

Review

Review on the Synthesis, Recyclability, Degradability, Self-Healability and Potential Applications of Reversible Imine Bond Containing Biobased Epoxy Thermosets

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Abstract: Epoxy thermosets need to be designed for simple recycling and biomass resource utilization in order to be fully sustainable building materials. The development of covalent adaptive networks (CANs) using adaptive covalent chemistry (ACC) may be helpful in this regard. Several reversible covalent bonds are incorporated into the epoxy polymer to overcome the challenge of reprocessability or recyclability, degradability and self-healability. The imine bond, also referred to as the Schiff base, is one of the reversible covalent bonds that can participate in both associative and dissociative reactions. This opens up possibilities for mechanical and chemical recycling as well as self-healing. This review summarises the progress related to the synthesis and mechanical and thermal properties of epoxy thermosets based on reversible imine bonds derived from different sustainable resources over the past few decades. The feedstocks, physical and thermal properties, recycling conditions, degradability and self-healability of the biomass epoxy thermosets are addressed along with the main obstacles, prospective improvements and potential applications.

Keywords: epoxy thermoset; bio-based; imine bond; recyclable; self-healable



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1. Introduction

The rapid expansion of plastic pollution and environmental concern motivate scientific research to use renewable resources and recyclability of the utilised polymeric materials that can be effective for packaging, construction, furniture and automotive industries [1–3]. There are two types of conventional synthetic polymer materials: thermoplastic and thermosetting polymers. While a certain temperature is applied, the thermoplastic polymer is broken its intermolecular connections, such as hydrogen bonds, Van der Waals forces and molecular chain entanglement, resulting in fluidity, and it can be easily reprocessed [4]. Among thermoset polymers, epoxy thermosets are considered the most adaptable and commonly used material due to their resilience to chemicals and heat, high mechanical strength and magnificent insulation [5,6]. Based on its chemical structure, the molecule has at least two epoxy groups and can be found in solid, viscous and liquid forms [7]. Therefore, it is often used in construction, electronic packaging, adhesives, coatings and composites [8]. However, diglycidyl ether of bisphenol A (DGEBA), which is not renewable, makes up about 90% of the epoxy thermosets used today [9]. However, after the completion of their service life, this thermoset decreases the composite material's feasibility and creates massive environmental and waste resource difficulties. Concerning environmental and human health issues, the utilization of bisphenol A BPA in materials that come

into touch with food is also prohibited by several nations, and they are concentrating on BPA replacement in research [10–12]. Keep focusing on petroleum availability and price uncertainty; the biobased materials and chemicals have to be synthesised from renewable resources. Therefore, epoxy made by BPA can be replaced by using renewable chemicals and derivatives [10]. Biomass renewable resources are cellulose [13–15], lignin [16–18], vanillin [19–21], vegetable oil [22–24], furan [25–27], cardanol [28–30], rosin [31–33], itaconic acid [34–36], quercetin [37,38] and so on.

Moreover, conventional and biobased thermosetting polymeric materials cannot be recycled or mended due to irreversible crosslinking networks, so they are treated as less environmentally friendly than thermoplastics [39–41]. The problems of the recycling and degradation, reprocessability, and self-healing of epoxy thermosets can be solved by incorporating reversible dynamic covalent bonds in the polymer network. Wuld and coworkers first proposed the concept of adaptive covalent chemistry (ACC) in 2002 [42], while Bowman and coworkers initially used the term covalent adaptive networks, also known as CANs, regarding crosslinked polymer networks with reversible bonds [43]. If certain stimuli and equilibrium controls allow for the reversible formation and breaking of covalent bonds, these bonds can be categorised as dynamic. In addition, these covalent bonds will be constructed as sustainable thermosets, eliminating the use of petroleum-based components and the depletion of fossil resources [44–47]. Several numbers of reversible covalent bonds are disulfide linkages [48–50], boronic ester bonds [31,51], ester bonds [37,52,53], acetal linkages [54–56], Schiff bases [2,57], carbamate linkages [58,59], Diels–Alder additions [60,61] and silicon oxygen bonds [62,63]. The dynamic covalent bond containing crosslinked network demonstrates repairability, malleability, degradability, reprocessability and self-healing properties under several extrinsic stimuli, such as solvent, pressure, light and heat [1,64–66]. CANs may be divided into two general categories according to how their dynamic structures are created: either bond exchange done kinetically (associative), expressed in Figure 1, or through equilibrium changes that result in reversible depolymerization (dissociative), expressed in Figure 2 [67,68]. In the case of associative dynamic bonds, a new bond is formed as the previous one breaks at the same time, keeping a constant crosslink density (Figure 1) [68,69]. In the case of dissociative dynamic bonds, the covalent networks are initially disrupted and then rebuilt at a different location within the network (Figure 2). During crosslinked network breakdown, the molecular density declines, resulting in network connectivity to be lost or completely degraded. This breakdown of the network might result in either the recovery of molecules or the formation of free chains, according to the composition of the dissociative network. Photo-triggerable reactions and Diels–Alder adducts are two of the most well-known examples of dissociative reversible networks [70,71]. In both situations, the polymeric thermosets are malleable and reshapable, and the crosslinks can be reformed to restore their original mechanical characteristics.

Recently, it has been established that various chemical linkages have adaptive abilities, making the resulting polymer network characteristics typically of CANs [72]. Moreover, the imine bond is a viable choice for CANs and epoxy thermosets among the many dynamic bonds. An imine (C=N) bond is formed in the reaction between the activated carbonyl and primary nucleophilic amine groups [2]. These linkages give polymers exceptional characteristics, including stimuli adaptability, reprocessability, degradability and self-healability. Taking into account the significant perspective of ACC for the formation of reworkable and regenerable sustainable thermosets, this review highlights the improvements in terms of synthesization and the mechanical and thermal properties of sustainable epoxy thermosets based on imine bonds and various bio-resource substances over the past few decades. The feedstocks, physical and thermal properties, recycling conditions, degradability and self-healability of the biomass epoxy thermosets are addressed along with the main obstacles, prospective improvements and potential applications.

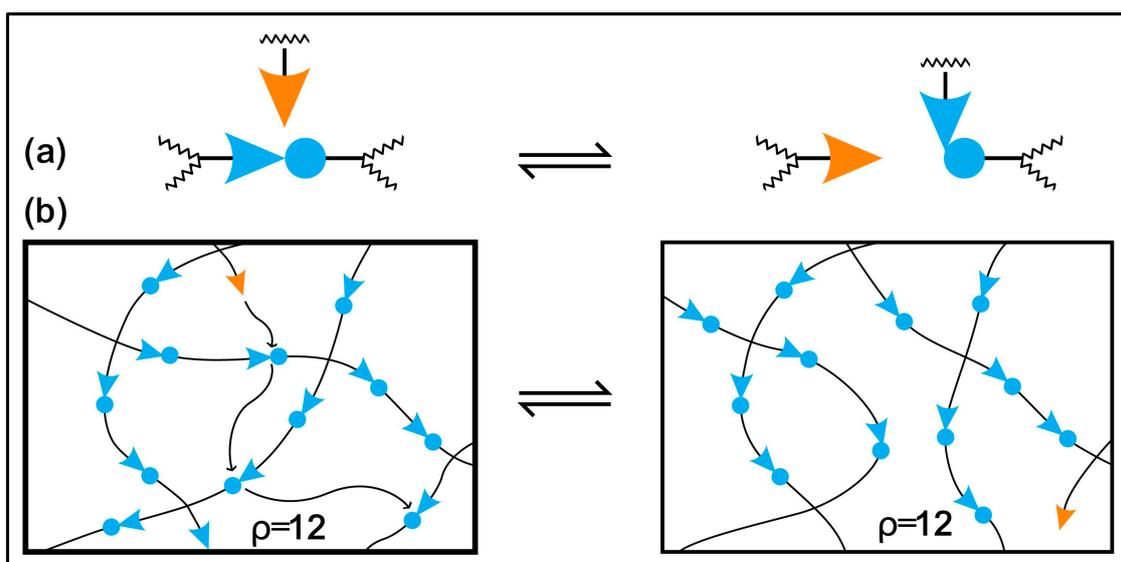


Figure 1. The mechanism of bond exchange in the polymer networks: (a) an exchange reaction that an active species goes through results in a bond exchange and the creation of a new active species, which then goes through more exchange reactions; (b) effective dispersion of reaction events rearranges the overall network connectivity while maintaining the total bond and crosslink density when the exchange reaction takes place in the backbone of a polymer network.

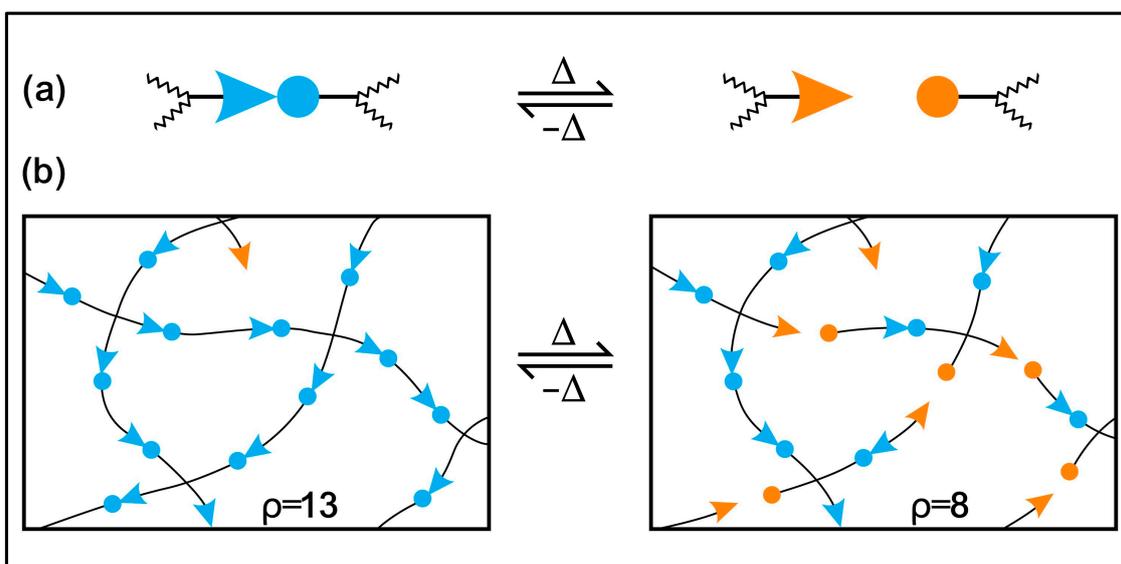


Figure 2. Reversible polymerization mechanism in a polymer network: (a) depolymerization event enabled by reversible crosslinking and (b) covalently modification of a crosslinked network.

2. Imine-Based Adaptive Covalent Chemistry

A well-known process that produces imines is the condensation reaction of an aldehyde or ketone with a primary amine. Water and acidic environments, in particular, can cause the imine to hydrolyse, which results in the reformation of the original functions (Figure 3a). In addition to this dissociative process, two exchange reaction-based associative pathways can occur without water: transamination (Figure 3b) and imine metathesis (Figure 3c) [73,74]. Transamination is defined as the process of changing an imine into an additional imine and another primary amine. On the other hand, the metathesis route involves an interaction between two imines that produces two new imines. According to some reports, the transamination route does not need a catalyst and typically takes place

when so many amines exist, resulting in the generation of aminal precursors [75]. L-proline is an example of an organic base accelerator that might enhance imine metathesis [76]. As a result, the imine linkages can induce the materials to have qualities such as self-healing, degradation and recyclability.

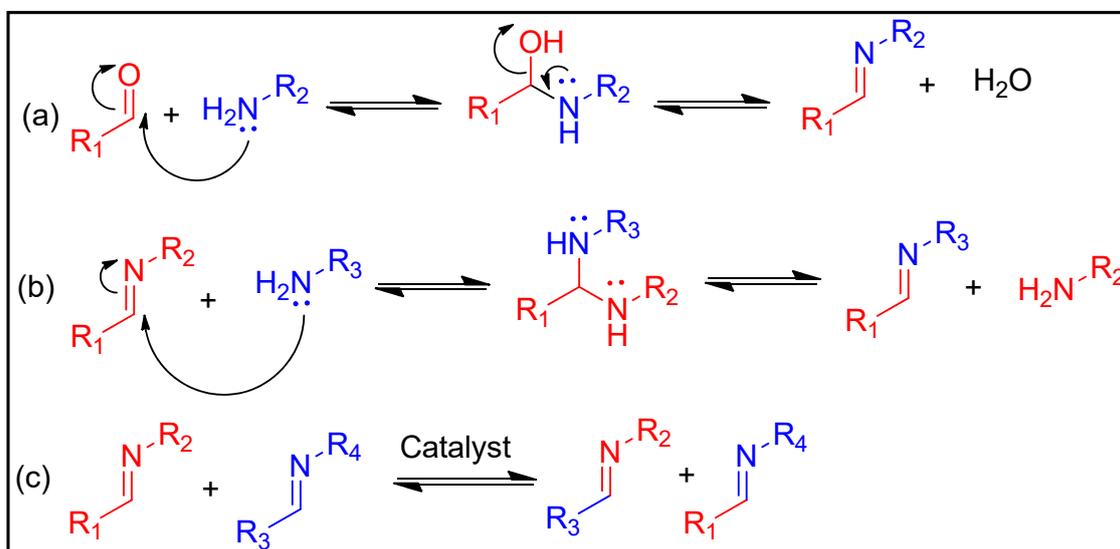


Figure 3. Basic exchange reaction of imine linkages: (a) imine hydrolysis, (b) transamination and (c) imine metathesis.

The water-based solubility of imine linkages is a common problem of imine chemistry, although the possibility for imine linkages to undergo heat-induced associative techniques has been utilised to generate thermally reprocessable thermosets [77–79]. However, this characteristic has also produced chemically recyclable polymers [80]. For example, Taynton and coworkers developed a reworkable and reproducible polyimine compound using the associative and dissociative imine systems [81]. The polyimine structures were developed using readily existing aldehyde, diamine and triamine combinations, demonstrating 100% recycling efficiency, stress-relaxation and Arrhenius-like malleability performance. Moreover, these thermosets also showed water-induced relaxation and were chemically recoverable at an ambient temperature. The imine metathesis and transamination were used to explain the malleability and rapid stress-relaxation of polyimine thermosets. In contrast, the combined reaction of imine dissociation and transamination caused by accessible amine functions was used to describe the quick water-induced stress relaxation. Besides water-induced methods, organic chemicals are additionally examined to promote the reversible reaction of imine linkages. In this context, Zhang and coworkers produced an imine-crosslinked self-healing organogel and exhibited that the synergistic impact of extra primary amine and organic solvent could accelerate the transamination process [78]. Schoustra and coworkers emphasised the effect of polar elements in molecular networks on the exchange of imine linkages to gain a deeper understanding of the associative connections of imine linkages and the impact of network and molecular components on the dynamics of the associative networks [82]. According to the study, adding higher polar elements, such as ethylene oxide, could increase the imine exchange reaction rate five times more than adding less polar components, such as aliphatic carbon chains. Based on the finding, cured polymer products containing polar functionalities in their network exhibited much higher temperatures for the glass-to-rubber and rubber-to-liquid phase transitions than polar components. The examination of stress-relaxation activity of polymer chains revealed a progressive three-phase relaxing approach that largely involved chain rearrangement inside the polymeric structure, imine interchange on a regional scale and imine interchange following diffusion across the chain.

3. Imine-Based Vitrimer Properties

One of the most significant characteristics of vitrimers is their malleability, which is achieved by heating and redistributing the dynamic links of the vitrimer throughout the structure while keeping the crosslink density constant. The viscosity of vitrimers is mainly regulated by the exchange reactions at elevated temperatures, resulting in an Arrhenius law, and the drop in viscosity with temperature (Figure 4). The topological freezing temperature (T_v) and the glass transition temperature (T_g) must be introduced to describe the viscoelastic nature of the vitrimer [83]. The bond exchange period shifts faster above T_v than the observation period, leading to a viscous flow. The network architecture seems to be preserved below T_v because the exchange reaction's kinetics are so sluggish, and the substances are then used as standard thermosets or elastomers [68]. Conventionally, the T_v is defined as the temperature at which the viscosity approaches 10^{12} Pa·s. [83]. Figure 4 displays the viscosity characteristics of vitrimers [68]. Depending on the placement of the T_v with relation to the T_g , two possibilities can be recognised [68,69]. When $T_v > T_g$ (Figure 4a), the product initially changes from a glassy state ($T < T_g$) to a rubbery state in which the network architecture remains stable ($T_g < T < T_v$) as the exchange reactions are still too slow. When the temperature rises over T_v , the exchange responses can be prominent and the product begins to exhibit Arrhenius law-compliant viscoelastic behaviour. While $T_v < T_g$ (Figure 4b), the inherently quick exchange responses above T_v are initially “entrapped” in a stiff, glassy polymeric structure, where the loss of segmental mobility restricts the topology from being reorganised. In this context, T_v is only a theoretical value that can be extrapolated from stress relaxation or creep tests, whereas the product performs as a glassy state until the temperature exceeds T_g . The renowned Williams–Landel–Ferry (WLF) theory predicts that the viscosity will decrease above T_g due to the beginning of segmental mobility, and then, it will follow an Arrhenius theory when exchange processes predominate. Because of this, vitrimers may be simply heated to change their shape, providing fantastic prospects for thermal recycling. Additionally, self-healing properties result from the ability to change the network architecture upon heating. These characteristics result in materials that have a longer lifespan, more regulated end-of-life and higher durability thanks to this unique recyclability.

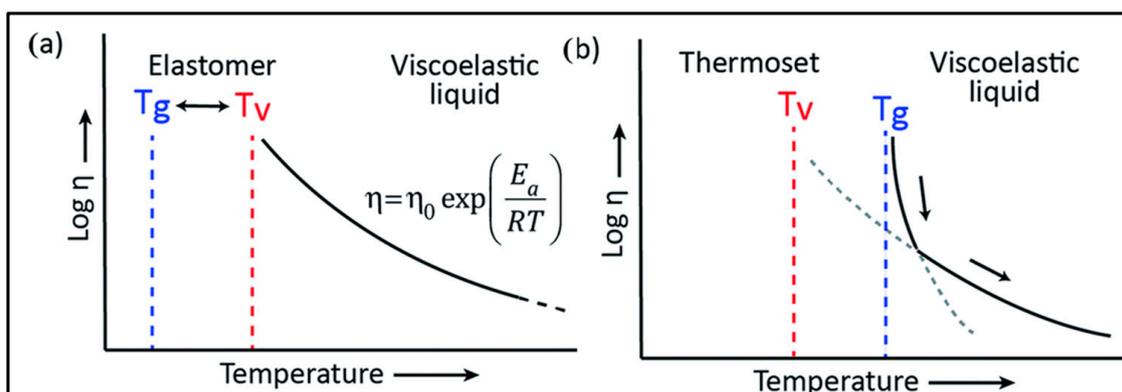


Figure 4. Demonstration of vitrimers’ viscoelastic performance regarding the topological freezing temperature (T_v) in relation to glass transition temperature (T_g): (a) T_g is lower than T_v ; the vitrimer follows Arrhenius equation and changes from a glassy solid ($T < T_g$) to an elastomer ($T_g < T < T_v$) to a viscoelastic liquid ($T > T_v$) while heated. (b) T_v is lower than T_g ; the vitrimer changes from a glassy solid to a viscoelastic liquid while heated, and its viscosity is regulated by diffusion (WLF) and exchange kinetics (Arrhenius). [Reproduced with permission from Du Prez et al.; published by RCS, 2016] [68].

4. Synthesis and Properties of Reprocessable Biobased Epoxy Thermosets Using Reversible Imine Bond

Growing sustainability concerns have encouraged the fast development of recyclable and ecologically friendly thermosetting polymers. Various renewable resources have been utilised to produce biobased epoxy resin, which can be reprocessed easily (see Table 1). Zhao and Omar prepared a partial biomass epoxy monomer (GE-VAN-AP) in a two-step process from biomass vanillin, aminophenol and epichlorohydrin as a replacement of petroleum-based product BPA through the imine exchange reaction, as illustrated in Figure 5a [84]. In this study, the malleability, degradability, recyclability and weldability properties of epoxy thermosets were obtained without any catalyst, as presented in Figure 5b–d. However, it has less water resistance than the conventional one, and its processing is complex because it applies high temperature and uses solvents during crosslinking as it has to evaporate after the curing. It is also mentionable that the thermo-mechanical attributes of the cured thermosets are lower than the conventional epoxy.

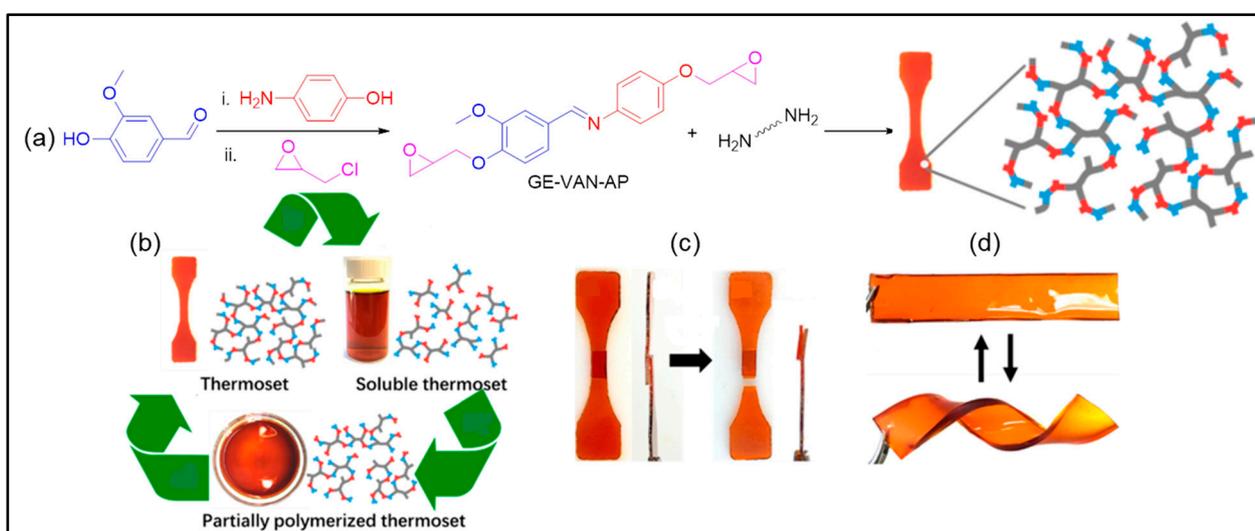


Figure 5. (a) Preparation process of imine bond containing partial biomass epoxy thermoset; chemical recyclability (b), weldability (c) and malleability (d) of the cured thermosets [Reproduced with permission from Zhao et al.; published by ACS, 2018] [84].

Liu and coworkers also synthesised an imine bond containing a biobased curing agent from vanillin and *m*-xylylenediamine, and finally, it cured with commercial DGEBA, detailed in Figure 6, which results in self-healable, remouldable, weldable and faster stress-relaxable behaviours [85]. The superior mechanical and thermal characteristics of thermosets were achieved because of the presence of aromatic *m*-xylylenediamine in the curing agent. Furthermore, thermosets retained 89% of their tensile strength and 94% of Young's modulus after 15 days of immersion in water.

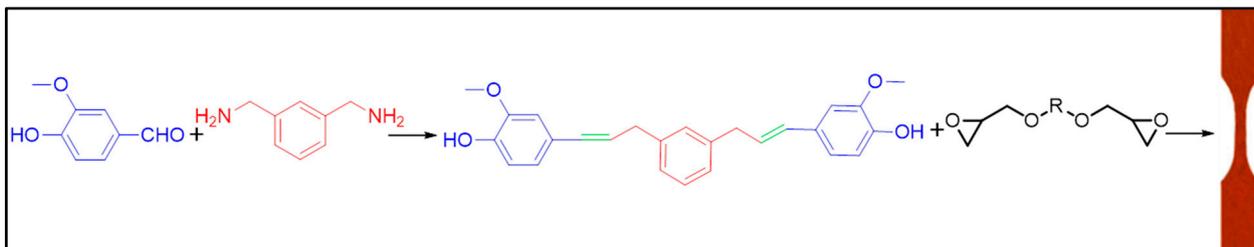


Figure 6. Synthesis procedure of imine bond including bio-source curing agent and its cured epoxy thermoset.

Further, Memon and coworkers established a reprocessable and chemically degradable biobased epoxy vitrimer with the single-stage condensation reaction of vanillin and isophorone diamine (IPDA) or methylcyclohexanediamine (HTDA) with commercial epoxy monomers, mentioned in Figure 7 [86,87]. These epoxy thermosets showed better tensile properties, an excellent storage modulus and a greater T_g value. Additionally, physically and chemically regenerated epoxy vitrimers can maintain significantly better or equal thermomechanical performance than traditional epoxy thermosets. Moreover, using these vitrimers as the matrix, higher mechanical properties and repairable carbon fibre-reinforced composite (CFRC) materials were introduced.

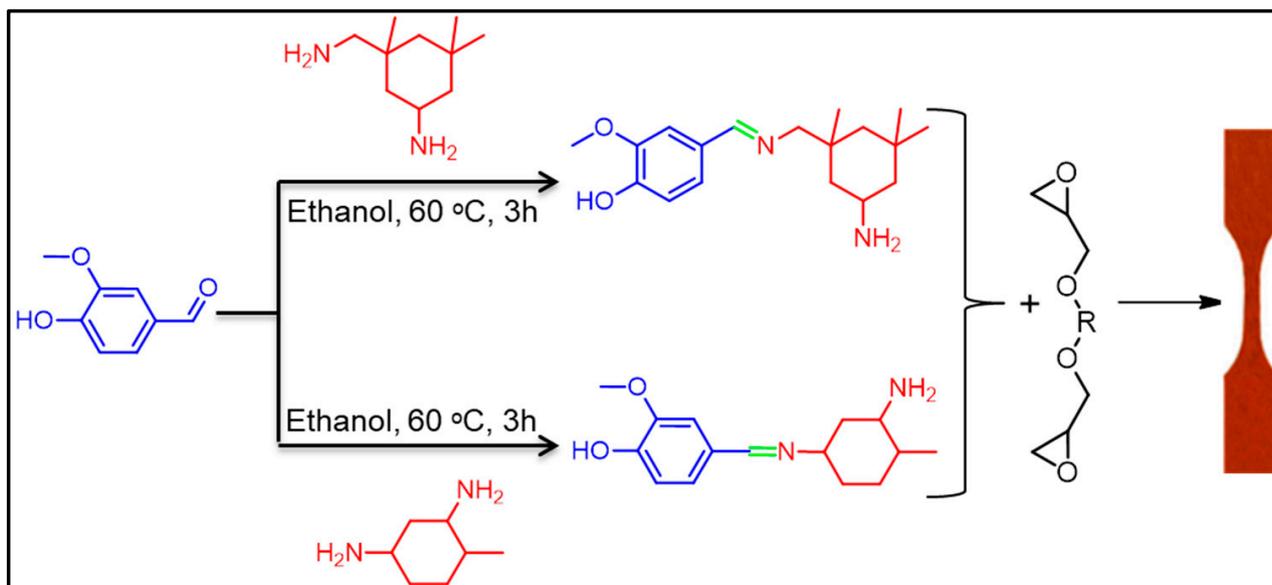


Figure 7. Synthesis pathway of dynamic imine bond containing biobased curing agents and their crosslinked epoxy thermosets.

Moreover, Rashid and coworkers prepared a partial biomass epoxy curing agent (VAN-BAC) in a single-step process from biomass vanillin and diamine as a replacement for the petroleum-based product through the imine exchange reaction and cured it with commercial diglycidyl ether of bisphenol F (DGEBF), as shown in Figure 8a [88]. These cured thermosets had remarkable mechanical and thermomechanical properties, solvent resistance, stress relaxation, closed-loop reprocessability and degradability. However, the prepared curing agent or hardener was completely solid and challenging to process [89]. Similar authors solved those problems by using 4-methyl-1,3-cyclohexanediamine (HTDA) as a co-curing agent and optimised their performances (original and recycling) [90]. Moreover, the curing agents were partially full biomass products. The same authors also prepared full biomass curing agents in a single-stage process from sustainable vanillin butanediamine and hexanediamine and cured them in DGEBF, as displayed in Figure 8b [91]. These cured thermosets had moderate mechanical and thermomechanical properties but excellent stress relaxation, solvent resistance, reprocessability, and degradability. The mechanical and thermomechanical properties were optimised using a cyclic co-curing agent (original and recycled) [89].

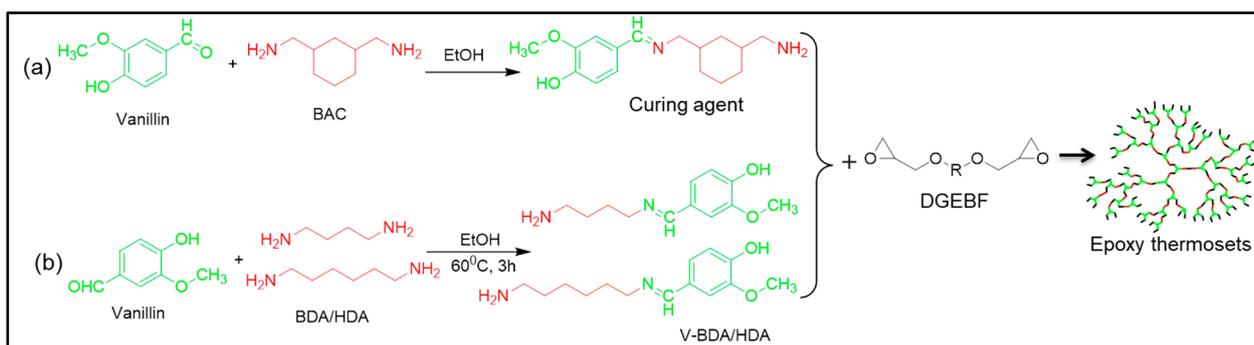


Figure 8. Synthesis of partial biomass (a) and full biomass (b) imine bond containing curing agent and their cured thermosets.

Table 1. List of resources for biobased epoxy thermosets and their thermo-mechanical properties original and regenerated. [T_g = Glass Transition Temperature, σ = Tensile Strength, ϵ = Elongation at break %, E = Tensile Modulus, σ_f = Flexural Strength, E_f = Flexural Modulus, G = Storage modulus].

Resources	Epoxy Resin	Curing Agent	Properties			Ref
			Original	Reprocessed	Recycled	
Vanillin and Syringaldehyde	DGEBF	Vanillin Bisaminomethyl Cyclohexane	$T_g = 92\text{ }^\circ\text{C}$ $\sigma_f = 106\text{ MPa}$ $E_f = 2.37\text{ GPa}$ $G = 3.08\text{ GPa}$	$T_g = 90\text{ }^\circ\text{C}$ $\sigma_f = 107\text{ MPa}$ $E_f = 2.63\text{ GPa}$ $G = 3.09\text{ GPa}$	$T_g = 84\text{ }^\circ\text{C}$ $\sigma_f = 111\text{ MPa}$ $E_f = 2.61\text{ GPa}$ $G = 3.14\text{ GPa}$	[88]
		Syringaldehyde Bisaminomethyl Cyclohexane	$T_g = 82\text{ }^\circ\text{C}$ $\sigma_f = 107\text{ MPa}$ $E_f = 2.35\text{ GPa}$ $G = 2.82\text{ GPa}$	$T_g = 86\text{ }^\circ\text{C}$ $\sigma_f = 107\text{ MPa}$ $E_f = 2.36\text{ GPa}$ $G = 3.03\text{ GPa}$	$T_g = 85\text{ }^\circ\text{C}$ $\sigma_f = 112\text{ MPa}$ $E_f = 2.37\text{ GPa}$ $G = 2.84\text{ GPa}$	
Vanillin	Glycerol triglycidyl ether (Gte)	VA	$T_g = 70\text{ }^\circ\text{C}$ $\sigma = 62 \pm 7\text{ MPa}$ $E = 1.6 \pm 1.1\text{ GPa}$ $\epsilon = 7.2 \pm 1.9\%$	$T_g = 70\text{ }^\circ\text{C}$ $\sigma = 76 \pm 1\text{ MPa}$ $E = 2.0 \pm 0.1\text{ GPa}$ $\epsilon = 8.9 \pm 1.7\%$	$\sigma = 63 \pm 5\text{ MPa}$ $E = 2.6 \pm 1.1\text{ GPa}$ $\epsilon = 2.7 \pm 0.1\%$	[92]
Vanillin	Vanillin-based epoxy resin (DADE)	D230	$T_g = 106\text{ }^\circ\text{C}$ $\sigma = 57.4 \pm 3.6\text{ MPa}$ $E = 2.52 \pm 0.12\text{ GPa}$ $\epsilon = 3.1 \pm 0.6\%$	$T_g = 97\text{ }^\circ\text{C}$ $\sigma = 47 \pm 4.4\text{ MPa}$ $E = 2.53 \pm 0.25\text{ GPa}$ $\epsilon = 2.2 \pm 0.2\%$		[21]
Vanillin	Hexa-vanillin terminated cyclophosphazene (HVP)	D230	$T_g = 98.4\text{ }^\circ\text{C}$ $\sigma = 58\text{ MPa}$ $E = 1.84\text{ GPa}$ $\epsilon = 5.6\%$	$\sigma = 56\text{ MPa}$ $E = 1.77\text{ GPa}$ $\epsilon = 5.9\%$		[93]
Vanillin	GE-VAN-AP	Jeffamine	$T_g = 71\text{ }^\circ\text{C}$ $\sigma = 46\text{ MPa}$ $\epsilon = 4\%$ $G = 2.00\text{ GPa}$		$T_g = 72\text{ }^\circ\text{C}$ $\sigma = 41\text{ MPa}$ $\epsilon = 3.8\%$ $G = 2.11\text{ GPa}$	[84]
Vanillin	DGEBA	Van2HMDA	$T_g = 88\text{ }^\circ\text{C}$ $\sigma = 85\text{ MPa}$ $\epsilon = 5.9\%$		$T_g = 63\text{ }^\circ\text{C}$	[66]
Vanillin	VAN-AC-EP	DDM	$T_g = 146\text{ }^\circ\text{C}$ $\sigma = 44 \pm 2.2\text{ MPa}$ $E = 2.69 \pm 0.11\text{ GPa}$ $\epsilon = 2.4 \pm 0.09\%$ $G = 3.35\text{ GPa}$	$\sigma = 29 \pm 1.3\text{ MPa}$ $E = 2.98 \pm 0.15\text{ GPa}$ $\epsilon = 1.1 \pm 0.06\%$		[57]
Vanillin	DGEBA	IH-VAN	$T_g = 121\text{ }^\circ\text{C}$ $\sigma = 60.1 \pm 1.5\text{ MPa}$ $E = 2.57 \pm 0.04\text{ GPa}$ $G = 2.50\text{ GPa}$	$T_g = 127\text{ }^\circ\text{C}$ $\sigma = 53.6 \pm 1.1\text{ MPa}$ $E = 2.83 \pm 0.04\text{ GPa}$ $G = 2.66\text{ GPa}$	$T_g = 119\text{ }^\circ\text{C}$ $\sigma = 60.9 \pm 1.0\text{ MPa}$ $E = 2.61 \pm 0.04\text{ MPa}$ $G = 2.12\text{ GPa}$	[86]

Table 1. Cont.

Resources	Epoxy Resin	Curing Agent	Properties			Ref
			Original	Reprocessed	Recycled	
Vanillin	DGEBA	IH-VAN	$T_g = 127\text{ }^\circ\text{C}$ $\sigma = 60.6 \pm 1.8\text{ MPa}$ $E = 2.60 \pm 0.04\text{ GPa}$ $G = 2.94\text{ GPa}$	$T_g = 135\text{ }^\circ\text{C}$ $\sigma = 52.4 \pm 0.9\text{ MPa}$ $E = 2.86 \pm 0.05\text{ GPa}$ $G = 3.07\text{ GPa}$	$T_g = 124\text{ }^\circ\text{C}$ $\sigma = 58.3 \pm 1.5\text{ MPa}$ $E = 2.62 \pm 0.03\text{ GPa}$ $G = 2.63\text{ GPa}$	[86]
Vanillin	AFG-90H	Vanillin and methylcyclohexane diamine	$T_g = 131\text{ }^\circ\text{C}$ $\sigma = 82\text{ MPa}$ $G = 2.96\text{ GPa}$		$\sigma = 79\text{ MPa}$ $G = 3.80\text{ GPa}$	[87]
Vanillin	Glycerol diglycidyl ether (GDE)	HVPA	$T_g = 118\text{ }^\circ\text{C}$ $\sigma = 38.8 \pm 2.1\text{ MPa}$ $E = 1.5 \pm 0.16\text{ GPa}$ $\epsilon = 20.9 \pm 1.90\%$		$\sigma = 35.2 \pm 2.1\text{ MPa}$ $\epsilon = 17.08 \pm 1.90\%$	[94]
Guaiacol and vanillin	Guaiacol-vanillin derivatives (GV-EP)	DDM	$T_g = 220\text{ }^\circ\text{C}$ $E = 4.49 \pm 0.06\text{ GPa}$ $G = 3.60\text{ GPa}$	$T_g = 237\text{ }^\circ\text{C}$ $E = 5.60 \pm 0.08\text{ GPa}$ $G = 2.31\text{ GPa}$		[95]
Lignin	PBE, VBE	DDM	PBE-DDM $T_g = 204\text{ }^\circ\text{C}$ $\sigma = 122 \pm 9\text{ MPa}$ $E = 2.65 \pm 0.1\text{ GPa}$ $\epsilon = 8.7 \pm 0.3\%$ VBE-DDM $T_g = 196\text{ }^\circ\text{C}$ $\sigma = 93 \pm 5\text{ MPa}$ $E = 2.17 \pm 0.09\text{ GPa}$ $\epsilon = 6.3 \pm 0.2\%$			[96]
Vanillin	Dialdehyde Monomer from Vanillin (DAV)	Diethylenetriamine and tris(2-aminoethyl)amine	$T_g = 60\text{ }^\circ\text{C}$ $\sigma = 51 \pm 3.99\text{ MPa}$ $E = 724 \pm 43.7\text{ MPa}$ $\epsilon = 13.01 \pm 1.51\%$	$\sigma = 53 \pm 2.27\text{ MPa}$ $E = 526 \pm 33.8\text{ MPa}$ $\epsilon = 18.29 \pm 2.68\%$		[97]
Vanillin	DGEBA	Van-OH	$T_g = 96\text{ }^\circ\text{C}$ $\sigma = 79.1\text{ MPa}$ $E = 2.47\text{ GPa}$ $\epsilon = 6.12\%$ $G = 2.65\text{ GPa}$	$\sigma = 48.8\text{ MPa}$ $E = 2.46\text{ GPa}$ $\epsilon = 2.82\%$		[85]
Soybean oil + Vanillin	Epoxidized soybean oil (ESO)	VA	$T_g = 27.6\text{ }^\circ\text{C}$ $\sigma = 7.7 \pm 1\text{ MPa}$ $E = 41.4 \pm 3.7\text{ MPa}$ $\epsilon = 144 \pm 14\%$ $G = 4.98\text{ MPa}$	$\sigma = 7.6 \pm 1\text{ MPa}$ $E = 41.4 \pm 3.7\text{ MPa}$ $\epsilon = 160 \pm 14\%$		[98]
Soybean oil + Vanillin	Epoxidized soybean oil (ESO)	VSB	$T_g = 66\text{ }^\circ\text{C}$ $\sigma = 37.4 \pm 4.1\text{ MPa}$ $E = 1.02 \pm 0.04\text{ GPa}$ $\epsilon = 6 \pm 1\%$	$\sigma = 37.4 \pm 4.1\text{ MPa}$ $E = 1.02 \pm 0.04\text{ GPa}$ $\epsilon = 6 \pm 1\%$		[24]
Vanillin	Mono-glycidyl structure of vanillin (Van-Ep)	Isophorone diamine (IPDA)	$T_g = 121\text{ }^\circ\text{C}$ $\sigma = 65 \pm 5.2\text{ MPa}$ $E = 2.30 \pm 0.23\text{ GPa}$ $\epsilon = 4.4 \pm 0.7\%$ $G = 3.56\text{ GPa}$	$\sigma = 65.7 \pm 2.8\text{ MPa}$ $E = 2.61 \pm 0.16\text{ GPa}$ $\epsilon = 3.7 \pm 0.4\%$		[99]
Vanillin	MB	PACM	$T_g = 172\text{ }^\circ\text{C}$ $\sigma = 81 \pm 1.2\text{ MPa}$ $E = 2.11 \pm 0.05\text{ GPa}$ $\epsilon = 15 \pm 0.8\%$	$T_g = 175\text{ }^\circ\text{C}$ $\sigma = 81 \pm 1.8\text{ MPa}$ $E = 2.28 \pm 0.03\text{ GPa}$ $\epsilon = 13 \pm 0.4\%$		[45]
Vanillin	GTE	VPDA	$T_g = 107\text{ }^\circ\text{C}$ $\sigma = 93 \pm 14.4\text{ MPa}$ $E = 1.41 \pm 0.21\text{ GPa}$ $\epsilon = 12.3 \pm 3.6\%$ $G = 2.51\text{ GPa}$	$T_g = 107\text{ }^\circ\text{C}$ $\sigma = 95 \pm 14.4\text{ MPa}$ $E = 1.51 \pm 0.49\text{ GPa}$ $\epsilon = 8 \pm 0.8\%$	$\sigma = 98 \pm 14.4\text{ MPa}$ $E = 1.51 \pm 0.49\text{ GPa}$ $\epsilon = 7 \pm 0.8\%$	[100]

Nevertheless, to solve the environmental problems and resource waste and to obtain greater mechanical and thermal properties, Jiang and coworkers synthesised a high-quality biomass epoxy monomer via the reaction of a Schiff base reacting with vanillin along with 4-amino cyclohexanol and epichlorohydrin and finally cured it with DDM as a curing

agent, as presented in Figure 9 [57]. This product showed recyclable, degradable and excellent stress-relaxed performance by including imine bonds in the crosslinked epoxy thermosets. It is also mentionable that this thermoset obtained 15.8% tensile strength and 36.8% tensile modulus, superior to traditional bisphenol A thermosets. Since the synthetic epoxy polymer demonstrated outstanding mechanical properties and could be applied in the fabrication of carbon fibre-reinforced composites (CFRCs). Imine bonds allowed for the carbon fibre to be recycled entirely without sacrificing its mechanical properties and to be put to use once more.

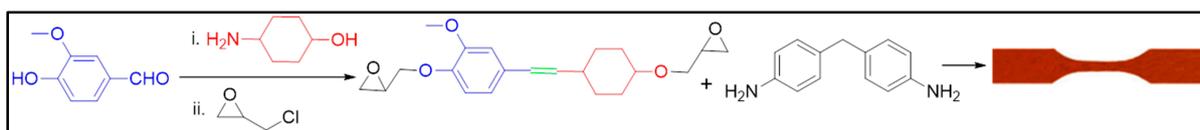


Figure 9. Synthesised imine bond, including biomass epoxy monomer, and its cured thermoset.

5. Reprocessability and Recyclability of Bio-Based Epoxy Thermosets Based on Reversible Imine Bond

The irreversibility of thermosets is considered their most serious drawback due to the challenge of recycling waste received at the end of their life or as a by-product during manufacturing [3,9,41]. Therefore, reprocessability and recyclability are the fundamental characteristics of the epoxy thermosets. The reprocessability and recyclability of epoxy thermosets can be solved by including reversible covalent bonds in their polymer network. Among them, various reprocessable and recyclable epoxy thermosets were produced by combining with dynamic imine bonds. Zhao and coworkers investigated the recyclability of EN-VAN-AP (vanillin-based epoxy thermosets) through a dissociative mechanism, as shown in Figure 10a [84]. In the dissociative mechanism, EN-VAN-AP was degraded completely in DMF and HCl solvent solution within 30 min at 65 °C. A viscous gel formed after evaporating the remaining solvent by the drying process at room temperature. Lastly, this gel was warmed up for 24 h at 120 °C to promote an aldehyde-amine reaction and reform the thermosets, expressed in Figure 10b. It is also mentionable that the thermal and mechanical properties of the recycled thermosets were almost similar to the original thermosets, as displayed in Figure 10c,d. Moreover, this method requires no catalyst or press heating compared to the associative mechanism.

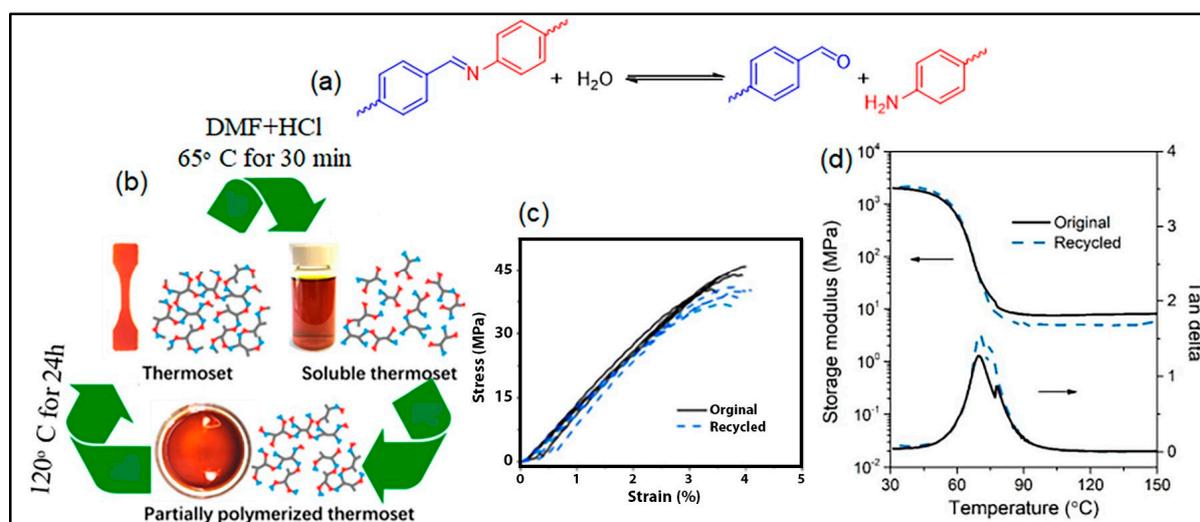


Figure 10. Dissociative mechanism (a), closed-loop recycling (b), mechanical (c) and thermal (d) properties of imine bond-containing thermosets [Reproduced with permission from Zhao et al.; published by ACS, 2018] [84].

In another study, a closed-looped recycling method was established to reuse the produced epoxy resin (ER) from vanillin and isophorone diamine (IPDA) or methylcyclohexanediamine (HTDA) via chemical degradation (Figure 11) [86,87]. In addition, the thermally reprocessed method without any catalyst was examined through hot press treatment (Figure 10). Crosslinked ER was shredded and pressed for 30 min at 170 °C in a steel mould for thermal reprocessing, and this epoxy powder reprocessed easily. After three (3) times reprocessing, this ER stored greater than 70% tensile stress and a more excellent Young's modulus and T_g values than the original samples. In addition, the ER is degraded in ethanol and IPDA/HTDA solution in the chemical recycling process at 60 °C. It can be reused because of a reversible imine exchange reaction between amino groups in IPDA/HTDA and epoxy molecules. The chemically recycled epoxy thermosets showed equivalent tensile and thermal properties to pristine ER. The authors also applied the recyclable ER on carbon fibres to produce carbon fibre-reinforced composites (CFRCs), which enables the recovery of both resin and the carbon fibres, resulting in the complete recyclability of CFRCs without compromising their physical properties.

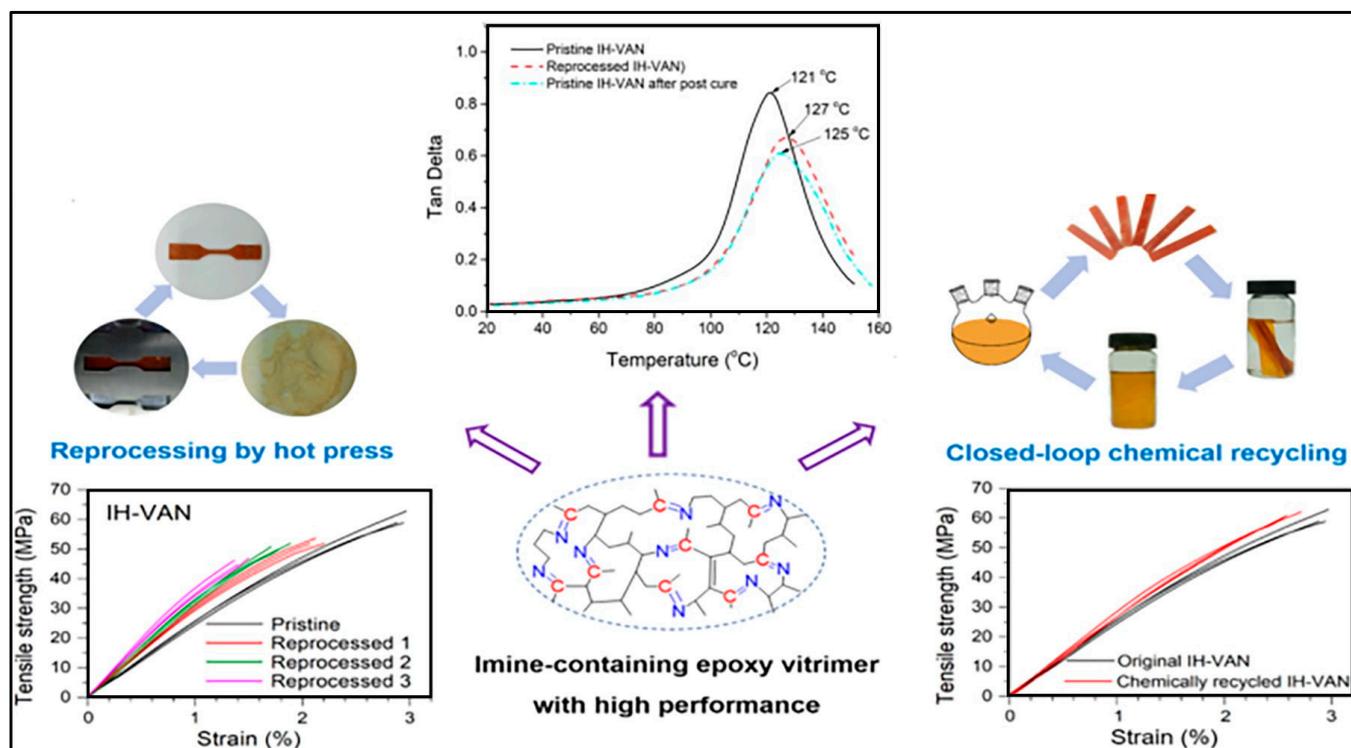


Figure 11. Physical and thermal properties of original and regenerated ERs [Reproduced with permission from Memon et al.; published by ACS, 2020] [86].

Further, Rashid and coworkers prepared reprocessable and recyclable ERs from biomass curing agents and commercial DGEBA [88]. These cured thermosets had remarkable mechanical and thermo-mechanical properties, solvent resistance and closed-loop reprocessability. However, the prepared curing agent or hardener was solid and challenging to process. Similar authors solved those problems using 4-methyl-1,3-cyclohexanediamine (HTDA) as a co-curing agent and optimised their performances (original and recycled) [90]. Moreover, the curing agents were partial biomass products. The same authors also prepared full biomass curing agents in a single-stage process from sustainable vanillin, butanediamine, and hexanediamine and cured them with DGEBA [91]. These cured thermosets had moderate mechanical and thermomechanical properties but excellent stress relaxation, solvent resistance and reprocessability. The mechanical and thermomechanical properties were optimised using a cyclic co-curing agent (original and recycled) [89]. Recently, high-

performance reprocessable biomass ER was developed from vanillin, rigid xylene diamine and DGEBF in a single-stage process [20]. The cured ER can be repeatedly reprocessed like thermoplastics owing to dynamic imine bonds in the polymer crosslinked networks and an almost 100% recovery of physical and thermal properties after three reprocessing cycles.

Peng and coworkers developed recyclable, degradable, self-healable, flame retardancy and anti-bacterial properties containing biobased epoxy thermosets with the combination of a multifunctional curing agent of cyclphosphazene-based amine (HVPA) and an epoxy monomer of glycerol diglycidyl ether (GDE0) [94]. To examine the reprocessability of the cured ERs, they tore up the crosslinked ER and then made a dumbbell shape after pressing at 100 °C under 1.5 MPa for 3 min with remoulding, expressed in Figure 12a. The elongation at the break (%) and tensile strength were retained at 81.7% and 90.8%, respectively, compared to the original thermosets, and other mechanical strength was significantly recovered after reprocessing (Figure 12b).

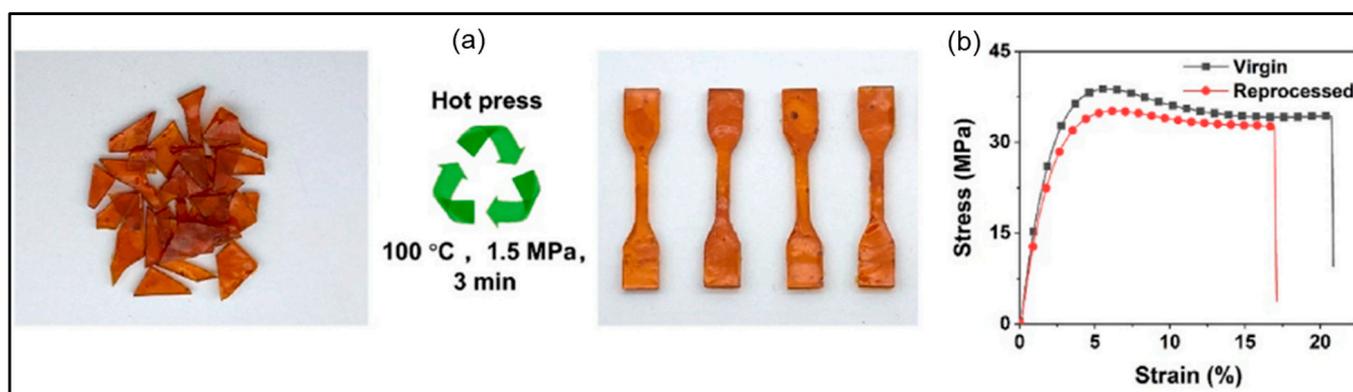


Figure 12. Reprocessing pathway (a) and physical properties (b) of the cured ERs [Reproduced with permission from Peng et al.; published by Elsevier, 2022] [94].

Su and coworkers prepared a reprocessable biobased epoxy thermoset from the vanillin-derived epoxy molecule (DADE) and commercial D230 curing agent, as demonstrated in Figure 13a [21]. The crosslinked ER showed excellent mechanical and thermal properties ($T_g \sim 106$ °C, tensile strength of ~ 57.4 MPa and elongation at break of $\sim 3.1\%$) compared to that of DGEBA-D230, as illustrated in Figure 13c,d. Additionally, DADE-D230 demonstrated remarkable malleability and reprocessability due to imine bonds in its polymer structure. Similarly, they prepared a dog bone-shaped mould after shattering the sample into powder and pressing it by applying 15 MPa pressure for 10 min at 150 °C, detailed in Figure 13b. The reprocessed DADE-D230 exhibited the same attributes as the commercial epoxy thermosets (DGEBA-D230), as shown in Figure 13c,d.

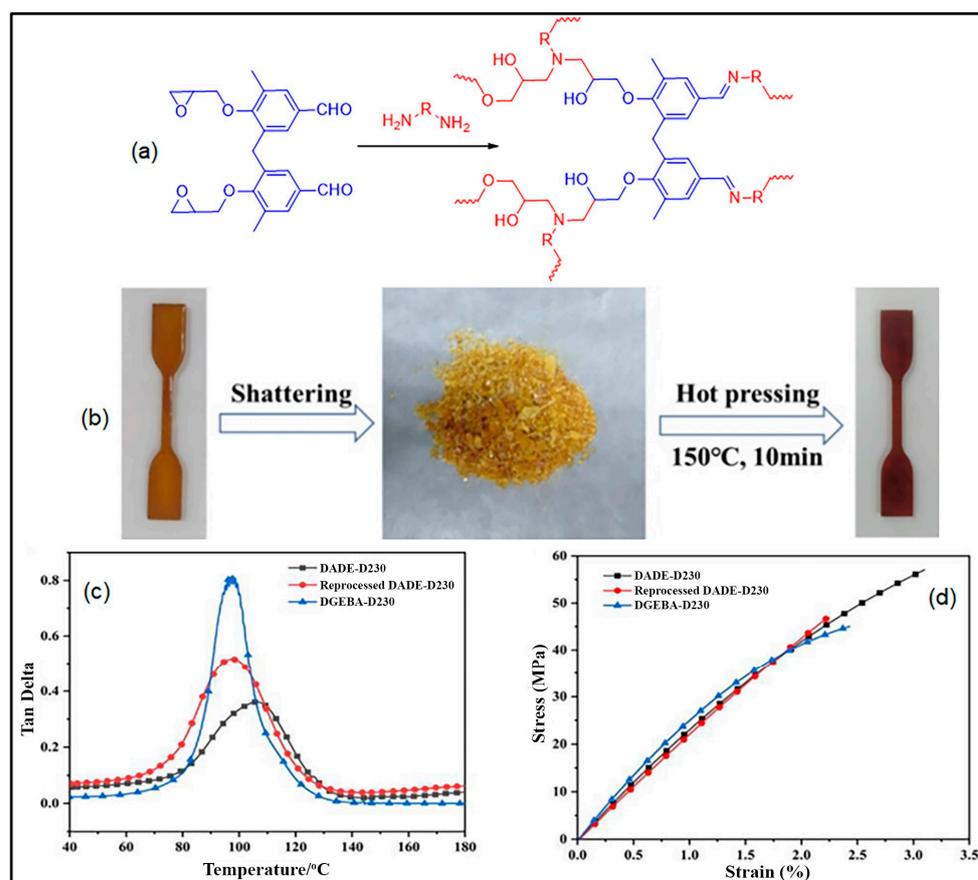


Figure 13. Curing mechanism (a), mechanical reprocessing (b), thermal (c) and physical (d) properties of the original and reprocessed ER [Reproduced with permission from Su et al.; published by Elsevier, 2020] [21].

6. Degradation of Bio-Based Epoxy Thermosets Based on Dynamic Imine Bond

After the service life of thermosets, existing commercial thermosets are frequently dumped in landfills or incinerated because of their irreversible covalently crosslinked networks. These disposal techniques provide financial and environmental difficulties due to their high cost and greenhouse gas emissions. Therefore, thermosets with labile bonds, such as imine, transesterification, disulfide, Diels–Alder, vinylogous urethane and acetal, may be recycled under benign conditions, and their environmental impact is reduced through rapid chemical degradation to their original constituent parts or other valuable substances. Li and coworkers developed biobased epoxy thermosets (GV-EP/DDM) that could be degraded in 0.1 M H_2SO_4 or HCl in the presence of DMSO/ H_2O volume ratio of 8:2 at 90 °C for 24 h, as expressed in Figure 14 [95]. Initially, it showed nearly no deterioration in the solution after soaking for 24 h at 25 °C and 50 °C temperatures. The sample was broken up into tiny fragments in less than 24 h as the solution temperature reached 90 °C due to rapid hydrolysis of the Schiff base, as seen in Figure 14. It was also discovered that the solute decomposed more quickly into H_2SO_4 than HCl solution under identical conditions. As a result, the ER has the potential to be used in advanced materials, such as temperature sensors and the driving of unfolding structures. After reaching the end of its service life, it can be chemically dissolved and separated into ERs and reinforced materials and finally reutilised.

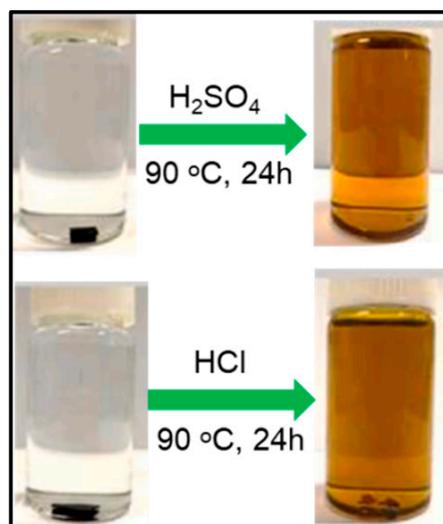


Figure 14. Degradation of crosslinked ER in 0.1 M H₂SO₄ or HCl in the presence of DMSO/H₂O volume ratio of 8:2 at 90 °C for 24 h [Reproduced with permission from Li et al.; published by Elsevier, 2022] [95].

Wang and coworkers prepared a recyclable biobased epoxy thermoset, known as MB-PACM, that can be fully degraded in a mildly acidic solution owing to imine bonds, as expressed in Figure 15 [45]. The degradation of crosslinked ER varied with the solvent, water-to-solvent ratio and time duration, as detailed in Figure 15. The systems required 233, 267, 340, 420 and 982 min with a methanol:water ratio of 8:2, 7:3, 6:4, 9:1 and 9.5:0.5, respectively, to dissolve in a 0.1 M HCl solution (Figure 15a). The capacity to dissolve the material after deterioration was reduced, as the solvent content was also reduced, causing the systems with methanol:water volume ratios of 7:3 and 6:4 to degrade more slowly. The system degrades more slowly with a volume ratio of 9:1 and 9.5:0.5 because of less water to drive hydrolysis. However, cured ER could not be entirely degraded in 8:2, 7:3, 9:1 and 9.5:0.5 volume ratio solutions in 48h at room temperature (Figure 15a). The dissolving time of cured ER in different solvents, such as methanol, THF, acetone and DMF solution, was also identical from 328 to 398 min when the volume ratio of solvent-to-water was 6:4 and the acidic concentration was 0.1 M (Figure 15b). It is also mentionable that the degradation time in ethanol was highest (583 min) because of the poor solvency of cured ER (Figure 15b). In addition, Figure 15d presents images of CF/MB-PACM composite degradation over time at room temperature in a solution of 0.1 M HCl (methanol/H₂O = 8/2, *v/v*) to recover carbon fibres without affecting their physical properties.

Yu and coworkers developed a degradable biobased ER that can be degraded in an acidic solution due to the incorporation of imine bonds in their polymer chains [99]. The cured samples were stirred in different acidic solutions (1 mol/L, 10⁻² mol/L and 10⁻⁵ mol/L) for 24 h at 70 °C. In 1 mol/L HCl solution, ERs were hydrolysed into yellow oil that adhered to the bottle wall. In contrast, partial hydrolysis produced a white powder in 10⁻² mol/L and 10⁻⁵ mol/L HCl solutions. Only 19.25 wt.% residuals in 1 mol/L of HCl solution prove that a robust acid solution is preferable for the degradation of ER and the rupture of an unsteady imine bond.

Nabipour and coworkers also developed a degradable, fully biobased EP from vanillin-derived epoxy monomer and 5,5'-methylenebis(2-furfurylamine) [101]. They investigated the impact of acidic conditions and temperature on the degradation of imine bonds containing cured ERs and found that the degradation increased with the increase in temperature in an acidic medium due to the hydrolyzation of imine bonds to produce amine and aldehyde reactant (Figure 16a). Further, it investigated the impact of the DMF:water ratio on cured ERs and found that an 8:2 ratio was prominent for degradation at 50 °C, as presented in Figure 16a. Again, cured ER degraded quickly in 0.1 M H₂SO₄ solution, although a

significant decrease was seen at 0.01 M and exposure to other weaker acids, such as HCl, H_3PO_4 and HNO_3 , as seen in Figure 16b. This characteristic ensures that cured ER has excellent degradability in moderately acidic medium and remarkable stability in weaker or low-acid environments. The degradation performance of ER was also investigated in several solvents, such as THF, DMF, methanol, acetone and water. ER degraded more quickly in DMF and THF systems in comparison with water, methanol and acetone (Figure 16c), probably as a result of the ability of high polar aprotic solvents (DMF and THF) to break the azomethine bond of the polymer networks.

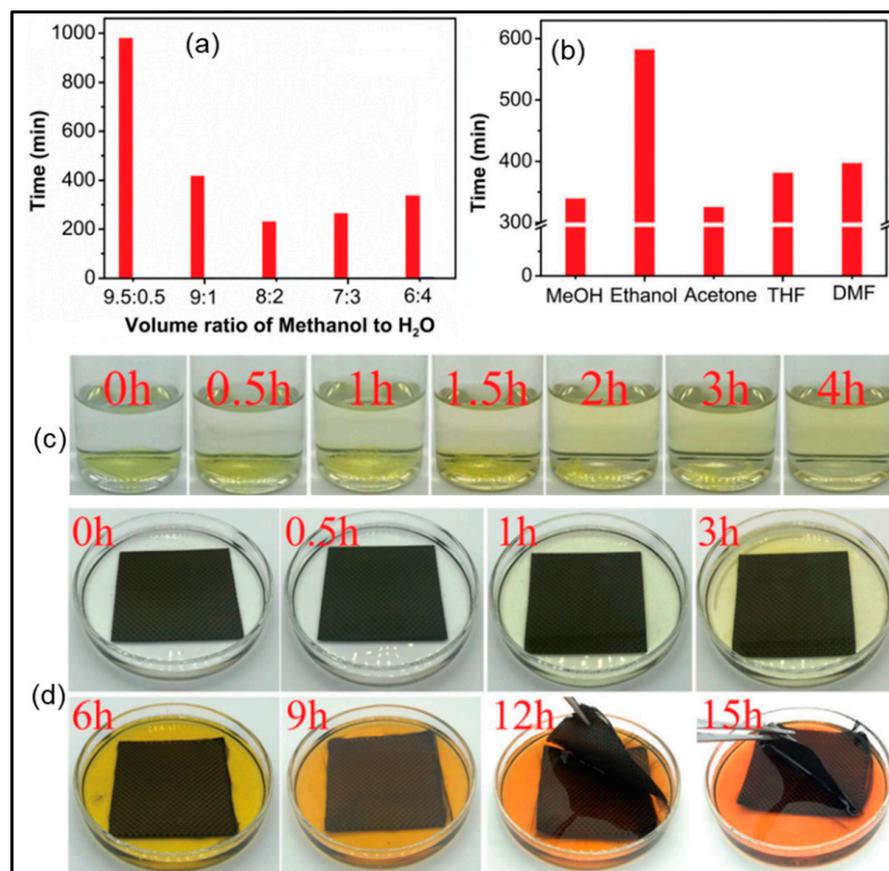


Figure 15. Degradation time of cured ER in different volume ratios of CH_3OH to H_2O (a) and different solvents (b) in the existence of 0.1 M HCl; (c) graphical presentation of degraded ER over time and (d) degradation way of carbon fibre composites over time [Reproduced with permission from Wang et al.; published by RSC, 2019] [45].

Xu and coworkers developed two command-degradable, Schiff-based ERs from lignin-derived epoxy monomers PBE and VBE and the curing agent DDM [96]. The degradation performance of Schiff-based ERs is affected by the water-to-THF ratio and temperature, as displayed in Figure 17a. The degrading process of ERs can be accelerated with a higher water content (Figure 17a). In addition, the solubility of degraded products would be reduced if the water was too high, harming the degradation. Moreover, the optimal water/THF ratio for the degradation of the two Schiff-based ERs is 2:8. Furthermore, practically no degradation happened at 23 °C, and it could happen smoothly and quickly at 50 °C (Figure 17a). In addition, the degradation of cured ERs is also influenced by acidity, such as acid concentration and strength, as well as solvents, as presented in Figure 17b,c. Both ERs degraded quickly in 0.1 M H_2SO_4 solution, while the rate of degradation was significantly slowed down by lowering the acid content to 0.01 M or by using weaker acids, such as HCl, H_3PO_4 and CH_3COOH , in place of H_2SO_4 (Figure 17b). Furthermore,

compared to other solvents, such as methanol, DMF, acetone, ethanol and water, the two samples degraded rapidly in THF (Figure 17c).

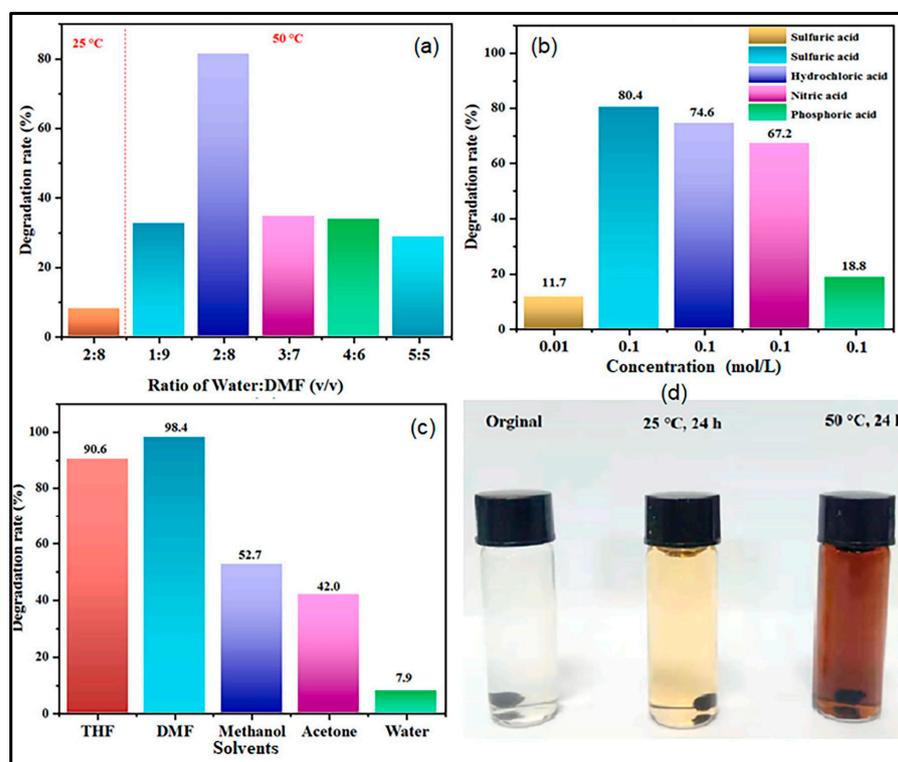


Figure 16. (a) Rate of crosslinked ER degradation at 50 °C and 25 °C in 0.1 M H₂SO₄ solution with several H₂O:DMF ratios; (b) degradation rate of crosslinked ER in different acid solutions at 50 °C with varying H₂SO₄ concentrations (H₂O:DMF = 2:8); (c) degradation rate of crosslinked ER at different solvents with 0.1 M H₂SO₄ solution and (d) the digital image of crosslinked ER degradation [Reproduced with permission from Nabipour et al.; published by Elsevier, 2021] [101].

A recyclable biobased vitrimer was synthesised by Liu and coworkers using the vanillin-modified monomers HVP and D230, as presented in Figure 18a [93]. This material can be fully degraded in an acidic solution (1 M HCl) and THF ($v/v = 2/8$) in 2 h at 25 °C while recovering virtually all of the HVP, as shown in Figure 18b [93]. Further, the developed vitrimers were applied on carbon fibres to make a carbon fibre composite (CFRC), as shown in Figure 18c. The non-destructive closed-loop recovery of HVP monomers and CFs from the composites is made possible by the dynamic imine linkages, which is crucial for maintaining the structure of virgin CFs and HVP molecules (Figure 18c). The properties of the rebuilt CFRPs were similar to those of the virgin ones and could be regenerated and healed quickly at suitable temperatures.

Yang and coworkers prepared a degradable imine bond containing ER from vanillin-modified monomers and D230 in different ratios, as shown in Figure 19a [102]. Under an acidic environment, the developed ER can be fully dissolved due to the reversible imine bonds in its polymer networks, as presented in Figure 19b. Furthermore, biobased ER was used to prepare CFRCs with closed-loop recycling, as displayed in Figure 19c. Interestingly, the recovered CFs retained the same molecular structure, physical properties and morphology as the virgin CFs.

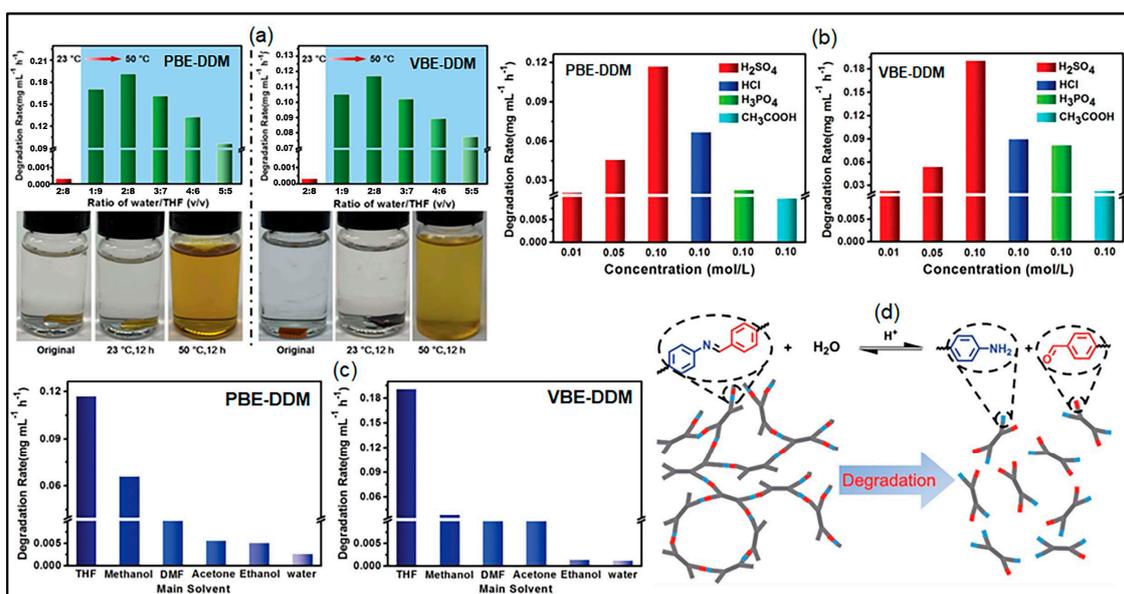


Figure 17. Degradation rate of crosslinked ER in sulfuric acid solution (0.1 M) with different temperatures and solvent ratios as well as their real photograph (a); degradation rate of crosslinked ER in different acid solutions with different concentrations (b) and different solvents (c) at 50 °C; (d) mechanism of degradation [Reproduced with permission from Xu et al.; published by RSC, 2019] [96].

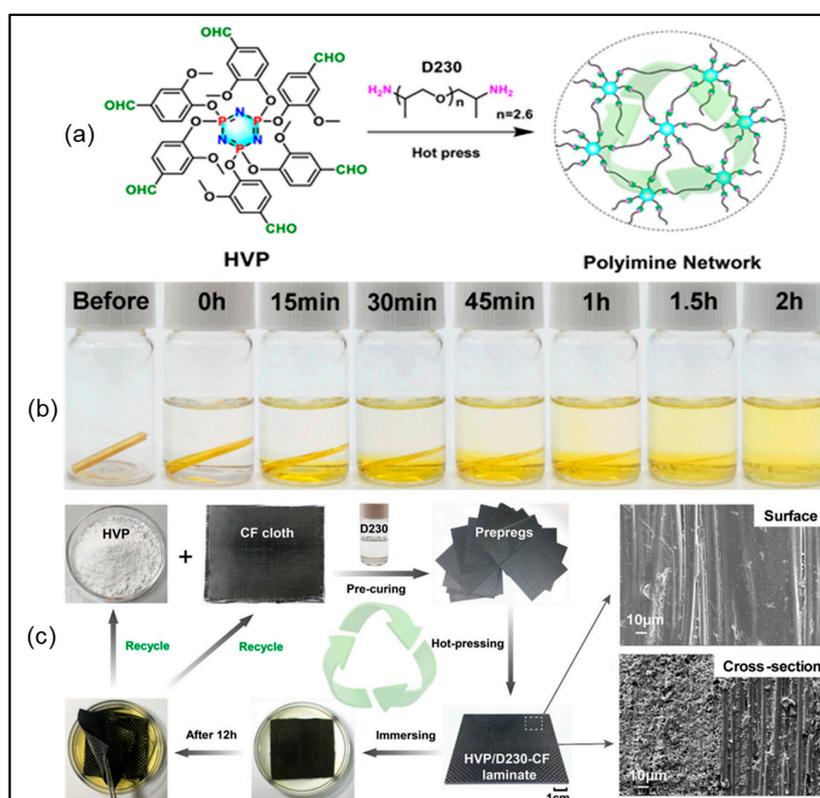


Figure 18. (a) Preparation of polyimine bond-containing recyclable biobased vitrimer; (b) degradation photographs of crosslinked vitrimer in acidic solution (1 M) for varying times; (c) preparation and closed-loop recycling of carbon fibre composite and its SEM view [Reproduced with permission from Liu et al.; published by Elsevier, 2021] [93].

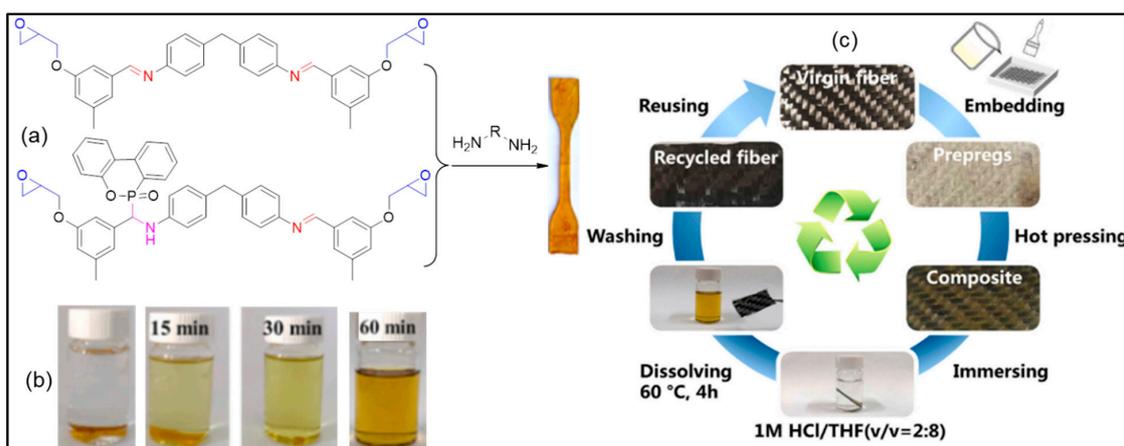


Figure 19. (a) Preparation of biobased imine bond-containing ER; (b) graphical presentation of degraded ER in acidic solution over time and (c) closed-loop recycling of carbon fibre composite [Reproduced with permission from Yang et al.; published by Elsevier, 2022] [102].

7. Self-Healability of Biobased Epoxy Thermosets Based on Imine Bond

Epoxy thermosets used in composite materials tend to be brittle and prone to micro or macro cracks due to their high level of 3D crosslinking. As a result, the integrity of the conventional thermosetting material will vary after being fractured. Scientists developed many reversible bonds to solve this problem. Among them, reversible imine bonds have frequently been used in the dynamic design of materials. To assess the self-healing or repairing performances, the biobased cured epoxy thermosets were scratched on surfaces and placed between two steel plates at 170 °C for 30 min in a convection oven, as displayed in Figure 20a [91]. Finally, an optically visual microscope was used to evaluate the changing scratch widths of thermosets over time (Figure 20b). The treatment of effectively self-healed or repaired epoxy thermosets by removing scratches and regenerating smooth surfaces, owing to the effective rearrangement of dynamic imine linkages, is precise.

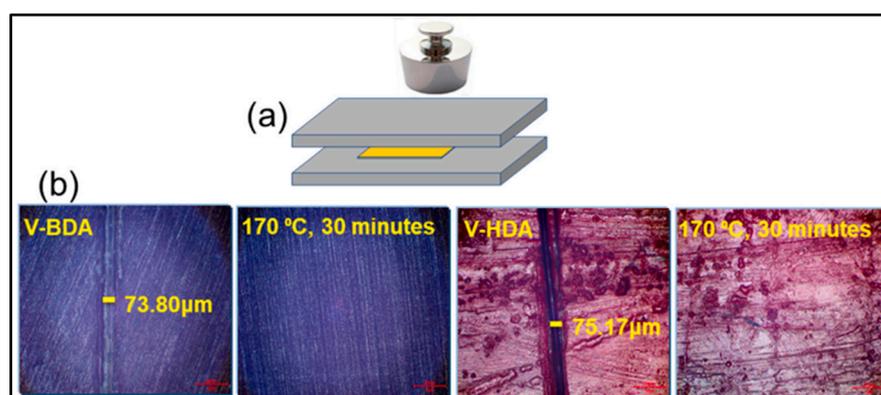


Figure 20. (a) Set-up of self-healability and (b) visual images of epoxy thermosets before and after healing [Reproduced with permission from Rashid et al.; published by Elsevier, 2023] [91].

Liu and coworkers incorporated the reversible imine bond inside the epoxy network, and a polarizing microscope was used to investigate the self-healing property with a hot stage [85]. The cured epoxy surface was slightly scratched using a knife (Figure 21a). After that, the fractured surface was heated at 120 °C over time. The fractured sample's self-healing capability was dissatisfactory for a shorter time; even heating for an additional 30 min might not produce satisfactory results. However, the fractures might vanish after 30 min of warming at 140 °C. In addition, the fracture width significantly decreased at 150 °C over time, as shown in Figure 21b. The epoxy thermoset materials can self-heal at

temperatures over their T_g value, and the higher the temperature, the more influential the self-healing performance. The fracture-repairing capacity increases due to the material's internal polymer chain moving more quickly after being heated over T_g and a severe imine metathesis response.

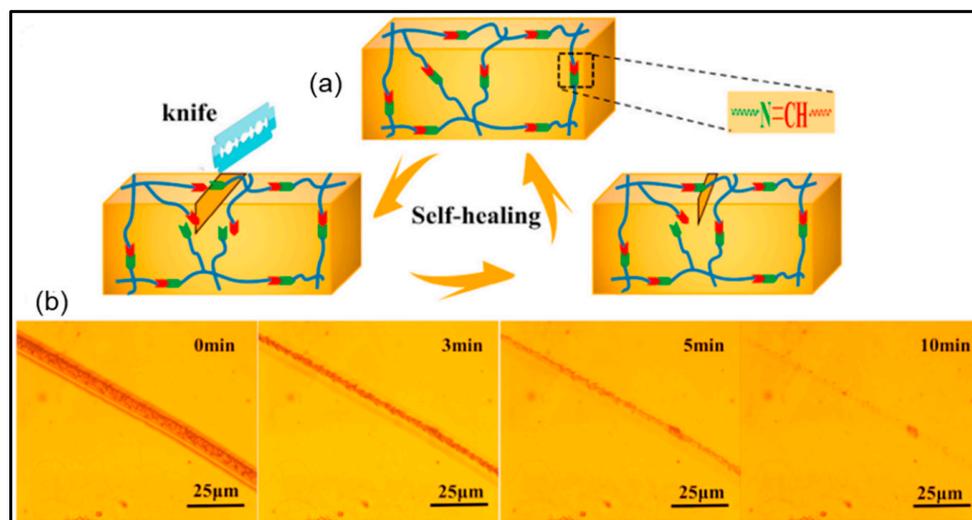


Figure 21. (a) Graphically illustrate the self-healing process through imine metathesis response, (b) optical microscopy photograph of before and after heating at 150 °C for various times [Reproduced with permission from Liu et al.; published by Elsevier, 2020] [85].

Mai and coworkers prepared a reversible biobased epoxy thermoset that can be thermally healable [66]. The experiment was conducted by making a fracture (~50 μm) on the surface of the cured thermoset and observing the reduction in the fracture width over time at 90 °C (Figure 22a). Finally, the fracture was healed on a hot plate at 90 °C for 5 min, as presented in Figure 22b. This occurred because temperatures higher than T_g resulted in the initiation of segmental motion, allowing for the polymer structures to diffuse into each other and exchange reactions and imine bond metathesis.

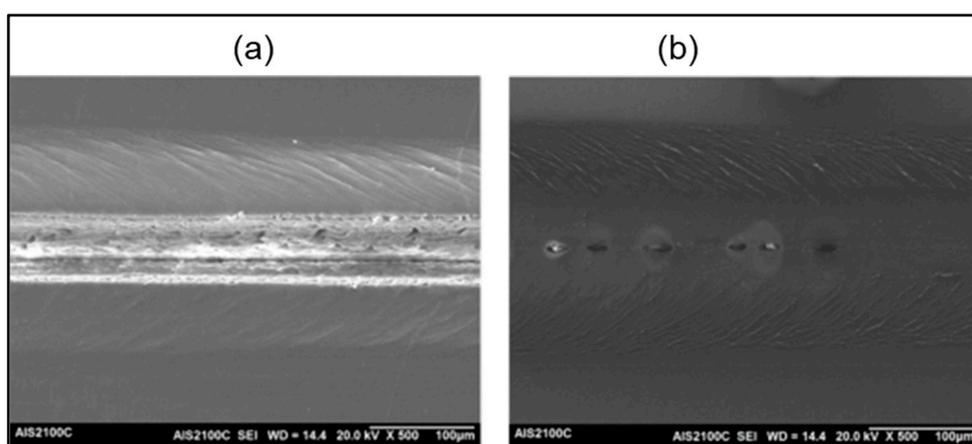


Figure 22. SEM photographs of cracking (a) and repairing (b) surface of epoxy thermoset [Reproduced with permission from Mai et al.; published by MDPI, 2019] [66].

Zamani and coworkers developed Schiff base CFRP from vanillin-modified monomers and 4,4-diaminodiphenylmethane (MDA), as illustrated in Figure 23a [103]. The Schiff base CFRP performed excellently in reparability after cracking under stress. As shown in Figure 23c, after the initial repair, the flexural strength dropped from 461 to 326 MPa, and after the subsequent restoration, it reached 267 MPa. Figure 23b demonstrates the heat

pressing process to repair the composite by re-adhering the cracked polymer at the carbon fibre interface.

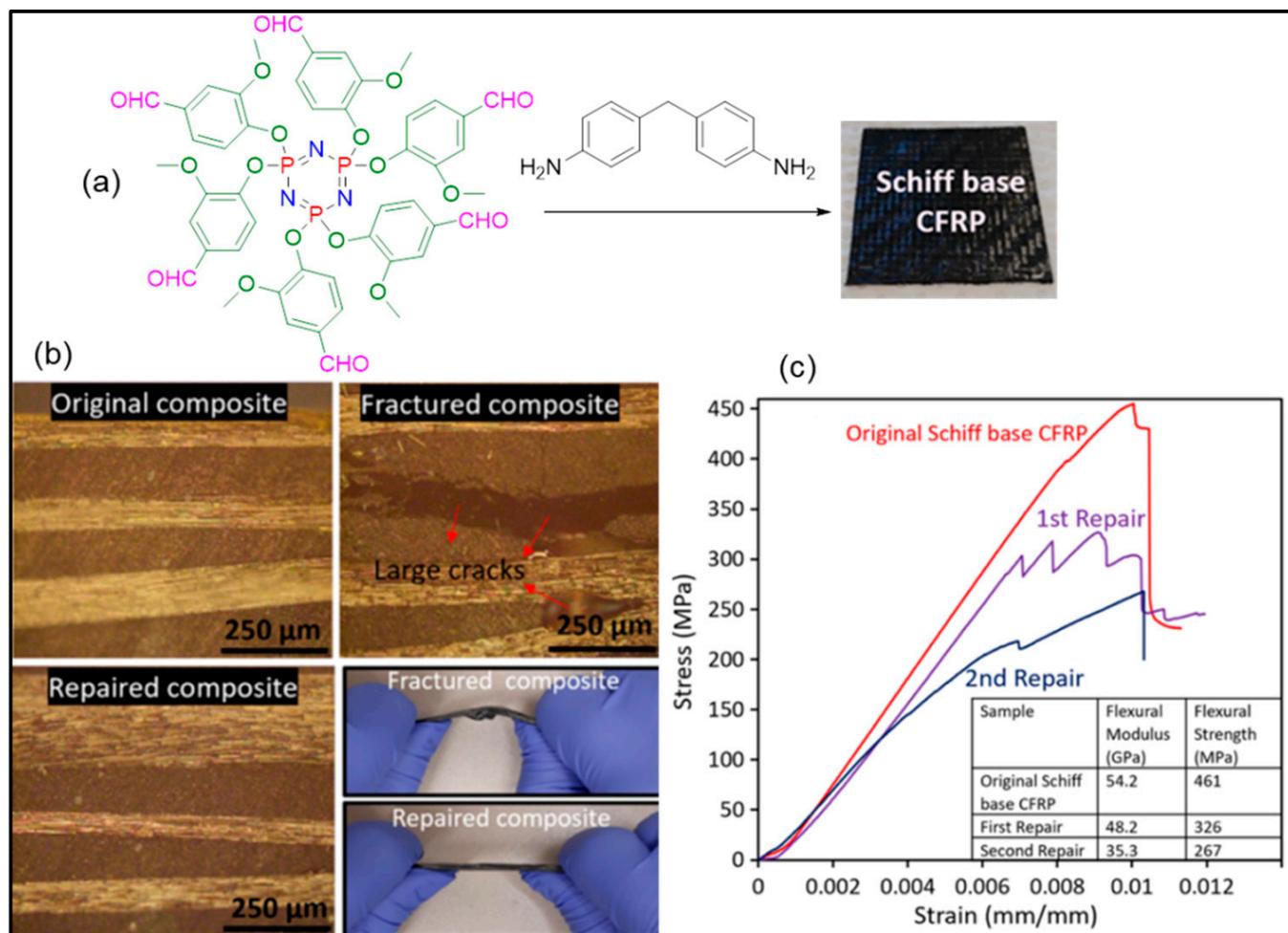


Figure 23. (a) Preparation of Schiff base CFRP; optical microscopic images (b) and mechanical properties (c) of original, fractured and repaired composite [Reproduced with permission from Zamani et al.; published by ACS, 2022] [103].

Peng and coworkers prepared an imine bond containing a fully biobased epoxy thermoset (HVPA/GDE) from a vanillin-functionalized monomer and glycerol diglycidyl ether [94]. This synthetic HVPA/GDE demonstrated outstanding self-healing characteristics due to their crosslinked system's evenly distributed reversible imine links. As depicted in Figure 24, a cut was formed on the surface of the HVPA/GDE material, which was then placed in an oven at 100 °C, and the repairing process was observed under an optical microscope. The repairing rate of epoxy thermoset can achieve more than 80% for 3 min in absence compression and 100% after just 8 min. An appropriate temperature can rearrange the linkage and eventually heal the thermosets' cracks by promoting the exchange response of imine bonds and accelerating the migration of free polymer chains (Figure 24).

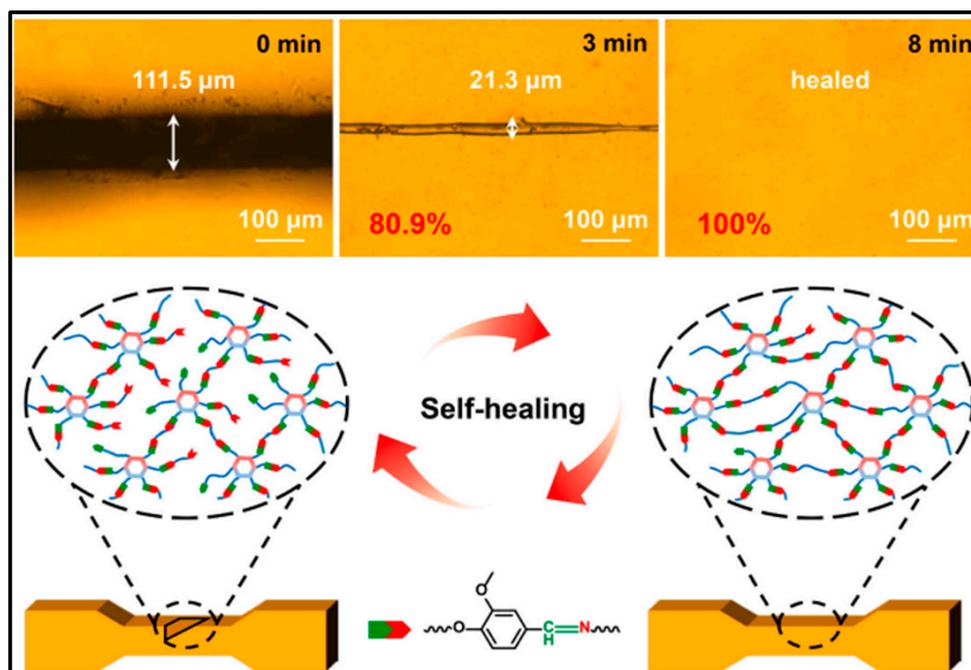


Figure 24. Optical photograph and mechanism of crack healing at 100 °C for different times [Reproduced with permission from Peng et al.; published by Elsevier, 2022] [94].

Yang and coworkers developed a vanillin-based epoxy thermoset that exhibited excellent self-healing performance [102]. It can be noticed that, after 12 h of treatment, the cracked samples were progressively healed, and subsequently, after 24 h of treatment, the cracks completely vanished, confirming that the epoxy thermoset exhibited outstanding self-healing performance owing to the presence of reversible imine linkages, as presented in Figure 25.

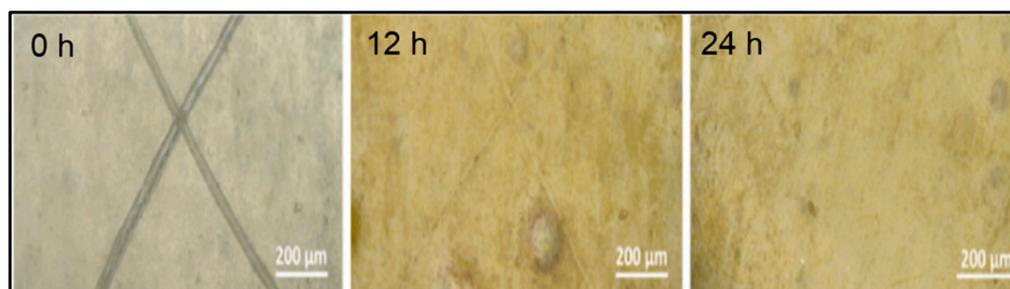


Figure 25. Optical image of crack healing at 60 °C for various times [Reproduced with permission from Yang et al.; published by Elsevier, 2022] [102].

8. Potential Application of Epoxy Resin

Reversible imine bonds comprising epoxy thermosets are produced from renewable, harmless and bio-source elements, which are reusable, repairable and self-healable. The remarkable qualities of epoxy thermosets can be used in various applications, as illustrated in Figure 26.

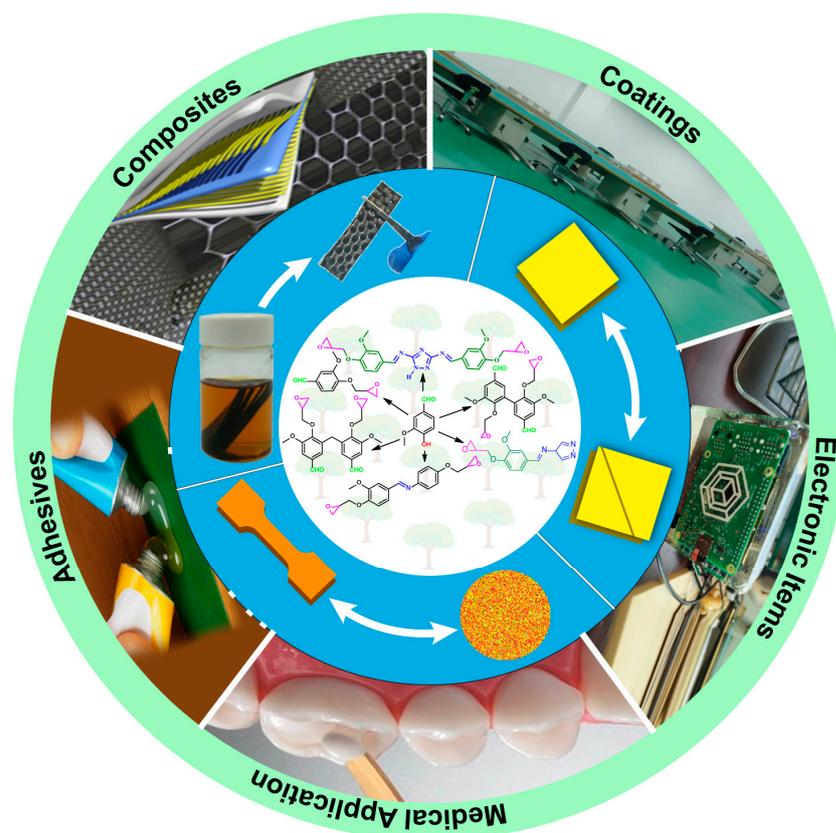


Figure 26. Synthesis, recyclability, repairability and potential application of dynamic imine bond-containing bio-mass epoxy thermosets.

8.1. Coating

The main benefits of biomass polymer coatings over petrochemical-based laminates and coatings are that they are more ecologically friendly [104]. Kadam and coworkers assessed the performance of biodegradable ER for two years in paper lamination and found that the coating was unaffected by humidity, dirt or bacteria [105]. ER has also been extensively used to create self-healing coatings [106]. These coatings are microencapsulated as healing agents inside the polymer, and they are widely utilised in the automotive and aerospace industry because of their long-term stability [107]. Due to their outstanding characteristics, ER is widely employed as effective coatings for preventing corrosion. Metal and containers coated with ER are commonly utilised for packaging purposes to avoid rusting, especially for acidic foods. Additionally, ERs manufacture ornamental flooring materials, including terrazzo, chip and coloured aggregate floors [108–110]. The dependence on petroleum-based chemicals can be mitigated using vegetable epoxies in the coating. It reduces the cost of paints and coating, sacrificing longevity and performance. Epoxied fatty acids can also be utilised for coating purposes [111].

8.2. Adhesives

There are several industrial uses of ER as an adhesive, including in the construction, boat, automotive, electrical and electronic equipment, aerospace, snowboard, bicycle, golf and ski industries [112]. Epoxy adhesives, also called “structural adhesives”, make up a large portion of the category of adhesives [40]. Commercial epoxy adhesives are designed for maximum tensile strength by adding stiff inorganic particles, rubber particles or phase-separated thermoplastics to the matrix [113]. Moreover, Liu and colleagues revealed the adhesive properties of ER from biomass vanillin [114]. ER connected the iron plates using heat compression at 120 °C. The adhesive remains noticeable on metal plates after investigation, indicating that lap-shear damage at the metal plates and ER interactions,

is caused by a cohesive failure instead of adhesive failure. Interestingly, vanillin-derived ER showed identical adhesive performance compared to other biomass [115–117] and conventional adhesives [118,119].

8.3. Electronics

ER is most frequently employed in electronics, such as generators, switches, transformers, insulators, motors and bushing. It shows the insulation property for electricity that shields the electrical parts from moisture, short circuits and dust [120]. To effectively protect semiconductor devices from moisture and unfavourable atmosphere conditions, such as moisture content, heat, UV light, physical harm and mechanical abrasion; mobile-ion contaminants and semiconductor moulding, ERs are utilised [121,122]. Electronic packaging applications have employed epoxy composites with particle fillers, such as mineral silica, glass powder and fused silica, as substrate materials [123,124].

8.4. Biomedical

ERs are widely employed in applications in the biomedical industry, such as the use of transplanted biofactors (cells, genes and proteins) for tissue healing and tissue grafting within biodegradable and porous scaffold materials. For numerous human therapeutic applications, including valves, vascular grafts, wound dressing and aortic heart, collagen-based polymers are employed [125,126]. In cosmetics and healthcare, epoxy thermosets can be utilised to make various goods, including drug carriers, because they exhibit more significant biodegradation rates, more antimicrobial properties, lower moisture absorption and exceptional mechanical qualities [19]. The biomedical system has widely used nanodiamond-epoxy derivatives because they exhibit a remarkable blend of chemical stability, rigidity, optical purity, less electrical conductivity, superior thermal conductivity and other unique features [127–129].

8.5. Environmentally Friendly Polymer Matrix for Fibre-Reinforced Composite

Recyclable biobased ER can be used as a matrix to manufacture composite materials with natural/synthetic fibres. Liu and coworkers developed a recyclable and reprocessable carbon fibre-reinforced composite fabricated with an imine bond containing biobased epoxy resin manufactured from epoxidized soybean oil [98]. It showed a greater Young's modulus (1.18 GPa) and tensile strength (145.4 MPa). Because of incorporating an imine bond, this composite can be reprocessed and recycled without destroying its properties. After degrading or removing the matrix, carbon fibre might undergo complete recycling, and it would be utilised efficiently in aerospace and wind power generation fields. Similarly, various kinds of research have been studied to develop a carbon fibre composite using renewable sources, such as vanillin and methylcyclohexane diamine [87]; vanillin-based monoepoxide and diamine [45]; m-xylylenediamine, vanillin and 1, 6-hexanediamine [130]; adipic acid and bio-based methane diamine [116].

9. Challenges and Future Prospects

Recently, the manufacturing of biobased epoxy resin has been rising, with exceptional improvement in reprocessability or recyclability, self-healing and degradability, incorporating the reversible imine bond. Several limitations and prospects were found and discussed below:

Most epoxy resins are partially biobased and produced from natural sources. Making biobased epoxy resin from natural sources at a reasonable cost is the main challenge and barrier in commercialising biobased epoxy. The complex synthesis procedure and complicated molecular structure of biological resources are other obstacles to market availability. Natural curing agents require a solvent to dissolve it because of its solid nature, making it difficult to process. The degradation temperature, water resistance and glass transition temperature of biobased epoxy resin is lower compared to conventional epoxy thermosets, limiting their application. Another challenge is the difficulties with manufacturing issues,

such as high curing time and temperatures. Manufacturing fully recyclable biobased epoxy thermosets is the most challenging due to less energy in renewable covalent bonds than conventional ones.

The future study on the imine bond-based chemistry will enhance the synthesis and fabrication process of biobased epoxy as a replacement for conventional epoxy thermosets, and it will help to make them commercial in our daily lives and to gain the desired properties of biobased epoxy thermosets. An investigation can be done on designing the epoxy resin to develop the easiest thermal reprocessability or chemical recyclability and stability. The higher number of –OH molecule-containing compounds, such as myricetin, may be synthesised to enhance molecular weight and reactivity performance, which also helps to improve mechanical properties, degradation temperature and water resistance. The epoxy monomers containing tri and tetra-functional epoxide groups can enhance mechanical properties. It is also essential to develop the biodegradable epoxy vitrimers that can be able to react with multiple responses, such as solvent, light, magnetism, electricity and solvent, to reduce the required higher time and higher energy consumption, which will make the easy malleability, reprocessing and self-healing.

10. Conclusions

This review paper focused on the synthesis, reprocessability, degradability and self-healability of bioresource epoxy thermosets based on the dynamic imine bond. These promising properties led to biobased epoxy thermosets in renowned platforms among various thermoset polymers, making them a fantastic replacement for petroleum-based epoxy resins. To produce recyclable or reprocessable, self-healable, degradable biobased epoxy vitrimers, imine bonds, among different reversible bonds, can be inserted into the epoxy. Enhancing important properties, such as toughness, flammability, brittleness and anti-bacterial properties, is vital, which will enlarge its application field. Researchers and the scientific community should come forward to overcome the limitations of manufacturing biobased epoxy thermosets, such as complex synthesis procedures, poor performance and solvent resistance, which will create profitable opportunities to increase consumption and production.

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