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Review of Recyclable Bio-based Epoxy Resins with Dynamic Chemical Bonds

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ABSTRACT

Epoxy thermosetting resins are usually reliant on fossil fuel-based resources, commonly diglycidyl ether bisphenol A (DGEBA) type epoxy monomers. Most raw materials of these thermoset resin are toxic to the health of human, and their eternal cross-links make them difficult to reuse and recycle. To alleviate concerns about the environment and human health, it is an effective way to design new bio-based epoxy thermosetting materials to replace petroleum based thermosetting materials. The introduction of cleavable and dynamic bonds for bio-based thermosetting materials can also realize the recycling of bio-based epoxy resin. In this way, the damaged thermosetting materials can be recovered to prolong their service lifetime and reduce the thermosetting waste. This review article aims to outline the latest improvements in intrinsically recyclable bio-based epoxy thermosetting materials. This review first describes the synthesis method of recyclable bio-based epoxy, then reviews the structure, recyclable and other properties of bio-based epoxy containing different dynamic bonds, and finally summarizes the challenges and opportunities for the recyclable bio-based epoxy.

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1. Introduction

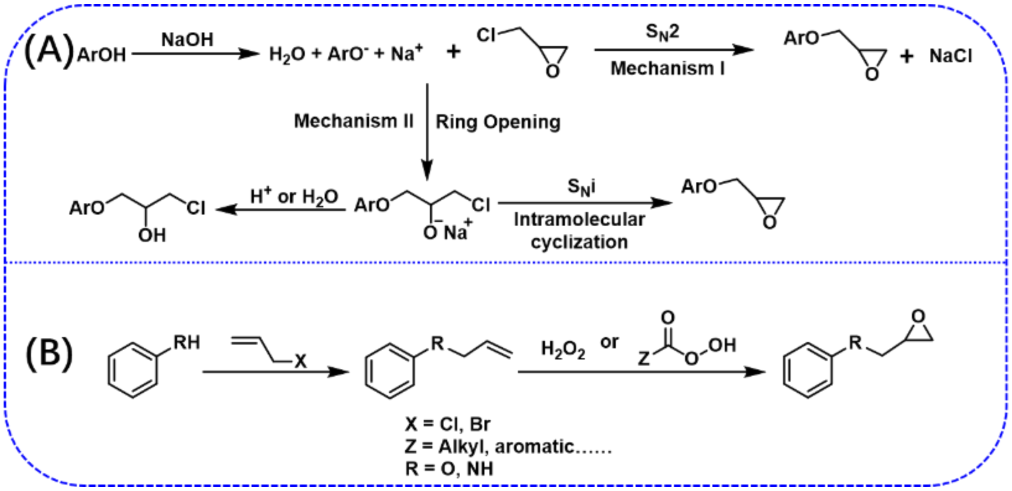
Epoxy monomer refers to linear organic polymer compounds containing two or more epoxy groups in their molecules [1-4]. However, after crosslinking reaction between epoxy monomer and curing agent, a three-dimensional network polymer with insoluble and infusible properties can be generated [5-7]. The synthesis of epoxy resin began in the 1930s and industrialization began in the late 1940s [7]. In recent years, the categories and production of epoxy resin have been increasing year by year. Due to its strong bonding performance, excellent mechanical properties, chemical resistance, weather resistance, good electrical insulation, and dimensional stability, epoxy resin has become one of the main matrices for polymer based composite materials [7-9], widely used in industrial sectors such as machinery, electrical machinery, chemical industry, aerospace, shipbuilding, automotive, and construction [10-12].

In recent years, bio-based epoxy resins with excellent properties have been prepared from magnolol, eugenol, casposol and so on [13-29]. However, it is precisely because epoxy resin has the characteristics of being insoluble and non melting after curing that a large amount of discarded epoxy resin based composite materials are difficult to degrade and recycle [7-9]. The resulting environmental pollution and resource waste have become prominent problems that hinder the application and development of epoxy resin materials. Usually, discarded epoxy resin materials are treated by incineration and landfill, causing serious environmental pollution and resource waste [30-32]. Especially traditional epoxy resins mostly use bisphenol A disrupting endocrine as the raw material [10, 33, 34]. The deposition of bisphenol A in soil and rivers poses a threat to human health. In addition, carbon fiber/epoxy resin composite materials can be directly mechanically crushed through physical methods and used as fillers, but the mechanical properties of the crushed carbon fiber composite materials are poor, and the added value of recycled products is low [35-37]. In order to better recover and utilize carbon fibers with excellent performance and high cost, thermal decomposition and supercritical/subcritical solvent decomposition methods can be used to recover carbon fibers, but their degradation conditions are harsh and the cost is high.

Recently, many researchers have introduced dynamic bonds into bio-based epoxy networks and designed biodegradable and recyclable thermosetting resins. Due to the presence of these dynamic bonds, thermosetting epoxy networks can be decomposed into monomers or oligomers under mild conditions. After being processed through extrusion molding, injection molding, and other processes, it can be reused [30]. The development of this bio-based epoxy resin with dynamic bonds not only extends the service life of the material and reduces the generation of waste plastics, but also reduces the dependence of thermosetting materials on non-renewable materials, resulting in lower carbon emissions. Additionally, the extraction of raw materials for bio-based resins from plants also contributes to the advancement of the agricultural industry to some extent [35]. This article mainly reviews the synthesis, performance, and degradation mechanism of bio-based epoxy networks with dynamic bond structures such as disulfide bonds, Schiff base bonds, acetals, ester groups, and boron ester bonds.

2. Synthesis Methods of Recyclable Bio-based Epoxy Resin

The synthesis of recyclable bio-based epoxy monomers is similar to that of commonly used epoxy monomers as shown in Scheme **1**. One approach to obtain the bio-based epoxy monomers is the glycidylation reaction between plant phenols and excess ECH using a phase transfer catalyst in alkaline conditions (Scheme **1A**). In this method, polyphenol intermediates containing dynamic chemical bonds, such as imine bonds, disulfide bonds, etc., are usually synthesized first, and then react with ECH. This method is most commonly used for the synthesis of inherently recyclable bio-based epoxy monomers. Another method to the preparation of bio-based monomers is the peroxidation of a carbon-carbon double bond in biomass employing the H2O2 or stronger oxidative reagents such as m-chloroperbenzoic acid (m-CPBA) (Scheme **1B**) [38]. This method is often used to prepare recyclable bio-based epoxy monomers from biomass containing C=C double bonds. In addition, the introduction of bio-based epoxy curing agent with dynamic covalent bonds or the formation of reversible dynamic covalent bonds (such as ester bonds) during the curing process are also valid methods to prepare recyclable bio-based epoxy resins [7].



Scheme 1: Synthesis of epoxy resins from phenolic compounds *via* glycidylation reaction (**A**) and double bond oxidation (**B**).

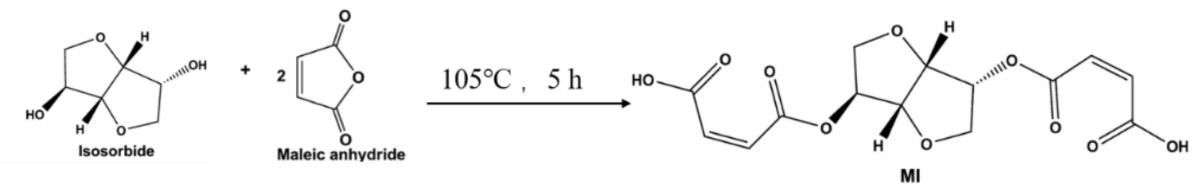
3. Structures of Recyclable Bio-based Epoxy Resin

3.1. Ester Bonds

The ester bond is a reversible covalent bond that is unstable under high temperature, acidic or alkaline conditions [39-47]. In the high temperature environment, ester bond of C-O bond reptures caused by ester exchange reaction [48-59]; In acidic or alkaline environments, acids or bases can catalyze the hydrolysis of esters [60-64]. The epoxy resin can be degraded under certain conditions by introducing ester bond structure into the molecule.

3.1.1. Hydrolyze

The carboxylic acid produced by hydrolysis of ester bond under alkaline conditions will neutralize with base to form carboxylate, so this process is irreversible, and also makes the epoxy resin containing ester bond have better degradation effect under the catalysis of base [60-64]. For example, Ma *et al*. synthesized a dicarboxylic acid oligomer (MI) from the melt reaction between isosorbide and maleic anhydride as shown in Scheme **2**. The dicarboxylic acid oligomer, MI, was used as a cross-linker for epoxidized sucrose soyate (ESS). The thermosetting resin (EMI1) could be degraded rapidly and completely dissolved in 1 M NaOH aqueous solution in 12 min at 50 ℃. Instead, the thermosetting resin was stable in 1 M HCl aqueous solution, as shown in Fig. (**1**) [65].



Scheme 2: Synthetic Route of Maleic Anhydride-Isosorbide Trimer (MI).

Similarly, Mariana Allasia *et al*. reported that fully green epoxy thermosets were synthesized by a catalyst-free curing process from epoxidized soy oil (ESO) and a series of naturally occurring dicarboxylic acids (DCAs) as shown in Scheme **3** [66]. ESO is well-cured by the natural DCAs in the absence of any catalyst. All materials showed similar degradation behavior with good thermal stability. Due to the ester bonds connecting DCAs with ESO and most of these groups present in the triglyceride molecule would be degraded, the ESO-based thermosets could be dissolved in an alkaline medium. Dissolve these epoxy resins in a 1M NaOH aqueous solution. It can be observed that E-C10 completely degraded after 42 hours, while E-C4 and E-C6 lost 75% and 93% of their mass respectively at the end of the experiment. E-C19 was degraded completely after 66 hours. In addition, the thermosets can be readily attacked and degraded by lipases secreted by fungi and bacteria found naturally in the soil.

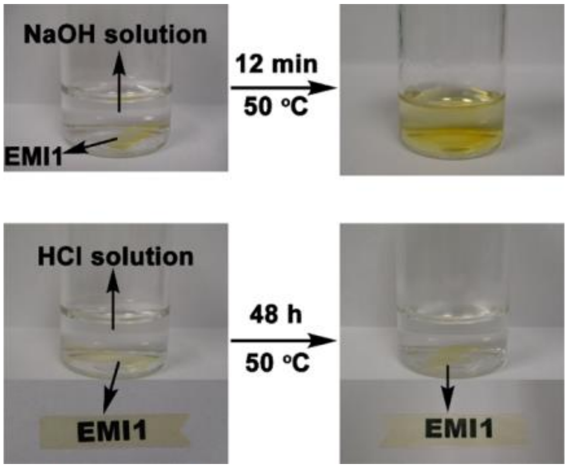
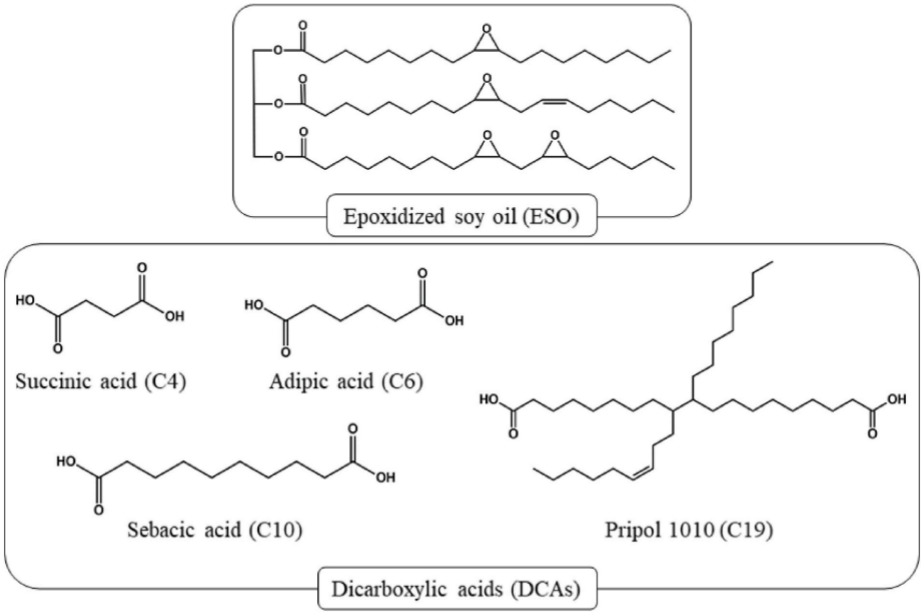


Figure 1: Appearance of EMI before and after immersing in 1 M NaOH aqueous solution (top) or 1 M HCl aqueous solution (bottom). Adapted with permission from ref. [65]. Copyright 2016 American Chemical Society.

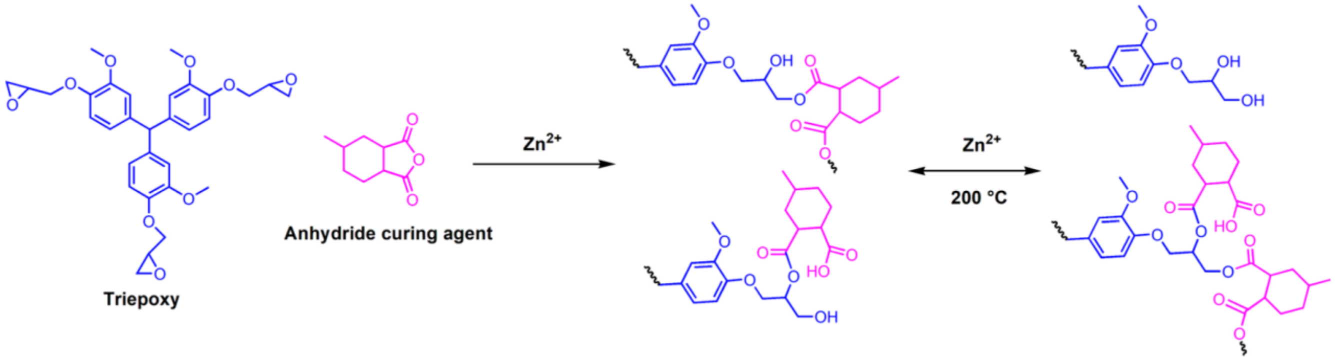


Scheme 3: Chemical structure of ESO and the explored DCAs.

3.1.2. Transesterification

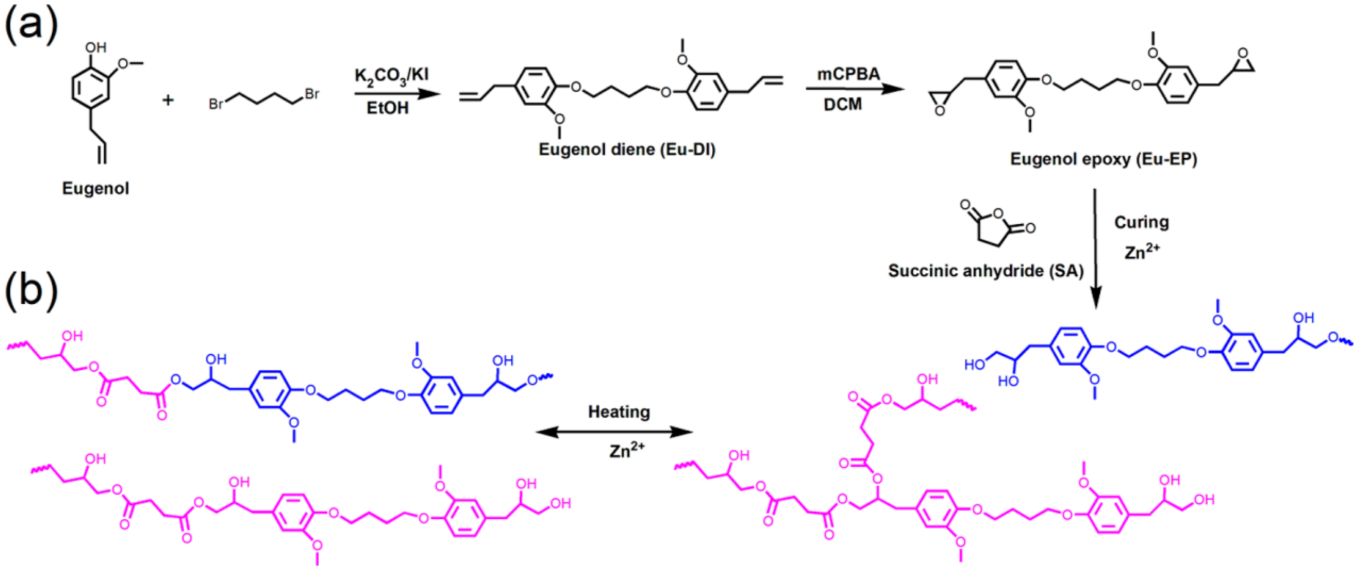
In a cross-linked polymer network, the hydroxyl group produced by the ring-opening reaction of the epoxy resin can undergo dynamic transesterification with the ester bond at high temperatures (>150°C), allowing the material to have multifunctional properties such as shape change, repair and reprocessing [48-59]. At high temperature, the cross-linked network reacts, and the strain-induced stress promotes the debonding of weak dynamic bonds and the movement of chain segments, resulting in transesterification reaction, leading to rapid relaxation. These reactions result in the rearrangement of the cross-linked network and confer the repairability of the material. Epoxy/acid or epoxy/acid anhydride curing system is widely used in industry to achieve transesterification reaction, and excessive zinc salt is used to catalyze the transesterification reaction. In industrial production, the stoichiometric ratio of epoxy resin to anhydride is usually 1:0.7 to 1:1. However, to achieve excellent crack healing and reprocessing properties, epoxy and anhydride are often formulated by stoichiometric ratios of 1:0.5 [67].

For example, Tuan Liu *et al*. synthesized a triepoxy (TEP) with renewable lignin-based vanillin and guaiacol as raw materials. TEP and anhydride (4-Methylcyclohexane-1,2-dicarboxylic anhydride, MHHPA) were reacted at different stoichiometric ratios (R = epoxy/anhydride) as shown in Scheme **4** [68]. The epoxy vitrimer materials were prepared by the curing reaction between TEP and an anhydride, which not only has high T_g (>180°C) and mechanical properties but is equipped with effective heat-activated stress relaxation and self-healing properties. The sample with surface cracks was placed between two metal plates at 220 ℃. The width of the crack on the cured TEP with R = 1/1 (TEP-1) decreased for over 70% in just 5 min. TEP with R = 1/0.5 (TEP-2) which was slightly pressed under a hot press at 220 ℃ that the width of the crack decreased over 90% in just 5 min. $Zn(acac)_2$-H_2O was used to catalyze the curing reaction and also served as the catalyst for subsequent transesterification in the formed crosslinked material at elevated temperatures.



Scheme 4: Curing Reaction of TEP and Anhydride and the illustration of Dynamic Transesterification Reactions (TERs) in the Cross-Linked Network Structure.

Tuan Liu *et al*. synthesized eugenol-based epoxy resin (Eu-EP) using eugenol as raw material by two-step procedure. Succinic anhydride (SA) mixed to react. Zinc acetylacetonate was chosen to catalyze the curing reaction and also used as the catalyst for subsequent transesterification in the formed material. The curing reaction of Eu-EP/SA results in the formation of ester bonds and hydroxyl groups, which could undergo transesterification bond exchange reactions (TERs) at hyperthermia (Scheme **5**) [67]. In this process, a recombination of the cross-linked covalent network resulting from a thermally induced dynamic exchange reaction occurs. Eu-EP/SAs can be recovered by physical and chemical methods. Eu-EP/SAs can be decomposed in ethanol at 160 ℃ for chemical recovery. The decomposed polymer can be transformed into a new thermosetting polymer after being exposed at 190℃ for 3 hours. In addition, Eu-EP/SAs can physically recover the debris by simple hot pressing at 200 °C (when the molar ratio of epoxy/anhydride of Eu-EP/SAs is 0.5).

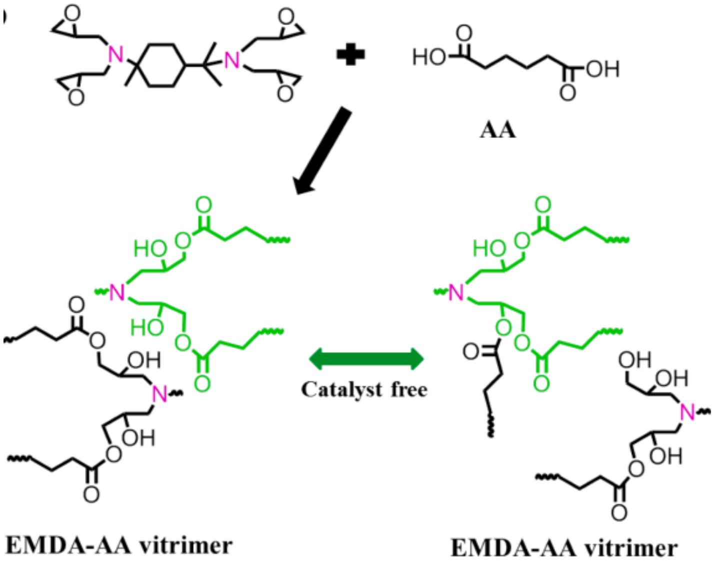


Scheme 5: (**a**) Synthetic Route of Eugenol Epoxy (Eu-EP); (**b**) Curing Reaction of Eu-EP and SA and illustration of Heat Induced Transesterification Reactions (TERs) in the Presence of Zinc Catalyst.

3.1.3. Amidation Reactions

It's typical that soybean oil (SO) derivatives are usually cured by amine or anhydride hardeners. Importantly, the amine-based hardeners require shorter cure times and lower reaction temperatures than anhydrides [69]. Amine curing agents are more extensively used.

For example, Xu *et al*. synthetize a degradable epoxidized menthane diamine-adipic acid (EMDA-AA) vitrimer matrix for carbon fiber reinforced composites (CFRPs) obtained from bio-based menthane diamine and adipic acid (Scheme **6**) [69]. The vitreous network utilizes the self-catalytic effect of tertiary amines in EMDA-AA vitreous to achieve topological rearrangement through ester exchange reactions. In addition, EMDA-AA vitreous matrix resin can undergo acylation reaction with ethanolamine under mild conditions, rapidly degrading into polyols. When the EMDA-AA scratched by a razor is heated in a 180 ℃ oven for 60 minutes, as shown in Fig. (**2**), its scratches are almost invisible and the sample completely heals. The topological rearrangement catalyzed by tertiary amine endows EMDA-AA materials with excellent self-healing ability. In addition, they utilized the autocatalysis of tertiary amine to carry out the amidation reaction by Ethanolamine (EA) at 60 ℃ to degrade the network of the EMDA-AA-CF composite. EA enters the polymer network, causing the matrix to expand. Amino and ester groups undergo acylation reaction under the catalysis of tertiary amine in the EMDA-AA matrix, resulting in partial degradation of the EMDA-AA network. After 30 minutes, all ester groups in the matrix are degraded by EA. The mechanism of this process is shown in Scheme **7**.



Scheme 6: the curing reaction of the EMDA-AA vitrimer.

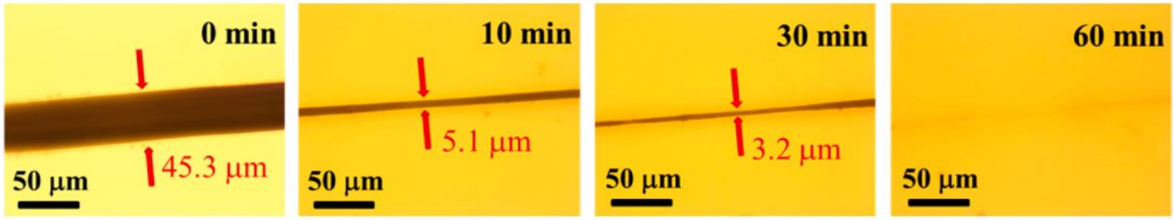
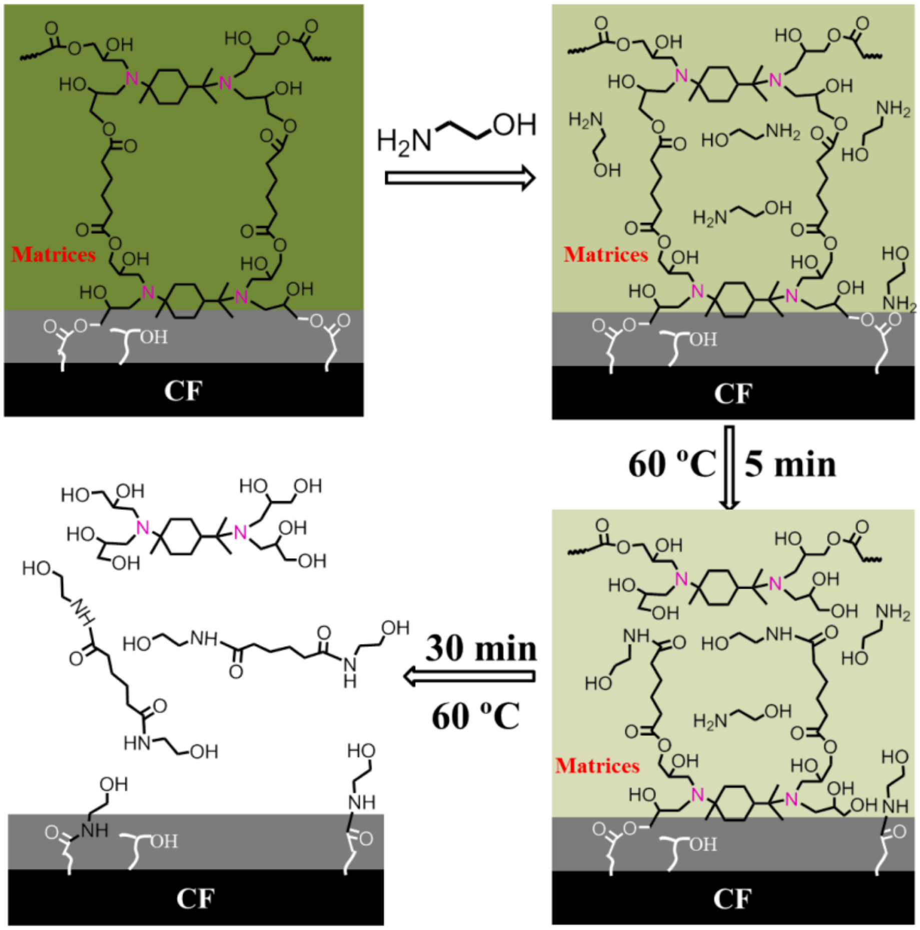


Figure 2: Healing of EMDA–AA with different heating times. Adapted with permission from ref. [69], Copyright 2022, Elsevier.

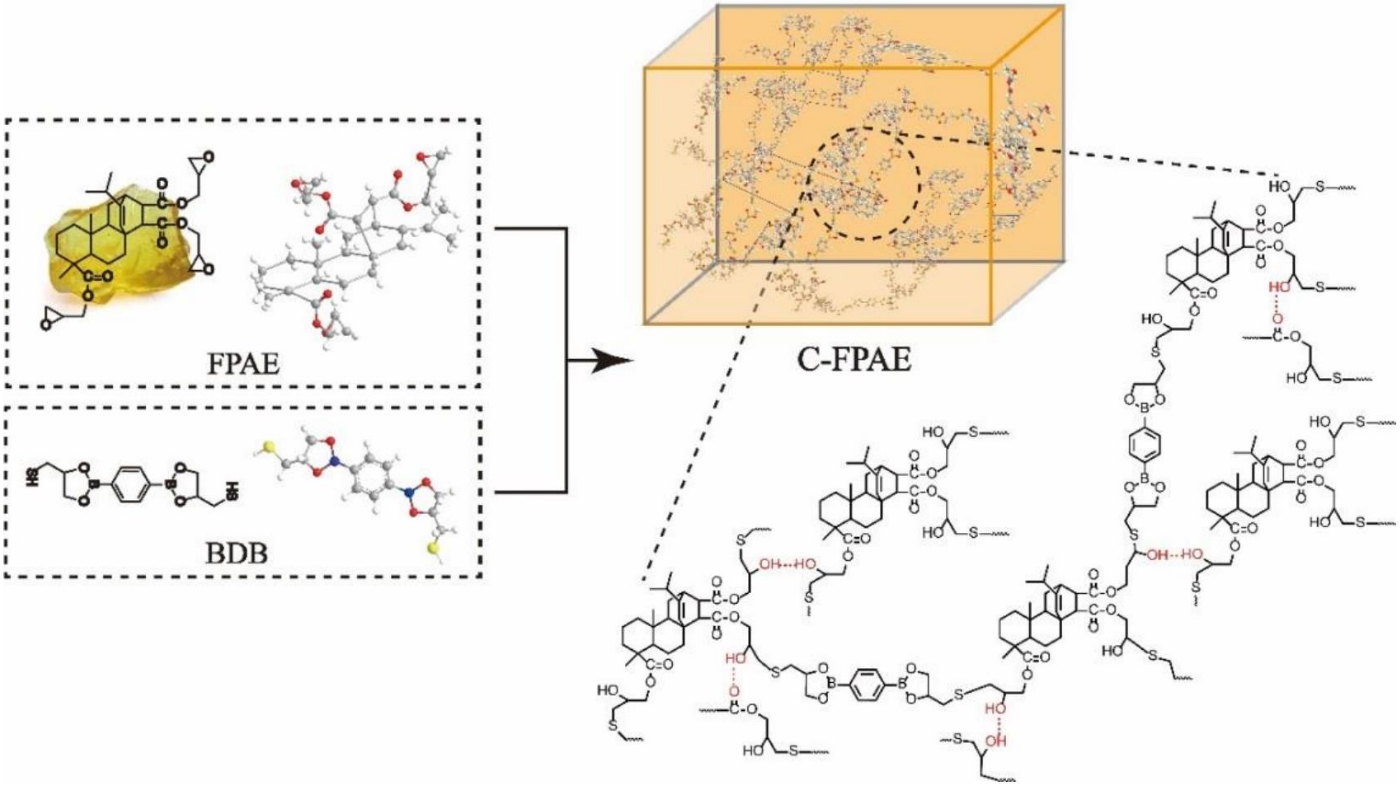
3.2. Borate Ester Bonds

Borate ester bond (B-O-C), as a dynamic reversible bond, has attracted much attention due to its mild alcoholysis conditions. Boric acid and its derivatives can be complexed with alcohols in aqueous solution to form reversible borate ester bonds, whose stability can be adjusted by the pH value or temperature of aqueous solution. Borate ester bonds have the advantage of green degradation at room temperature [70-73]. One side, the boronic ester undergoes an associative transesterification reaction in a permanent crosslinking network, which provides network rearrangement and contributes to a gradual Arrhenius-like viscosity dependence, giving the network the ability to be reshaped in a solid state. Moreover, boronic ester bonds are highly sensitive to reactive oxygen species, and in acidic media with a pH much lower than their pKa, boronic ester bonds are more prone to hydrolysis and cleavage into boric acid and diol [70-73].



Scheme 7: Degradation mechanism of the EMDA-AA-CF composites in EA at 60 ℃.

For example, Zeng *et al*. synthesized a rigid vitrimer monomer yielded by rosin. They used 2,2′–(1,4–phenylene)–bis(4–mercaptan–1,3,2–dioxaborolane) (BDB) as a curing agent reacted with the rosin-derived monomer by one-pot thermally initiated thiol-epoxy click chemistry, producing vitrimers with a framework of a rigid hydrogenated phenanthrene ring(C-FPAE) as shown in Scheme **8** [71]. Due to transesterification of boronic ester bonds, rosin epoxy vitrimer network topologies can be altered, equipped with recycle, self-healing, and shape memory abilities. Cutting the C-FPEA thin sample with a thickness of 0.7 mm using a razor to a width of 117 µm. The cut sample was subjected to a 30 minutes healing treatment at 170 ℃. C-FPEA can recover over 80% with only 30 minutes of healing treatment. Moreover, the C-FPAE strip sample was heated in an oven to 130 ℃ to form a fixed oblique shape, then the temperature drops to room temperature. When the temperature rises again to 130 ℃, the shape returns to its original flat state within 2 minutes. Besides, rosin vitrimer can also be degraded under active oxygen and acidic conditions. C-FPAE powder samples were immersed in a mixed solution of THF/H_2O_2/HCl with different pH at 30 ℃ for 48 h under continuous stirring. Along with the pH decreasing from 6.5 to 0.0, the degradable weight percentages increased from 10% to 90% (Fig. **3**), and the degradation mechanism is shown in Scheme **9**. Therefore, it can be seen that the samples of C-FPAE are more easily degraded in strong acid solutions. Furthermore, C-FPAE exhibit high thermal stability, attributed to the enhanced covalent cross-linker at higher contents of BDB, the improvement of the rosin framework, and the hydrogen bond in the networks.



Scheme 8: Synthesis of a C-FPAE cross-linking network.

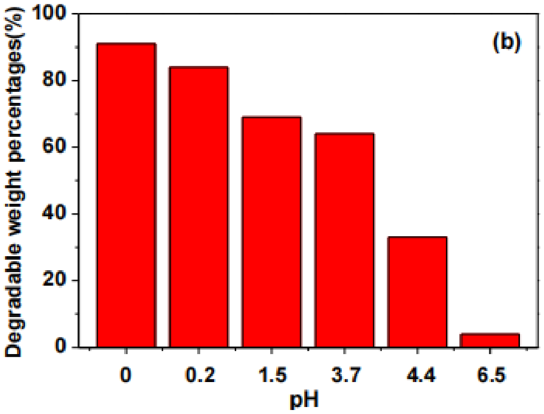
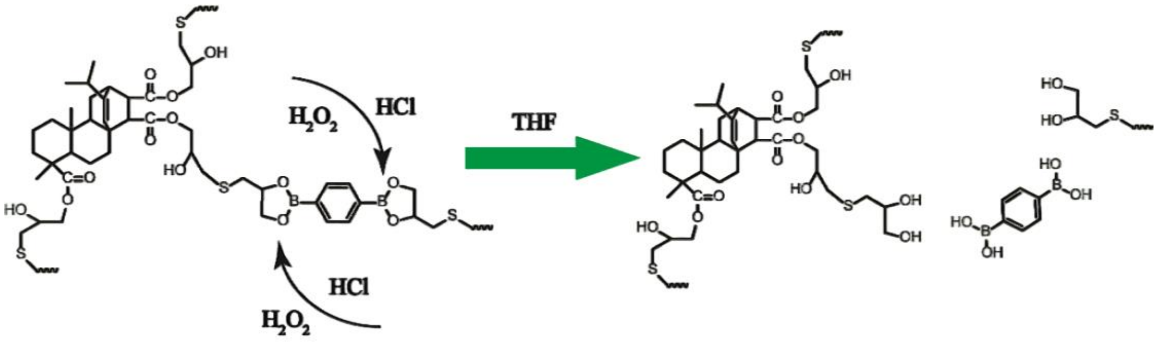
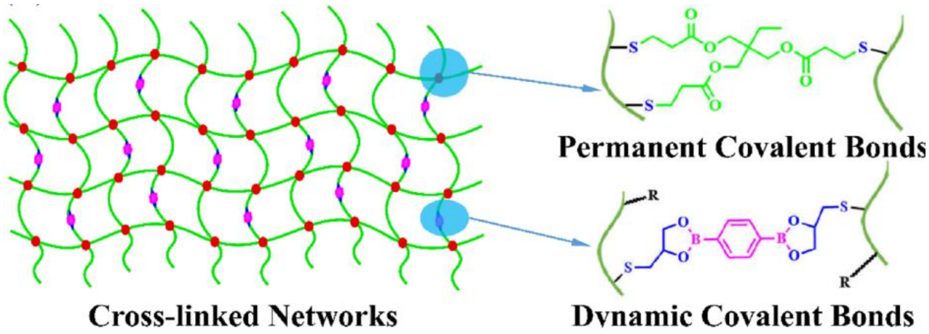


Figure 3: The degradation weight percentage of 20% C-FPAE in mixed solutions with different pH. (20% means that the content of BDB is 20mol%). Adapted with permission from ref. [71]. Copyright 2021, MDPI.



Scheme 9: Schematic representation of C-FPAE degradation.

Hu *et al*. synthesized epoxidized itaconic acid (EIA) through the esterification reaction of itaconic acid (IA) and epichlorohydrin (ECH). The hybrid cross-linked network as shown in Scheme **10** was achieved by thiol-ene reaction, thiolepoxy reaction and free radical copolymerization of double bonds, 1-thioglycerol, trimethylolpropane tris(3-mercaptopropionate) (TPMP), BDB and EIA [72]. Due to the esterification reaction of the borate ester group, this EIA-based epoxy thermosets material showed thermal repair properties. The crack width on the sample coating gradually decreased from 28.4 μm to less than 2.2 μm in just 30 min at 160 ℃ and no external stress. The fractured sample was subjected to further treatment at 160 ℃ and 2 MPa for 1 hour, resulting in a new sample with a tensile strength of 80 MPa (Fig. **4B**), slightly lower than the original sample (89 MPa), indicating that the EIA-based epoxy thermosetting material has excellent processability. The reason is that the covalent cross-linked network can be remodeled at the processing temperature due to the exchange of covalent bonds between the borate ester bonds at high temperatures (Fig. **4A**).



Scheme 10: Preparation of EIA-based epoxy thermosets.

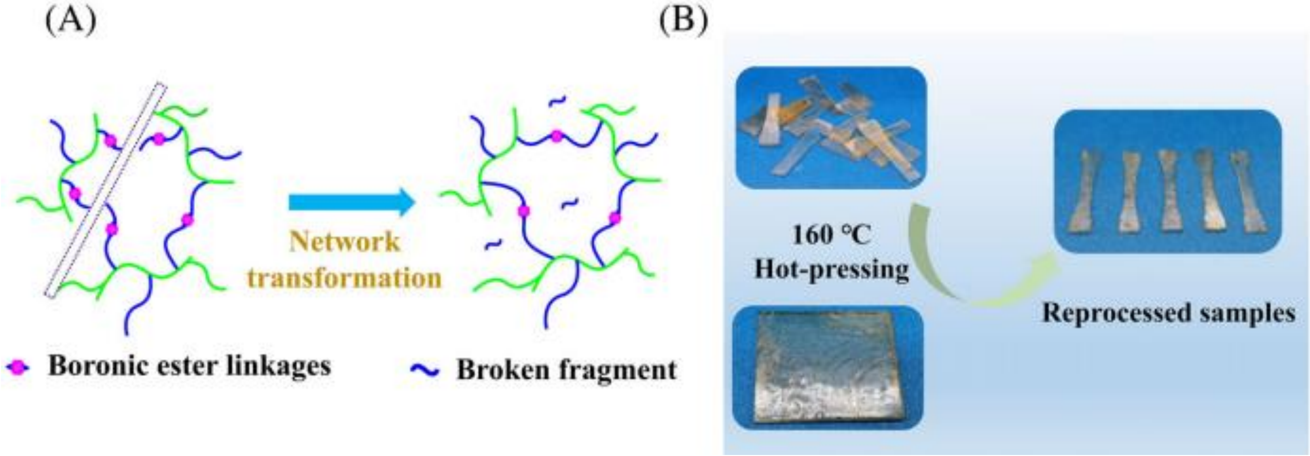
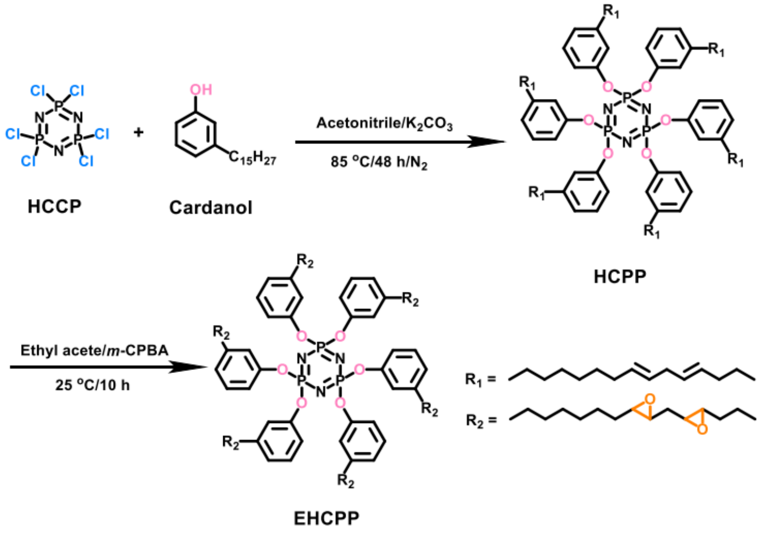


Figure 4: (**A**) The repair mechanism based on the boronic ester linkages; (**B**) The reprocessability ability of sample at 160 ℃. Adapted with permission from ref.

Ke *et al*. synthesized a bio-based epoxy monomer (EHCPP) (Scheme **11**) with hard core structures and multi-arms by cardanol with hexachlorocyclotriphosphazene, epoxidized by m-chloroperoxybenzoic acid (m-CPBA). Then, dynamic boron ester bonds were introduced by curing with BDB to prepared EHCPP-BDB networks. Due to the presence of dynamic reversible boron ester bonds, cardanol-based epoxy polymer showed recyclability. EHCPP-BDB networks cut into small pieces and then remolded to new samples by hot-pressing at 150 ℃ under a pressure of 10 MPa for 10 min [73]. As shown in Fig. (**5b**), EHCPP-BDB could be reshaped into a new coherent and homogeneous sample, due to covalent bond exchange of dynamic boron ester bonds. The reversible mechanism of boron ester in the BDB monomer of the cardanol-based epoxy polymer networks is shown in Fig. (**5a**). In addition, immersing the EHCPP-BDB polymer in 10% NaOH resulted in a 30% increase in the weight of the network. This is because the dynamically reversible boron oxygen bond is hydrolyzed into boric acid in aqueous solution, and then forms borate in the presence of sodium hydroxide.



Scheme 11: Synthetic route of EHCPP.

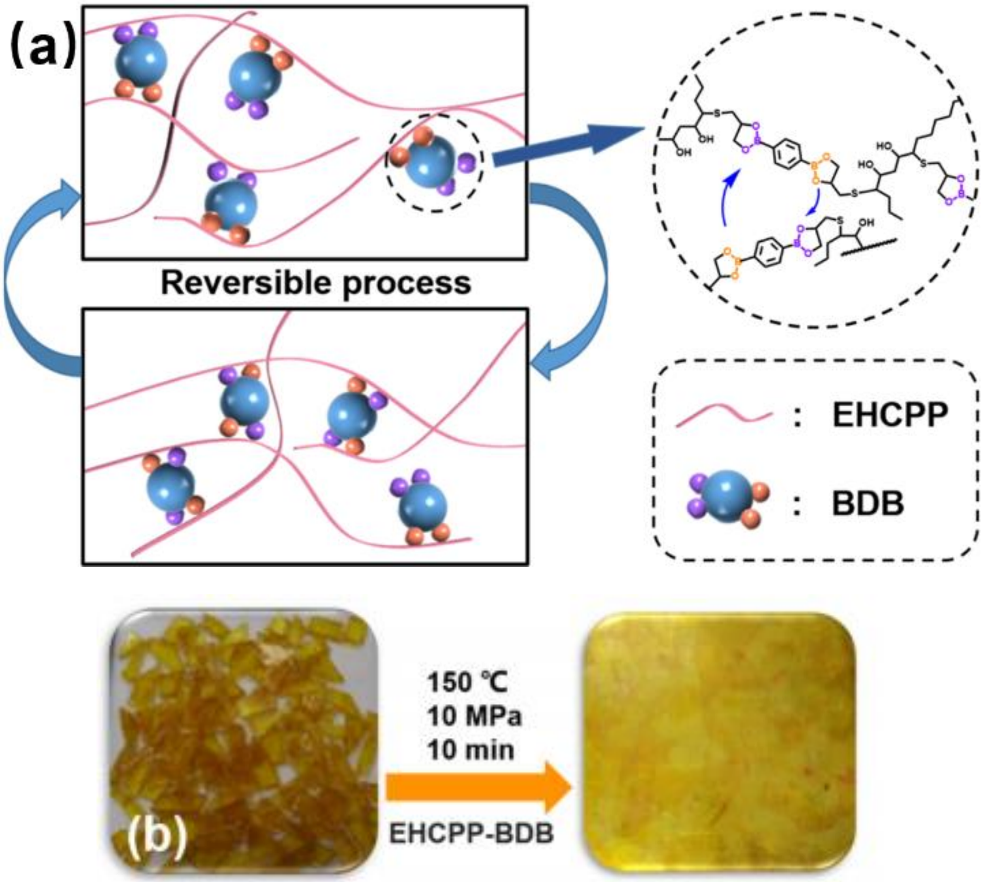


Figure 5: (**a**) Schematic illustration of the reversible mechanism of boron ester in BDB (SH monomer) of the cardanol-based epoxy polymer networks; (**b**) photographs of original and reshaped EHCPP polymer networks. Adapted with permission from ref. [73]. Copyright 2021 American Chemical Society.

3.3. Schiff Bases

Schiff base refers to the compound with the structure of $R_2C=NR'(R'H)$ formed by the addition reaction of aldehyde or ketone with primary amine [74-79]. Schiff base provides a new research way for the degradation of bio-based epoxy due to its unique associate reaction (imine-amine exchange) and dissociation reaction (imine hydrolysis and recombination) [80-85].

Vanillin and syringaldehyde are often used to prepare degradable epoxy resin containing Schiff base because of their CHO groups and good properties. For example, Su *et al*. synthesized bio-based epoxy monomer of DADE containing aldehyde group with vanillin as raw material, and cured with Poly (propylene glycol) bis (2-aminopropyl ether) (D230) to prepared the bio-based epoxy resin of DADE-D230 by in-situ forming Schiff base as shown in Fig. (**6A**). The cross-linked network of DADE-D230 can not only be recycled at 150℃ for 10 min (Fig. **6B**), but also has mechanical properties equivalent to bisphenol A epoxy resin [86]. Zhao *et al*. synthesized an epoxy thermosetting by using vanillin as a raw material by embedding imine bond in epoxy crosslinking network. It has high thermo-mechanical properties, and it can be degraded, recycled and repaired as needed when stimulated by acid, temperature or water. Degradation and recycling involve the hydrolysis and recombination of imine bonds, and the remodeling and repair of thermosetting materials are realized through imine exchange reaction. There is no need for metal catalysts, pressure heating or additional monomer during reprocessing, which greatly reduces the complexity of the reprocessing process [87].

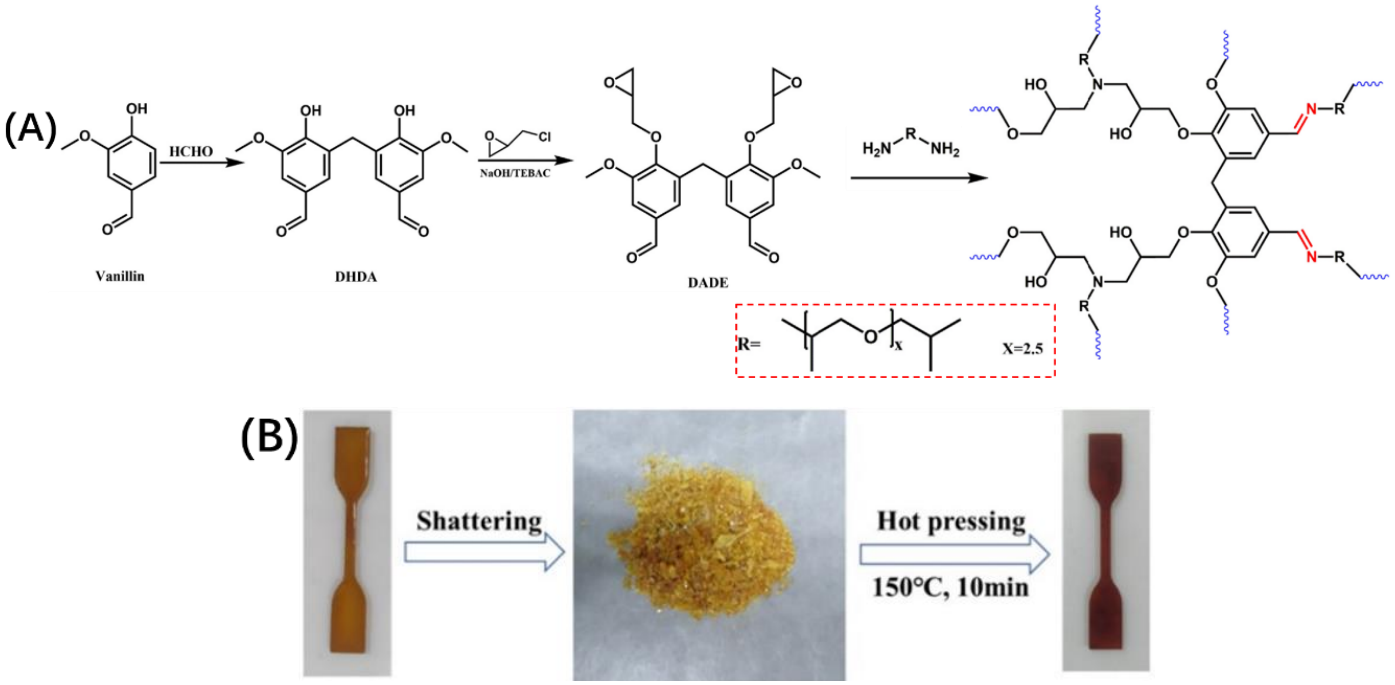


Figure 6: (**A**) Synthetic route of vanillin-derived epoxy monomer of DADE, and the curing mechanism between DADE and D230. (**B**) Reprocessing experiments of DADE-D230 in a hot pressing. Adapted with permission from ref. [86]. Copyright 2020, Elsevier.

The exchange reaction of imine bond endows the material with reprocess-ability, and usually the reprocessing process needs to be carried out at high temperature. Therefore, repeated thermal processing will lead to the oxidation and embrittlement of the material, which will greatly reduce the recycling performance of the material [88], so the fatigue resistance of recyclable bio-based epoxy resin material is important. Based on this, Memon *et al*. synthesized an imine-containing curing agent (IH-VAN) from vanillin and used it to synthesize an epoxy resin. Due to the addition of imine dynamic covalent bond, the cured epoxy resin is reprocessable and degradable. The retention rate of tensile strength of epoxy resin after three times of hot pressing recovery treatment is above 70%, and the degradation products and recovered solvent can be reused to prepare new epoxy resin, realizing complete closed-loop recovery. But its degradation is still dependent on pH and temperature [74]. Yu *et al*. used isophorone diamine (IPDA) as hardener to cure vanillin (Van-Ep) with monoglyceride structure, and prepared vanillin-based epoxy resin (Van-Ep/IPDA). Because of its imine structure, it is degradable in acidic solution. The reworked Van-Ep/IPDA vitrimer shows the same mechanical properties as the original vitrimer even after three times of hot pressing [89]. Geng *et al*. synthesized a bio-based Schiff base polymer from vanillin and a commercial amine crosslinking agent. By introducing dynamic imine covalent bonds into these crosslinked networks, the tensile strength and elongation at break of the obtained polymer can be recovered by more than 70% even after three times of heat recovery treatment, and sometimes even slightly higher. It has self-healing ability, hot reprocessing performance and chemical recoverability under acid hydrolysis. This work provides an important opportunity for designing self-repairing and chemically recyclable vanillin-based monomer polymer materials [90].

Combining the common properties (self-crosslinking, reversibility and rigidity) of Schiff base compounds, it provides new possibilities for designing functional epoxy thermosetting materials. The introduction of Schiff base network not only solves the degradability of bio-based epoxy, but also improves the mechanical properties, coating properties, flame retardant properties and antibacterial properties of the material [91-94]. At high temperature, the internal —CH=N— bonds of the bio-based epoxy containing imine bonds will be rearranged and cyclized, resulting in nitrogen-containing six-membered heterocyclic compounds. These heterocyclic compounds can make polymer chains self-crosslink, thus enhancing the char-forming ability of materials and improving the flame retardant properties of materials. It provides a new possibility for biodegradable bio-based epoxy resin to have flame retardancy. For example, Wang *et al*. used phosphorus oxychloride and vanillin as raw materials to synthesize a new type of trialdehyde monomer of TFMP (Fig. **7A**), and then reacted with three different diamines and TFMP through Schiff base to obtain Schiff base covalent adaptable networks (CANs). The films were cut into small pieces and then sandwiched between two steel plates, each covered with two layers of polyimide films. They were subsequently hot-pressed at 180℃ under a pressure of 15mpa for 10 minutes (TFMP-M), 8 minutes (TFMP-P), or 2 minutes (TFMP-H). After cooling to room temperature, the regenerated film is obtained. It not only can be reprocessed (Fig. **7B**), but also has high LOI (30%) and flame retardancy passing V0 level (Fig. **7C**), which solves the problems of recyclability and flammability of thermosetting materials at the same time for the first time [91]. Similarly, Xie *et al*. used aromatic syringaldehyde to react with 1,4-butanediamine (BDA) to prepare a bio-based epoxy prepolymer (SH-BDAEP) containing imine bond, and then cured with 4,4'- diaminodiphenylmethane (DDM) to prepare a bio-epoxy thermosetting resin SH-BDAEP/DDM. The introduction of imine bond makes it completely degradable in acidic medium. In addition, the limiting oxygen index (LOI) is 39.6%, and the flame retardant level is as high as V0. Its excellent fire resistance, mechanical properties and acid-catalyzed degradation are far superior to ordinary bisphenol A epoxy thermosetting resin [23].

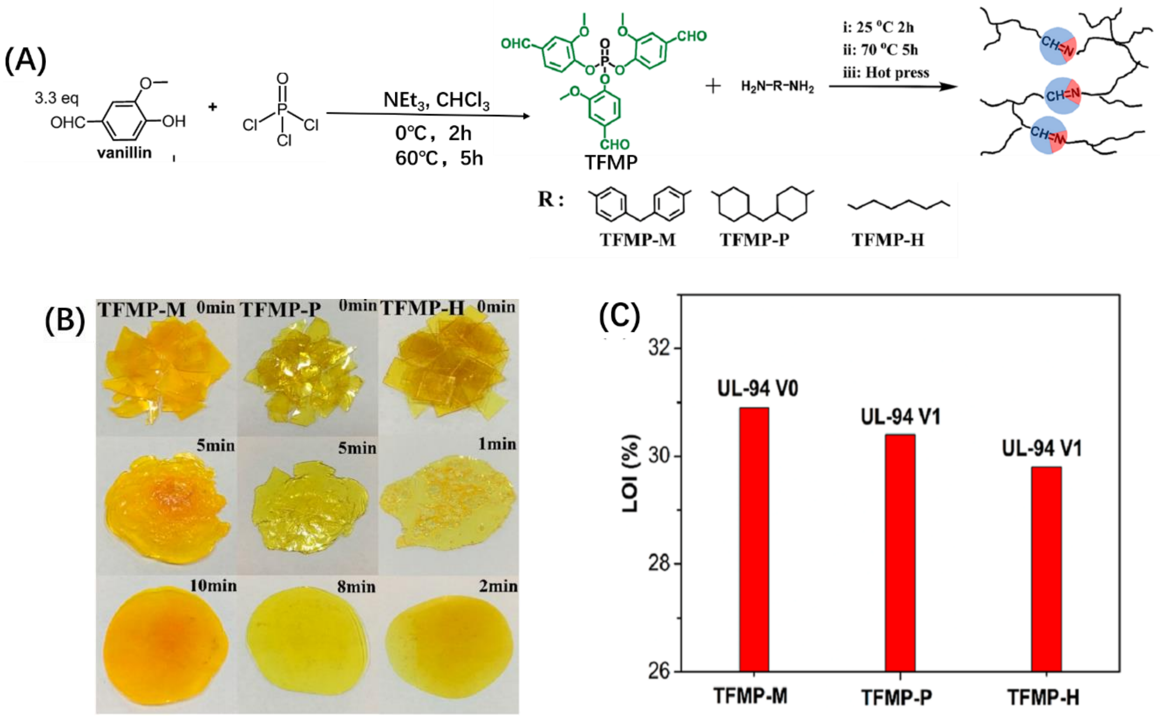


Figure 7: (**A**) Synthetic Route of TFMP and preparation of Schiff Base CANs, (**B**) Reprocess of Schiff base CANs at different times at 180°C under 15 MPa pressure, and (**C**) LOI and UL-94 rating of CANs. Adapted with permission from ref. [91]. Copyright 2018 American Chemical Society.

The use of a dynamic covalent bond has many limitations in dynamics, and it is often necessary to introduce another covalent bond synergy. Guo *et al*. studied the preparation of vanillin vitrimer by introducing dynamic disulfide bonds into the Schiff polymer with dialdehyde and amine monomers derived from vanillin as raw materials. The addition of disulfide bonds shortens the relaxation time and improves the mechanical properties of the material while maintaining the degradable and recyclable chemical properties. In addition, the addition of Schiff base also gives the coating properties of the material (acid and alkali resistance, strong adhesion and wear resistance, etc.) [92]. Although the addition of Schiff base will give the coating performance of the material, its sensitivity to water will reduce the service life of the coating. In order to solve this problem, Liu *et al*. synthesized Van-OH curing agent with dynamic imine bond from vanillin derived from lignin and m-diamine. Subsequently, DGEBA was cured to obtain Van-EP bio-based vitrimers (Fig. **8A**). After soaking in water for 15 days, the material still maintained high mechanical properties (70.5Mpa, 79.1 Mpa; before soaking; See Fig. **8B** for details). This is because the internal network of the material is highly crosslinked, which makes the material have excellent water resistance compared with other imine-based materials [93]. On the premise of solving the problem of water resistance, the addition of Schiff base makes it possible for bio-based epoxy resin to have antibacterial properties. For example, Xu *et al*. synthesized diphenyl ring conjugated Schiff base dioxygen monomer and crosslinked it with 4,4- diaminodiphenylmethane. The obtained epoxy resin not only has acidity, temperature degradation and water resistance, but also has a killing rate of 91% for *Escherichia coli* [94]. The addition of Schiff base provides an important foundation for the development of degradable functional materials.

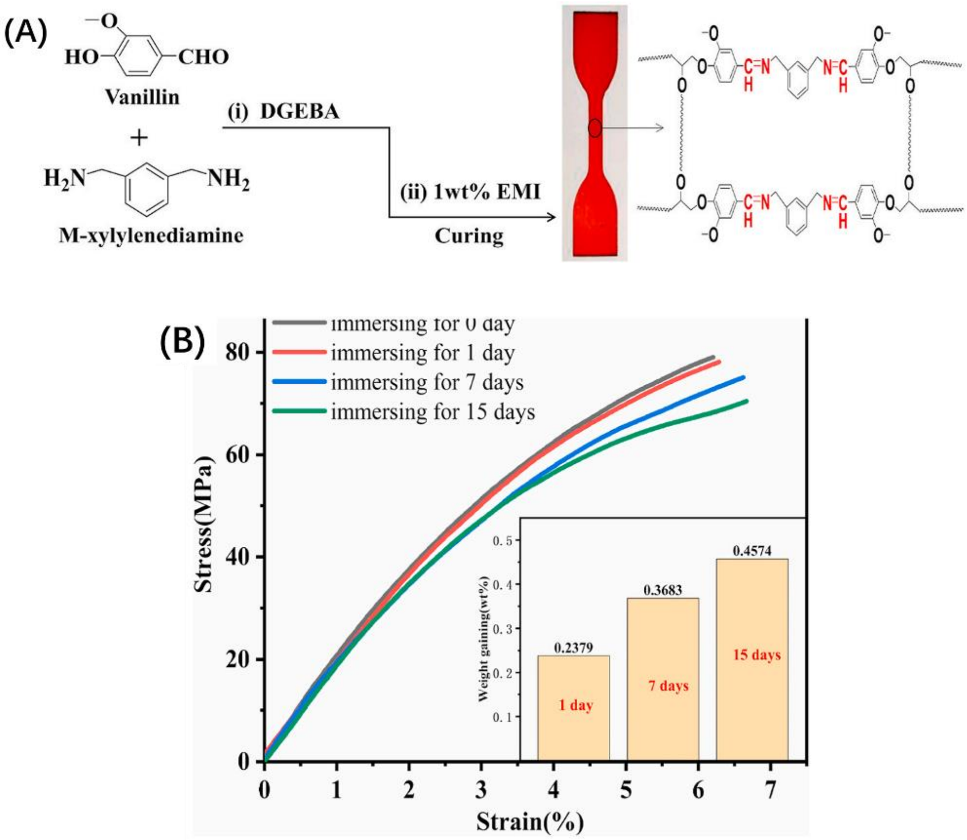


Figure 8: (**A**) Synthetic route of Van-EP bio-based vitrimer, (**B**)Typical stress-strain curves and weight gaining of Van-EP bio-based vitrimers after immersed in water for different times. Adapted with permission from ref. 93. Copyright 2020, Elsevier.

Carbon fiber reinforced composites (CFRP composites) based on epoxy thermosetting are widely used in aerospace, automobile transportation and other fields because of their excellent mechanical properties. However, the permanent cross-linking structure inside the traditional epoxy resin makes it not malleable, so its composite materials can not be processed any more [35-37]. Although most degradable composites are of great scientific significance, they have some defects, such as complex process and damage of recycled carbon fiber, which directly or indirectly limit their industrial application. How to recover carbon fiber from epoxy resin matrix effectively and without damage under mild conditions is still a challenge [84]. The reversible exchange reaction of imine bond provides a new research idea for this. For example, Wang *et al*. used formyl monofunctional epoxy resin and diamine-type PACM (4,4 '-methylene dicyclohexylamine) as raw materials to prepare high-performance Schiff base epoxy resin of MB-PACM for the first time by a simple method of in-situ generation of Schiff base during the curing process of epoxy resin. The CFRP composite prepared with this matrix can be degraded at room temperature and acidic conditions, and the recovered carbon fiber can still maintain the surface morphology and mechanical properties of the original carbon fiber. See Fig. (**9**) for details [80]. Liu *et al*. synthesized a bio-based epoxy vitrimer (Gte-VA) with triglyceride ether (GTE) and imine-containing hardener (VA) as raw materials. The specific structure and synthetic route are shown in Scheme **11**, and the CFRP composites prepared with it can also realize the full recycling of carbon fibers [95]. Liu *et al*. used vanillin, m-diamine and 1,6- hexamethylenediamine as raw materials to synthesize two kinds of dynamic imine bond curing agents, and cured DGEBA respectively to prepare two kinds of bio-based imine epoxy resins. The recyclable carbon fiber reinforced polymer composites prepared by these two kinds of vitrimer can be completely degraded under weak acid conditions, realizing the lossless recovery of carbon fiber composites [84]. The introduction of imine bond not only realizes the recovery of carbon fiber under mild conditions, but also provides the possibility for the full recycling of carbon fiber.

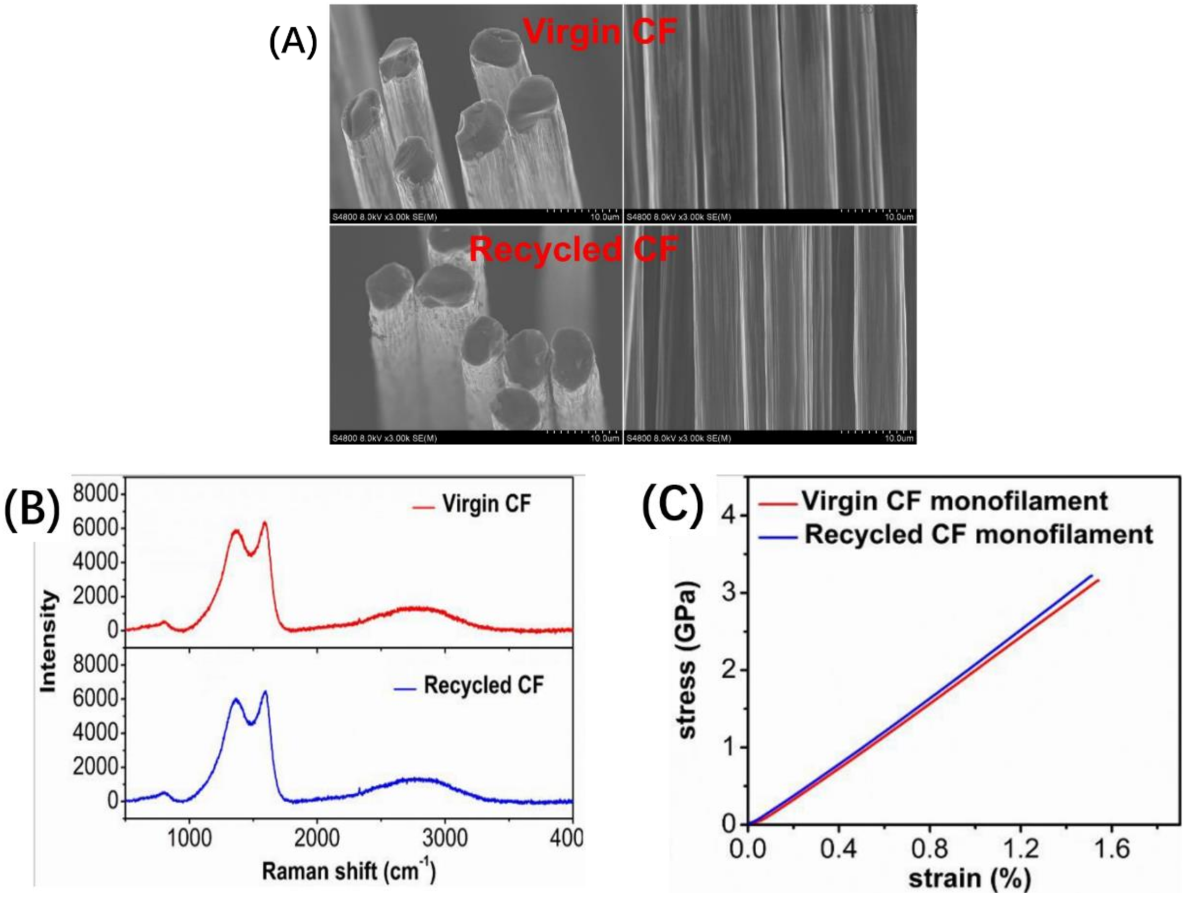
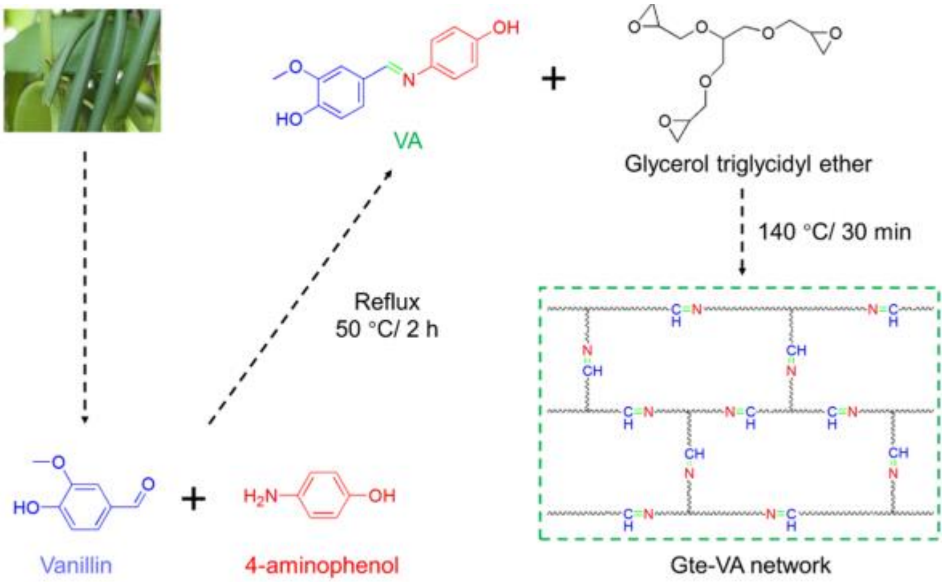


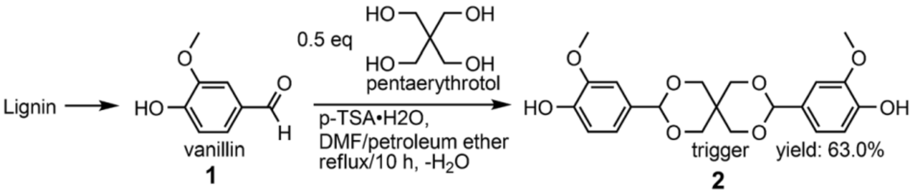
Figure 9: (**a**) The surface morphology of the virgin and recycled CF; (**b**) Raman spectra of the virgin and recycled CFs; (**c**) representative tensile stress-strain curves of the virgin and recycled CF monofilaments. Adapted with permission from ref. [80]. Copyright 2019 The Royal Society of Chemistry.

3.4. Acetal Structure

Aldehydes or ketones can react with polyols under acidic conditions to form an acetal structure, which is stable under alkaline conditions, but will be broken down into the original aldehydes (ketones) and alcohols under acidic conditions. The introduction of acetal structure in the epoxy resin network can make the epoxy resin have degradable properties. Moreover, due to the high rigidity of the acetal structure, the resin introduced with this structure has excellent thermal and mechanical properties [96-99]. For example, Ma *et al*. synthesized a vanillin-based helical diacetal structure using vanillin and pentaerythritol. The synthetic route is shown in Scheme **12** below [96]. It reacted with epichlorohydrin to produce epoxy resin monomer, and then cured with isophorondiamine to produce thermosetting resin. This epoxy resin can be completely dissolved in 1M HCl (acetone/H_2O=9/1, v/v) solution within 183 minutes at 23 ℃. At 50 ℃, the degradation time is reduced to 19 min, and the degradation time can be achieved in 11 min and 9 min, respectively, in solutions with concentrations of 0.5 M and 1M HCl.



Scheme 11: Synthetic route of VA and the preparation of epoxy vitrimer.



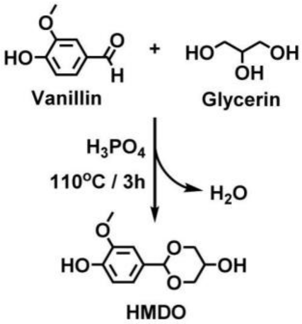
Scheme 12: Synthetic route to spiro diacetal triggered from a renewable resource.

Binbo Wang *et al*. synthesized a bisphenol (HMDO) with acetal structure by using vanillin and glycerol. The synthetic route of HMDO is illustrated in Scheme **13**. HDMO reacts with epichlorohydrin and then cured with 4,4'-diaminodiphenylmethane (DDM) to form a bio-based epoxy system (DGHMDO-DDM), which showed much higher mechanical properties (stronger and tougher) and comparable thermal properties relative to a commercial high-performance counterpart based on bisphenol A (BPA) [100]. As shown in Scheme **14**, HDMO can be hydrolyzed under acidic conditions, so HDMO-based epoxy resins can also be degraded. A DGHMDO-DDM sample with dimensions of 8 mm × 8 mm × 1 mm was completely destroyed after being immersed in 0.1 M acetone hydrochloride/water (9/1, v/v) at 50 ℃ for 5.5 h (Fig. **10**).

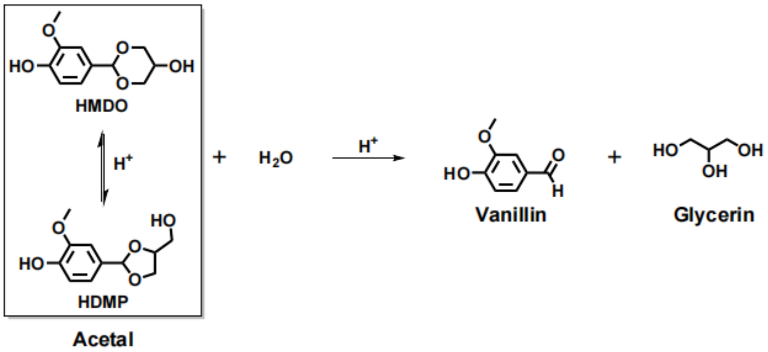
3.5. Disulfide Bonds

The dynamic reaction of disulfide bonds involves many mechanisms. When the external force causes the mechanical fracture of disulfide bonds, sulfhydryl radicals are generated and can be quickly exchanged with other disulfide bonds, resulting in the self-healing or reprocessing of cross-linked networks. The dissociation property of disulfide bonds provides a new solution for the degradation of epoxy resin under reducing or alkaline conditions [101].

Epoxidized vegetable oil (evo), mainly including epoxidized linseed oil (ELO) and epoxidized soybean oil (ESO), have the structures as shown in Scheme **15**. Vegetable oil is considered as one of the most important renewable substitutes because of its easy-to-obtain, cheap and sustainable characteristics. The unique triglyceride structure and three soft long fatty acid chains with 8 to 24 carbon atoms and 0 to 7 carbon-carbon double bonds make vegetable oil a good platform for developing high value-added monomers and polymers. A multifunctional vegetable oil-based epoxy resin was developed by introducing epoxy groups into unsaturated parts of vegetable oil and then curing with various hardeners (such as amine, anhydride, bisphenol and acid). Functional bio-based epoxy resin extracted from renewable vegetable oil can effectively alleviate various disadvantages caused by excessive dependence on petroleum-based monomers [102].

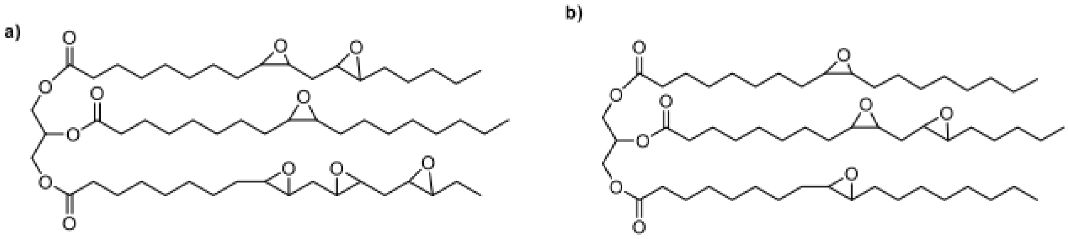


Scheme 13: Synthetic route of HMDO.



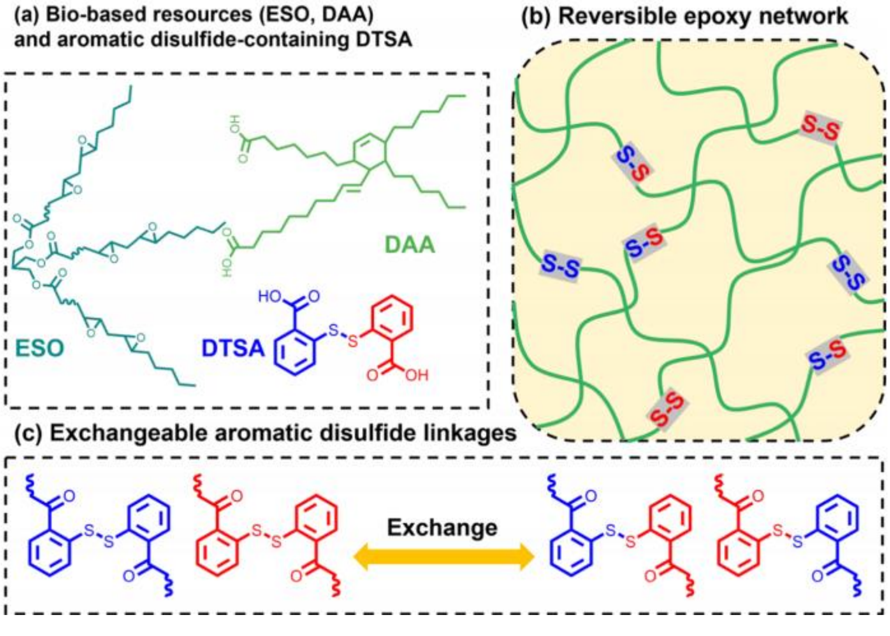
Scheme 14: Hydrolysis mechanism of HMDO.

Figure 10: Chemical degradability of the HMDO-based thermosetting plastic. Adapted with permission from ref. 100. Copyright 2020, Elsevier.

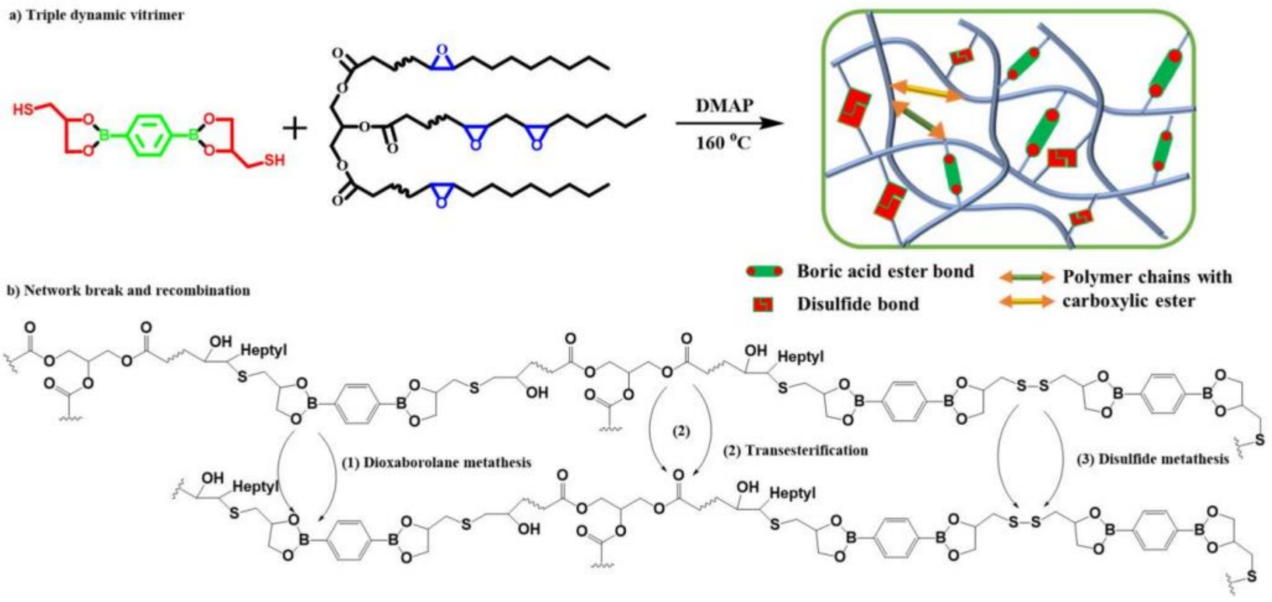


Scheme 15: Chemical structure of starting materials: ELO (**a**), ESO (**b**).

MAURO *et al*. crosslinked the mixture of ELO, ESO and (ELO+ESO) of epoxidized vegetable oil with a carboxylic acid hardener containing disulfide, and obtained a thermoreversible and chemically reversible dynamic covalent network. The synthesized thermosetting material has good chemical recycling and mechanical reprocessing ability. Chemical recycling of the prepared mesh material has little effect on the mechanical properties of the material after reprocessing [103]. In fact, the unique flexible fatty acid chain structure of triglyceride is weak and soft, and the limited active reaction sites of vegetable oil leading to low crosslinking density, which will lead to poor thermophysical and mechanical properties of epoxy resin to a certain extent, and it is neither degradable nor recyclable. Therefore, when designing vegetable oil-based epoxy resin, it is a challenge to have high mechanical properties, degradability and reprocessability at the same time. Because the main disadvantage of vegetable oil-based polymers is low mechanical properties. An effective way to solve the low mechanical properties is to introduce hard segments, such as aromatic rings, into the polymer network. Shan *et al*. used dicarboxylic acid functionalized aromatic disulfide (DTSA) and dimerized fatty acid (DAA) to cross-link epoxidized soybean oil (ESO) to prepare a bio-based epoxy elastomer with toughness and extensibility. The synthesis process and the mechanism of aromatic disulfide bonds are shown in Scheme **16**. Dynamic aromatic disulfide bonds can be exchanged even at room temperature, which gives it self-healing ability and reprocessability. At the same time, the inherent high flexibility of the fat segment is also conducive to self-healing. Generally speaking, the mechanical properties of materials with good self-healing ability are often poor. However, the epoxy elastomer containing aromatic disulfide bonds not only has high toughness during deformation, but also shows good healing efficiency without additional stimulation [104]. In addition to introducing aromatic rings, the introduction of various covalent bonds will also improve this defect to some extent. Zhang *et al*. used epoxidized vegetable oil and dithiol functionalized boron ester as raw materials, and synthesized a new type of bio-based epoxy resin by thermally initiated thiol-epoxy "click" reaction. The reaction mechanism is shown in Scheme **17**. Because it contains a large number of dynamic units (S-S bond, carboxylate and borate), epoxy resin has good self-healing and reprocessing properties. The tensile strength of the sample can reach 43.2 MPa, and the elongation at break can reach 25%, and the original mechanical properties of the obtained sample can be restored at different humidity and temperature, and it can be repeatedly treated for more than 9 times, the recycled samples prepared by epoxidized olive oil (EOO), epoxidized rubber seed oil (ERSO), epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) keep 121.9%, 89.9%, 105.0% and 93.0% after 9 cycles. The synergy of the three dynamic units opens up a new dimension for the synthesis of functional polymers [102].

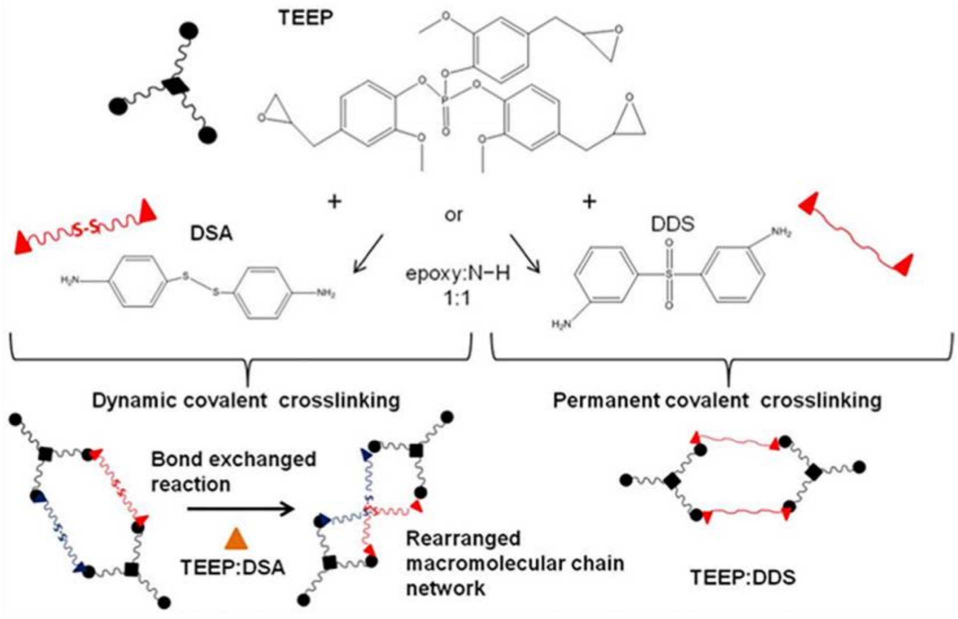


Scheme 16: (**a**) Chemical reagents of the epoxy network included epoxidized soybean oil (ESO), dimer aliphatic acid (DAA), and aromatic disulfidecontaining agent (DTSA). Both ESO and DAA are bio-based resources containing long saturated or unsaturated fatty acid chains. The obtained reversible epoxy network (**b**) contains exchangeable aromatic disulfide linkages (**c**) which constantly break and reform.



Scheme 17: The reaction mechanism of cross-linked bio-based epoxy resins.

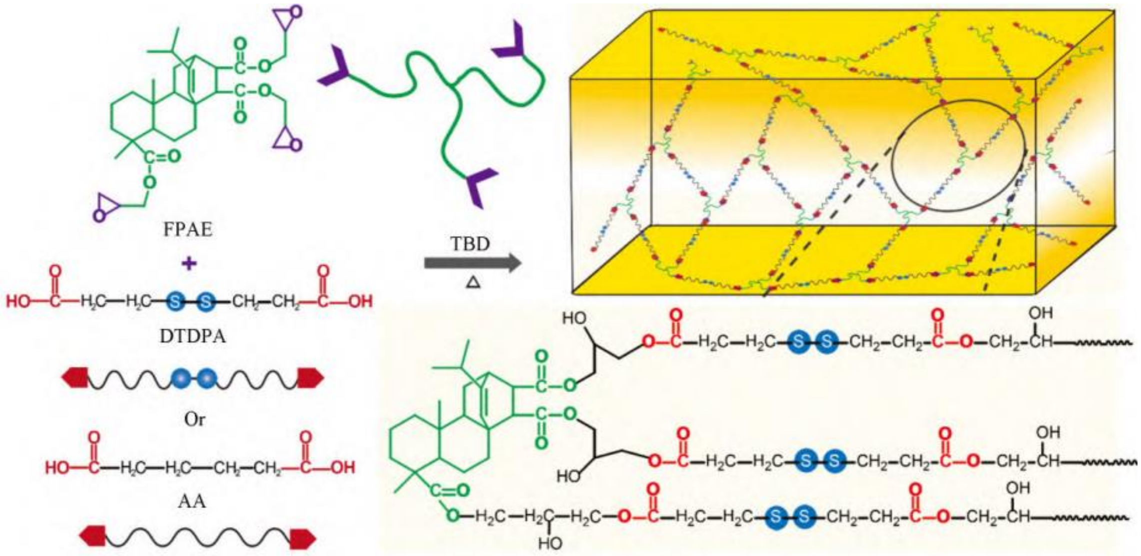
Besides vegetable oil, eugenol, isosorbide and natural rosin are also used in the synthesis of new epoxy resin. For example, eugenol is often used to prepare bio-based epoxy resin because of its unique CHO group. Ocando *et al*. successfully synthesized a sustainable dynamic eugenol-derived epoxy resin TEEP:DSA with high renewable carbon content and a petroleum-based epoxy resin TEEP:DDS without dynamic bond by crosslinking epoxidized eugenol oil with aromatic diamine containing disulfide functional groups (the synthetic route is shown in Scheme **18**). TEEP:DSA shows the same stiffness and higher T_g value as petroleum-based DGEBA. Dynamic covalent cross-linking is integrated into eugenol-based epoxy resin, which makes it have good remodeling, self-repair and recycling ability [105].



Scheme 18: General overview of the synthesis of the different partially bio-based epoxy networks.

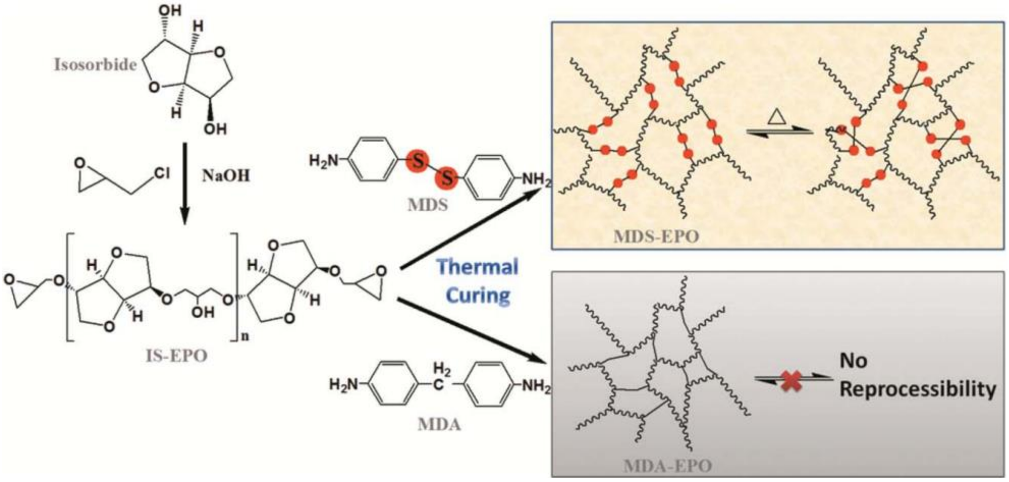
Natural rosin is an ideal material for preparing epoxy vitrimer polymers. Its rigid tricyclphenanthrene skeleton structure can improve the glass transition temperature (T_g), mechanical properties and heat resistance of epoxy vitrimer. Zeng *et al*. obtained rosin-based epoxy vitrimer polymer with double dynamic covalent bonds of dynamic ester bond and disulfide bond through polycondensation between fumaric acid-based epoxy resin (FPAE) and 3,3'-

tdpa (DTDPA). The preparation process is shown in Scheme **19**. The introduction of double dynamic covalent bonds can effectively accelerate the low-temperature exchange rate of dynamic covalent bonds. The relaxation time of the obtained RE-80 (cured products of a DTDPA crosslinker) network is only 74 s at 190℃, the topological transition temperature is 54.1℃, and the activation energy is only 93. 4 kJ/mol, which can realize reprocessing and self-repair under mild conditions (160 and 170℃). At the same time, the rigid framework of rosin can give the network excellent mechanical properties (tensile strength 37. 5 MPa, elongation at break 10. 2%, toughness 1. 86MJ/m^3) [106].



Scheme 19: Preparation of rosin-based epoxy networks with dual dynamic covalent bonds.

Isosorbide has high thermal stability, which is beneficial to the thermal post-treatment of epoxy resin. Ma *et al*. reported a bio-based vitrimer polymer composed of isosorbide-derived epoxy resin and aromatic diamine containing disulfide bonds, and its synthetic route is shown in Scheme **20**. The prepared dynamic epoxy resin MDS-EPO has equivalent thermo-mechanical properties with similar epoxy resin mesh MDA-EPO cured by traditional curing agent. Rheological experiments show that the stress of the dynamic network relaxes rapidly at a temperature higher than the glass transition temperature due to the rapid decomposition of disulfide bonds. This feature allows the broken samples to be recycled and reprocessed many times by hot press. Dynamic epoxy resin also shows the shape memory effect. As shown in Fig. (**11**), the shape recovery ratio can be easily adjusted by controlling the stress relaxation in the temporary state at the programming temperature. In addition, the degradability of dynamic epoxy resin in alkaline aqueous solution was confirmed (see Fig. **12** for details) [101].



Scheme 20: Synthetic route of isosorbide-derived epoxy. (IS-EPO).

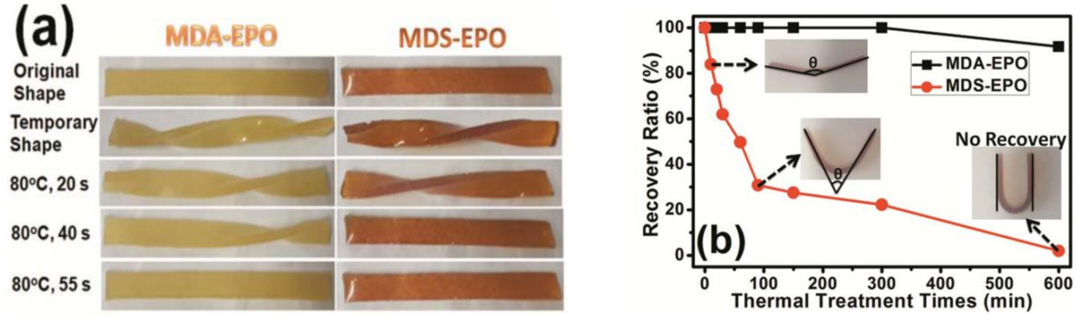


Figure 11: (**a**) Shape-memory effect of MDA-EPO and MDSEPO. (**b**) Shape recovery ratio of MDA-EPO and MDS-EPO treated at 80 ℃ for different times. Adapted with permission from ref. [101]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA.

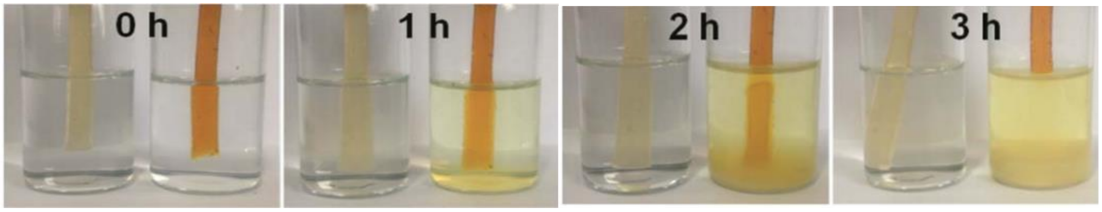
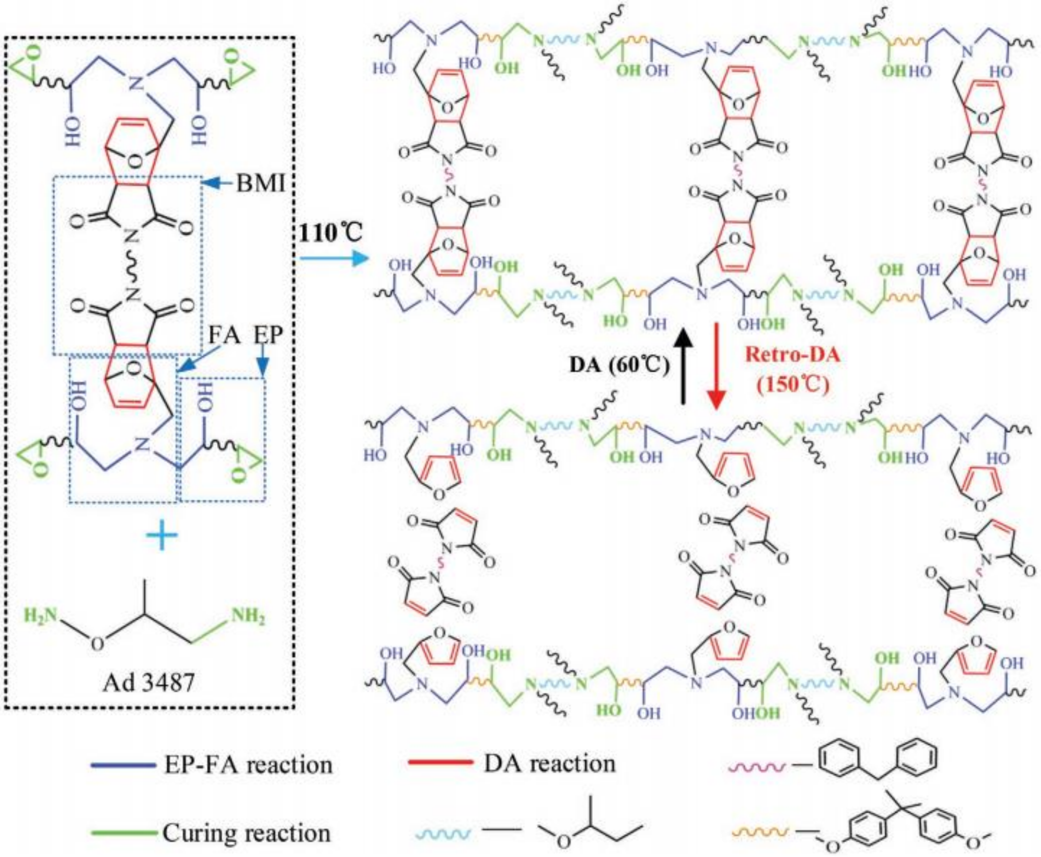


Figure 12. Photographs of MDA-EPO (left bottle) and MDSEPO (right bottle) immersed in 5 wt% NaOH aqueous solution. Adapted with permission from ref. [101]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA.

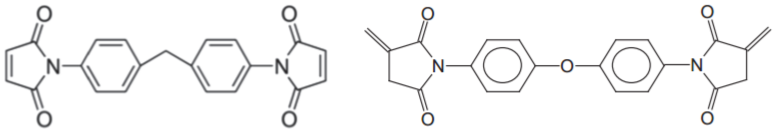
3.5. Diels−Alder Addition Structures

The DA reaction (Diels-Alder reaction) takes place between an electron-rich conjugated diene and an electron-poor electrophilic diene, and cyclohexene adducts are generated by [4+2] cycloaddition reaction, which does not need to add anything, and no by-products are produced in the reaction [107-109]. The DA bond can be reversibly cracked to form the starting materials, dienophiles and conjugated dienes. As an additional reaction, the reverse reaction of DA is an exothermic process, which requires a higher temperature [110]. The "click" characteristic of DA reaction makes it a popular choice in synthesizing epoxy networks with self-repairing and recyclable properties [111]. Bio-furan derivatives are considered as promising substitutes for petroleum-based epoxy resins, because their five-membered aromatic heterocyclic and diene structures can carry out DA reaction. In addition, furaldehyde contains an aldehyde group, which is an electrophilic reaction site and can be converted into methylene bond to connect other aromatic rings [112]. Based on the formation and cleavage of DA bond between furan (FA) and maleimide units, it is the most commonly used reversible crosslinking. Compared with other DA systems, the formation efficiency of cyclic adducts is higher, and the temperature of reverse reaction is relatively low, thus avoiding side reactions and main chain degradation. However, furan-based DA is renewable, and maleimide needs to be obtained from hydrocarbons, so in practical application, biological bismaleimide (BMI) is often used to replace maleimide group [113]. Wu *et al*. synthesized a thermal reversible DA compound composed of furan and bismaleimide, and introduced it into ordinary low-viscosity epoxy resin to prepare a self-healing epoxy-based system. Its self-healing mechanism is shown in Scheme **21** [114]. In addition, Lejeail *et al*. synthesized a bio-based furan epoxy resin with bisitaconic imide as raw material. The thermal reversibility of DA network made the cross-linked material repairable and recyclable after being damaged. When itaconic anhydride is replaced by itaconic imide, the formation of lactone acid can be avoided. Both bisitaconic and bismaleimide can be used as cross-linking agents with reversible bonds/chemical cross-linking based on DA in the resin. The structural comparison between bisitaconic imide and bismaleimide is shown in Scheme **22** [113].

Multiple thermal cycling self-repairing is of great significance to the recyclability of bio-based epoxy resin. The good reprocessing performance of materials makes it possible for waste epoxy resin to be recycled, and the introduction of DA reversible bond brings hope. For example, Zhang *et al*. prepared an epoxy resin (FA-FGE-BMI) with good self-healing and adhesive properties by DA reaction between an epoxy prepolymer containing polyfuran groups and bismaleimide groups (Scheme **23**). FA-FGEB-MI has good self-healing performance, and the higher the temperature, the faster the self-healing speed. Moreover, they also studied the bending strength and recovery rate of the material after four damage repair cycles. Surprisingly, after three times of damage repair, the bending strength is greatly improved. Although it is reduced in the fourth repair, its bending strength is also higher than that of the original material. This provides a new research idea for the research related to the recycling of epoxy resin [115]. Zhao *et al*. used epichlorohydrin to react with furfuryl alcohol to synthesize epoxy monomer with diene structure, and then reacted with bismaleimide with dienophile structure to prepare self-repairing epoxy resin (EP-DA) based on thermal reversible DA reaction. The synthetic route is shown in Scheme **24**. The introduction of DA bond into EP-DA endows epoxy resin with good thermal reversibility and reprocess ability, and enables epoxy resin to achieve self-repair. In addition, the experiment simulated the impact damage of epoxy resin in practical use, and the repair behavior and multiple repair ability of epoxy resin were investigated by combining macro qualitative observation with quantitative determination of bending load recovery. It was confirmed that this material had good self-repair performance and multiple repeated repair ability, and its one-time repair efficiency reached 77.1%. After three times of impact damage-heat treatment, the repair efficiency of the same sample was still as high as 53.9% [116].

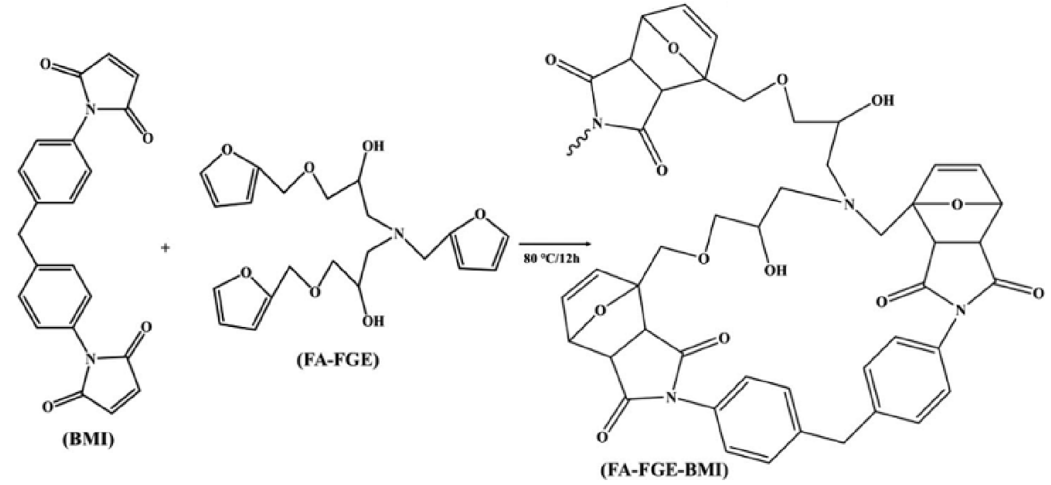


Scheme 21: Mechanism of the self-healing process.

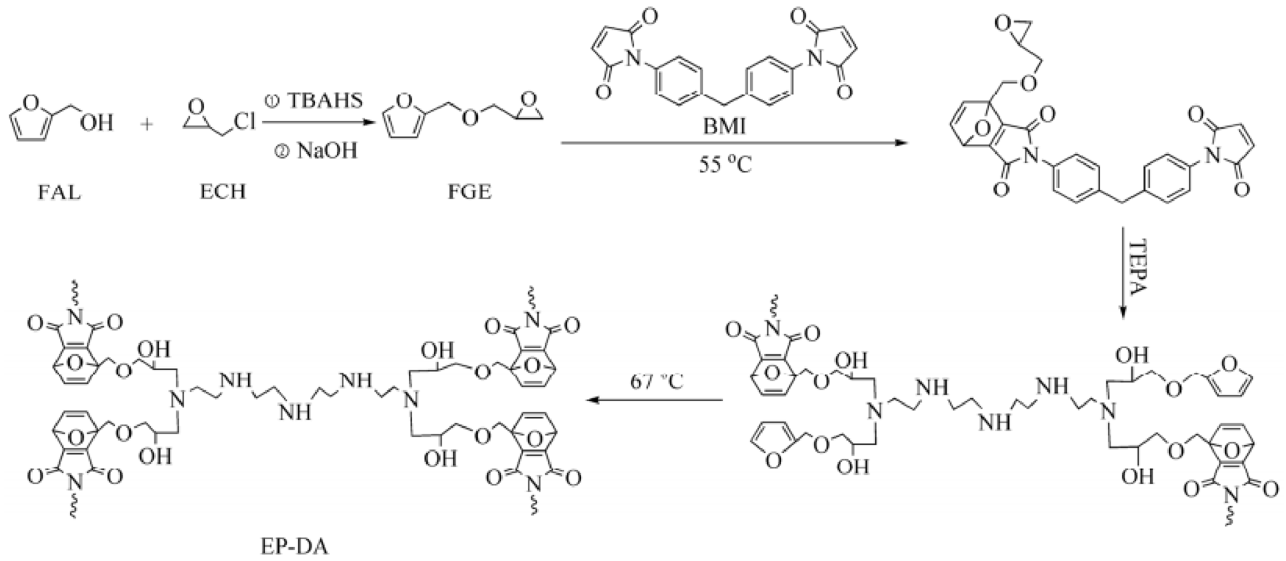


Scheme 22: Structure of bismaleimide (left) vs. structure of Bisitaconimide (right).

The introduction of DA bond has brought many advantages to degradable epoxy resin. Based on the properties of thermal reversibility and multiple thermal cycles, it has broadened the application prospect for the sustainable development of degradable epoxy resin.



Scheme 23: Synthesis of FA-FGE-BMI.



Scheme 24: Synthetic process of EP-DA.

4. Conclusions and Challenges

The research status of recyclable bio-based epoxy resin was presented. Recyclable bio-based epoxy thermosets can be prepared by introducing dynamic reversible bonds, such as ester, borate ester bonds, acetal structures, Schiff bases, disulfide bonds, or Diels-Alder addition structures into the bio-based epoxy monomers or bio-based curing agents. The introduction of dynamic covalent bonds or cleavable bonds can give the cross-linked networks of epoxy resins functional performances including degradability, reprocess ability, recyclability, repairability, etc. The aforementioned performances could be realized through two approaches. One is to de-crosslink and re-crosslink of the network structure by exchange reactions of dynamic bonds. Another method is to transform the network structure into small molecules or oligomers through hydrolysis reactions. It is worth noting that the first method to achieve reprocessing usually needs high temperature and pressure. While the realization of the second method is often affected by the pH value of the solution, or the need to add the catalyst. Moreover, a mixture of small molecules or oligomers is obtained after the hydrolysis reaction. If it is to be recycled, it takes a lot of purification steps. Therefore, it is necessary to develop bio-based epoxy resins that can be recycled directly by removing solvents after hydrolysis. In addition, in order to improve the efficiency of degradation or exchange reactions, it is often necessary to design multiple dynamic covalent bonds into an epoxy resin network to play a synergistic role.

The preparation of bio-based degradable epoxy resin from renewable biomass raw materials can alleviate the fossil energy crisis and reduce environmental pollution. This thermosetting resin can be extensively used in carbon fiber reinforced resin-based composites. The non-destructive recovery of carbon fiber can be achieved, and the properties of the recycled composite materials have not decreased significantly. In addition, this recyclable thermosetting resin can also be used for 3D printing materials. Components printed with this material can be recycled as new ink, used for the next round of 3D printing technology. Epoxy resin containing cleavable structural units can be degraded under mild conditions to achieve resource recovery and reuse to meet the needs of sustainable development of society. However, epoxy resin containing reversible covalent bond structure also has some deficiencies, such as epoxy resin containing Schiff base structure is sensitive to water, poor aging resistance to heat and humidity, and epoxy resin containing disulfide bond has poor heat resistance stability, these deficiencies will limit the application field of epoxy resin. In addition, research in the recycle bio-based epoxy resins is still in the initial stage, and there are still many challenges and problems that need to be solved. The raw materials of bio-based epoxy resins are mainly derived from renewable biomass resources, such as vegetable oil and biomass waste. However, the supply stability and sustainability of these raw materials still face challenges. On the one hand, the output and quality of raw materials may be affected by seasonal, climatic, regional and other factors; On the other hand, large-scale raw material collection and utilization may have a certain impact on the ecological environment. Moreover, biomass feedstocks are more expensive in production, collection and storage compared with fossil fuel-based feedstocks, and the production scale is small. How to improve the separation and purification technology of biomass, reduce the price of biomass monomer, and synthesize recycle bio-based epoxy resins in a high purity and economical and efficient way are the problem that needs to be solved at present.

Contribution

Mengting Wan and Xuemei Liu contributed equally to this manuscript.

Conflicts of Interest

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

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