Wang, W. Yuan, S. Zhou, S. You, J. Zhu, *Green Chem.* **2019**, *21*, 1484.
- [63] S. Guggari, F. Magliozzi, S. Malburet, A. Graillot, M. Destarac, M. Guerre, *ACS Sustainable Chem. Eng.* **2023**, *11*, 6021.
- [64] Y. Liu, B. Wang, S. Ma, T. Yu, X. Xu, Q. Li, S. Wang, Y. Han, Z. Yu, J. Zhu, *Composites, Part B* **2021**, *211*, 108654.
- [65] K. Sykam, M. Försth, G. Sas, Á. Restás, O. Das, *Ind. Crops Prod.* **2021**, *164*, 113349.
- [66] W. Yang, Q. Yi, F. Liu, X. Pan, Y. Zeng, *Eur. Polym. J.* **2023**, *196*, 112278.
- [67] L. Zhong, Y. Hao, J. Zhang, F. Wei, T. Li, M. Miao, D. Zhang, *Macromolecules* **2022**, *55*, 595.
- [68] Y. Tao, L. Fang, M. Dai, C. Wang, J. Sun, Q. Fang, *Polym. Chem.* **2020**, *11*, 4500.
- [69] S. Zhang, T. Liu, C. Hao, L. Wang, J. Han, H. Liu, J. Zhang, *Green Chem.* **2018**, *20*, 2995.
- [70] C. Hao, T. Liu, S. Zhang, L. Brown, R. Li, J. Xin, T. Zhong, L. Jiang, J. Zhang, *ChemSusChem* **2019**, *12*, 1049.
- [71] L. Zhou, G. Zhang, Y. Feng, H. Zhang, J. Li, X. Shi, *J. Mater. Sci.* **2018**, *53*, 7030.
- [72] W. Post, A. Cohades, V. Michaud, S. van der Zwaag, S. J. Garcia, *Compos. Sci. Technol.* **2017**, *152*, 85.
- [73] S. Wang, X. Xing, X. Zhang, X. Wang, X. Jing, *J. Mater. Chem. A* **2018**, *6*, 10868.
- [74] S. Ma, D. C. Webster, *Macromolecules* **2015**, *48*, 7127.
- [75] L. Lu, J. Pan, G. Li, *J. Mater. Chem. A* **2017**, *5*, 21505.
- [76] J. Han, T. Liu, C. Hao, S. Zhang, B. Guo, J. Zhang, *Macromolecules* **2018**, *51*, 6789.
- [77] M. Giebler, C. Sperling, S. Kaiser, I. Duretek, S. Schlögl, *Polymers* **2020**, *12*, 1148.



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