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Review

A Critical Review of Sustainable Vanillin-modified Vitrimers: Synthesis, Challenge and Prospects

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Abstract: Nearly 90% of thermosets are produced from petroleum resources, they have remarkable mechanical characteristics, are chemically durable, and dimensionally stable. However, they can contribute to global warming, depletion of petroleum reserves, and environmental contamination during manufacture, use, and disposal. Using renewable resources to form thermosetting materials is one of the most crucial aspects of addressing the aforementioned issues. Vanillin-based raw materials have been used in the industrial manufacturing of polymer materials because they are simple to modify structurally. Conversely, traditional thermosetting materials as a broad class of high-molecular-weight molecules are challenging to heal, decompose and recover owing to their permanent 3-D crosslinking network. Once the products are damaged, recycling issues could arise, causing resource loss and environmental impact. It could be solved by inserting dynamic covalent adaptable networks (DCANs) into the polymer chains, increasing product longevity, and minimizing waste. It also improves the attractiveness of these products in the prospective field. Moreover, it is essential to underline that increasing product lifespan and reducing waste is equivalent to reducing the expense of consuming resources. The detailed synthesis, reprocessing, thermal, and mechanical characteristics of partly and entirely biomass thermosetting polymers made from vanillin-modified monomers are covered in the current work. Finally, the review highlights the benefits, difficulties, and application of these emerging vanillin-modified vitrimers as a potential replacement for conventional non-recyclable thermosets.

Keywords: vitrimer; vanillin-modified monomer; dynamic covalent adaptable network; recyclable; synthesize

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1. Introduction

Thermosets are the most readily used materials in the polymer industry and allow outstanding chemical and electrical resistance, mechanical properties, and formability provided by their permanent extensively 3-D crosslinked network [1–3]. As a result, crosslinked thermosets perform excellently in applications such as composite materials, dental fillings, coatings, and 3-D printing that involve polymers with stable network formation, on-demand generation, and improved stiffness, as displayed in Figure 1 [4–6]. Despite the benefits that thermosets provide, stable and inflexible 3-D networks prevent flow at elevated temperatures, making them unfeasible for mechanical reprocessing [7,8]. Because of their unsatisfactory recyclability and repairability, most thermosets are burned or dumped after their lifetime [9,10]. A cutting-edge thermoset needs to be prepared which is inherently repairable, reusable, and self-malleable much like thermoplastic. In addition, it has exceptional thermal and mechanical properties granted by 3-D crosslinks due to extending the durability and lowering the landfilling rate [11–13]. Dynamic covalent adaptable network (DCAN) integration with a thermoset is an excellent solution to the preceding

problem [7,14,15]. DCAN can undertake exchange interactions with one another at thermal equilibrium conditions in their network system due to external triggers such as temperature, pressure, radiation, solvent, and chemicals [16–19]. The two potential mechanisms in DCANs are depolymerization/dissociative interaction (e.g., diels-alder) and integration/associative interaction (e.g., imination), as illustrated in Figure 2. Under the right processing conditions, DCAN-containing thermosets can be converted to a thermoplastic-like state with a depolymerization mechanism. However, this causes a sudden loss of structural stability and crosslinked density since the depolymerizing response is quicker than the reconnecting response (Figure 2a) [16,20]. Other DCAN-containing polymers with associative mechanisms exhibit a glassy tendency at the operating temperature and retain a consistent crosslinking density (Figure 2b) [21,22]. In 2011, Leibler and his team named those DCAN polymers "vitrimers" [15], which combine the distinctive properties of both thermoplastic and thermoset materials [23]. Topology freezing transition temperature (T_v) is a unique characteristic temperature seen in vitrimers. The change in viscosity of vitrimers follows Arrhenius's theory, in contrast to thermoplastics, which behave differently and flow by the Williams and coworkers' (WLF) hypothesis [15,24,25]. Vitrimers can perform as a viscoelastic fluid at the above T_v. However, they show superior qualities and formability below T_v [26–28]. Moreover, the vitrimer's network architecture can be changed without altering the crosslink density, which means that vitrimers retain their mechanical stability before degrading and are always insoluble in solvents [15,21,24,25]. As a result, polymer scientists and researchers focus on vitrimers in order to offer a broader range of polymer materials for different purposes [23].

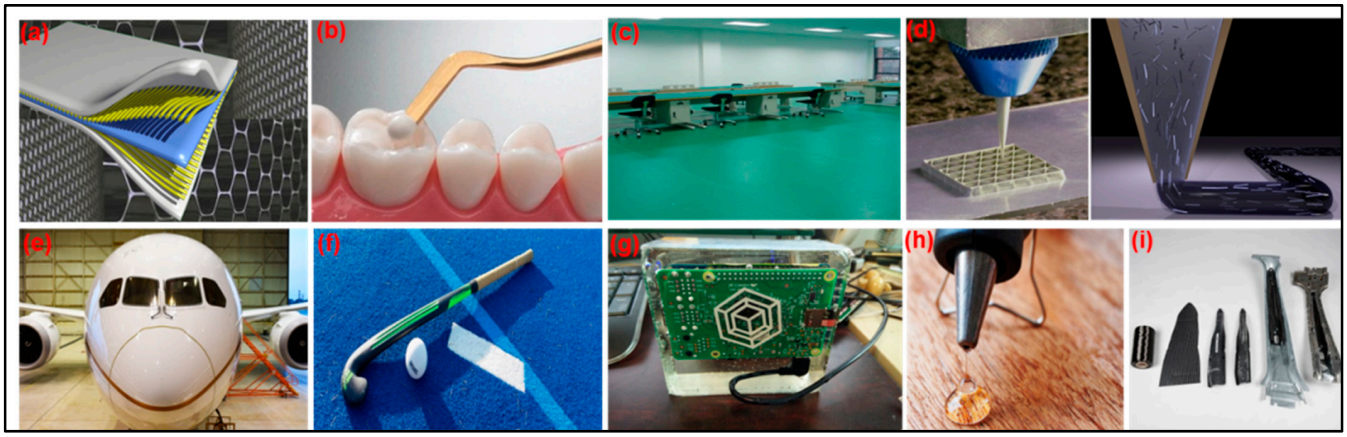

Figure 1. Potential applications of thermosets: (**a**) composite materials, (**b**) dental filling, (**c**) floor coatings, (**d**) 3-D printing, (**e**) plane body structure, (**f**) sports items, (**g**) electronics products, (**h**) adhesive, and (**i**) automobile parts.

Epoxy resins represent one of the most significant thermoset reversibly crosslinked networks. Over 70% of the global thermoset resin market is epoxy resin, which has a variety of uses in the aerospace, structural, electronic, adhesive, and coating industries [29–34]. Unfortunately, the most commonly produced epoxy resins are made from the hazardous bisphenol A (BPA) derivative diglycidyl ether of bisphenol A (DGEBA). In addition to being a known endocrine disruptor, BPA has negative effects on the immunological and central neurological systems [35–37]. DGEBA is also produced using petrochemicals, which have detrimental environmental impacts and are not renewable or sustainable [38]. These elements highlight the necessity of creating sustainable epoxy resin using sustainable feedstocks. Using renewable biomass as the polymeric component's feedstock can help lessen environmental issues by reducing petroleum use and carbon dioxide emissions [39]. Additionally, it reduces carbon emissions, uses fossil fuels in the material preparation process, and encourages the growth of related plant culture industries [3,40,41]. As a result, many studies used different types of renewable feedstocks instead of DGEBA, in-

cluding vegetable oil, lignin, furan, rosin, vanillin, cardanol, cellulose, and other biomass resources [3,42]. These feedstocks offer the opportunity of being plentiful, healthy for the environment, and nontoxic. Out of all these renewable feedstocks, vanillin was the most practical choice, which may be explained by its molecular reactivity, ease of handling, great abundance, and relative affordability [43–45]. A green and renewable epoxy resin can be formed by epoxidizing vanillin and then crosslinking it with a curing agent [46–48]. However, epoxy thermosets made from vanillin cannot be recycled and reprocessed without incorporating DCANs. Given the possibilities described above, a lot of focus has been placed on creating bio-based epoxy vitrimers from vanillin by including DCANs [49–52]. Different types of modified vanillin are used to develop green epoxy vitrimers by incorporating various DCANs into the polymer networks. Even though these cutting-edge green products provide sustainability and recyclability, it may be challenging to replace traditional epoxy thermosets in the application of different fields owing to their thermal and mechanical performances.

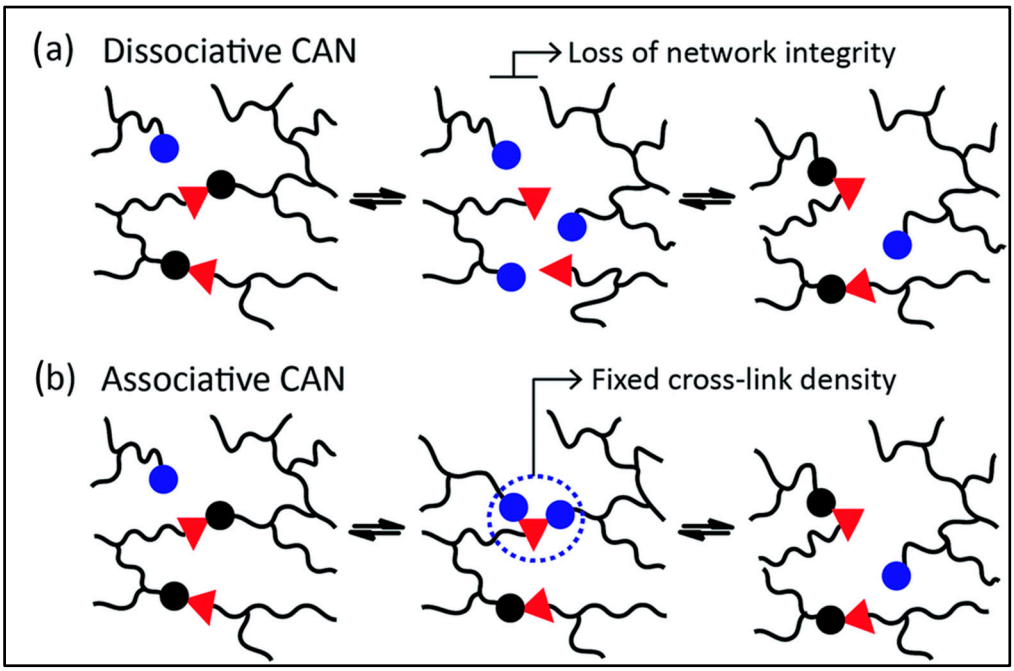

Figure 2. Recyclable mechanism of dynamic covalent adaptable networks (DCANs) [Reproduced with permission from Du Prez et al.; published by RSC, 2016] [21]. Blue and black dots, red triangles are used as active functional groups that can react each other at different conditions.

In this regard, the review's specific goal is to provide thorough yet focused information on the techniques used to synthesize epoxy vitrimers based on vanillin that exhibits extraordinary recyclability and good service properties. The review is segmented into several sections explaining the contribution of vanillin-modified epoxy monomers, curing agents, and vitrimers that are partially and fully bio-based thermosets. Additionally, we will discuss the benefits, difficulties, and application of these emerging vanillin-modified vitrimers as a potential replacement for conventional non-recyclable thermosets.

2. Vanillin-Modified Epoxy Monomers

Vanillin is an aromatic compound obtained from vanilla beans and lignin that is yieldable on a considerable scale [53,54]. It contains highly reactive aldehyde and phenolic hydroxyl groups, which have attracted interest in producing building block polymers [55]. The preparation of Schiff-base epoxy vitrimers with vanillin as a feedstock has been published recently, as illustrated in Figure 3. Their thermal and mechanical properties, as well as recycling conditions, are listed in Table 1.

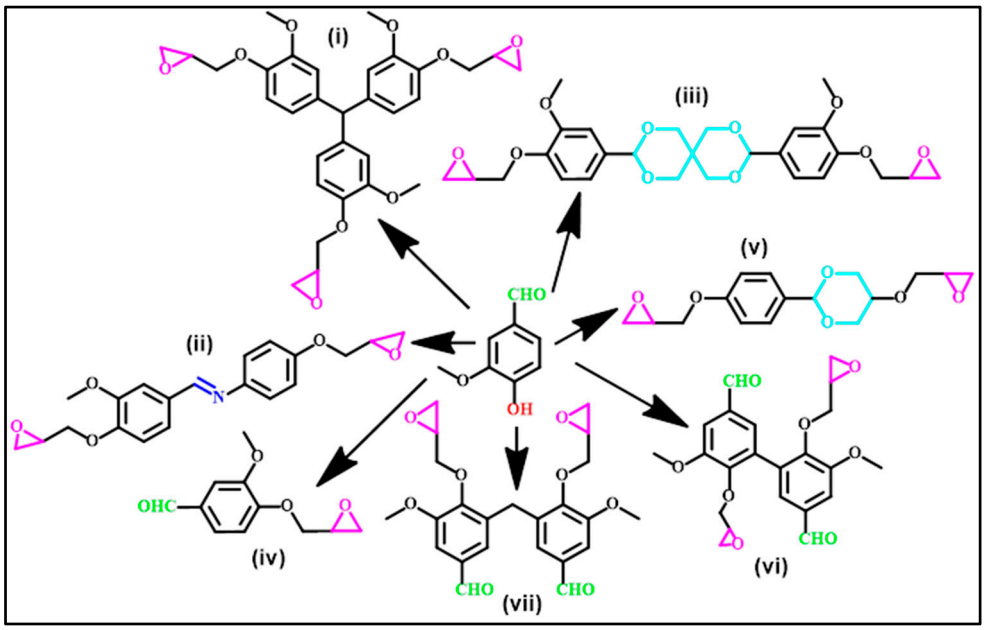

Figure 3. Potential modification of vanillin monomer to epoxy monomer.

Table 1. Thermal and mechanical properties as well as recycling conditions of vanillin-modified epoxy vitrimers.

Composition	Pristine Products		Recycling Conditions		Recycled Products		Ref.
	Strength (MPa)	T_g (°C)	Thermal	Chemical	Strength (MPa)	T_g (°C)	
TEP + MHHPA	69	187	220 °C, 10 m	-	-	-	[56]
GE-VAN-AP + Jeffamine	46	71	100 °C, 60 s	65 °C, 30 m, acid	41	72	[49]
VBE + DDM	93	181	-	50 °C, 12 h, acid	-	-	[57]
Spiro-acetal epoxy + IPDA	87	169	-	50 °C, 9 m, acid	-	-	[58]
MB + PACM	81	172	180 °C, 2 m	r.t., 4 h, acid	81	175	[59]
Van-EP + IPDA	65	109	130 °C, 5 m	70 °C, 24 h, acid	66	-	[50]
DGEVE + DDS	71	184		50 °C, 40 m, acid	-	-	[60]
DGHMDO + DDM	105	164	-	50 °C, 5.5 h, acid	-	-	[61]
DADE + D230	57	106	150 °C, 10 m	50 °C, 24 h, acid	47	97	[62]
GV-EP + DDM	-	220	230 °C, 2 h	90 °C, 24 h, acid	-	237	[52]

T. Liu et al. synthesized a unique triepoxy (TEP) using sustainable vanillin and guaiacol as feedstocks (Figure 3i) and cured it with anhydride hardener (MHHPA) in the presence of a metal catalyst [56]. The cured TEP had a better young's modulus (1.95 GPa), tensile strength (69.2 MPa), and T_g (187 °C) than the traditional epoxy thermoset. It also demonstrated remarkable stress relaxation and healability owing to the triggerable transesterification response. In addition, the cured TEP, along with an epoxy anhydride stoichiometric ratio (R) of 1/1, had the best healability, and the crack of it healed effectively within 10 min. However, a significant amount of catalyst and high temperature were required to respond to the exchange reaction.

Furthermore, Zhao and M. M. Omar used vanillin and p-aminophenol as raw materials to make diphenol-based compounds [49]. Then, these were epoxidized to produce epoxy resins with imine bonds and further cured with aliphatic diamine-based compounds as a hardener to make Schiff base vitrimers, as illustrated in Figures 3ii and 4I. In this design, the author embeds the imine bond in the epoxy resin before curing to facilitate the preparation of a Schiff base vitrimer with a high crosslinked density and robust mechanical properties.

The cured resins were degraded into solvents and polymerized again by evaporating those solvents, which were malleable, as shown in Figure 4II,III. The author also explored the performance of various solvents on the deterioration of the vitrimer under acidic conditions (Figure 4IV) and claimed that the optimal degradation solvent should have the following properties: (1) good consistency with the substance and its degradation products; (2) moderate boiling point and quick removal; and (3) no impact on the efficiency of recycled materials. DMF, on the other hand, is an excellent solvent since it possesses all three properties mentioned above. Moreover, two fractured dog-bone-shaped samples were bonded together in the center at 120 °C for four hours, and the welded sample's fractured sections revealed tensile failure rather than cohesive failure (Figure 4V). The cured thermoset also demonstrated water-driven malleability (see Figure 4VI). The authors claim that their thermoset is entirely reusable; however, it has inferior thermal and mechanical properties due to the longer aliphatic chain in the curing agent. In addition, this epoxy is too challenging to process and can only be operated at extreme temperatures, i.e., using melt polymerization or high boiling point solvents, which bounds its processing.

Figure 4. (**I**) Synthesis method of epoxy resin; (**II**) chemical reprocessing stages of cured epoxy resins: (a) solubilized in DMF and HCl solvents; (b) partly polymerized viscous solution; (c) viscous solution restored cured epoxy resin; (**III**) malleability; (**IV**) solvent resistance; (**V**) weldability of the cured epoxy resin: front view (a) and side view (b) of the welded (c) and broken (d) samples; (**VI**) water-driven malleability: (a) 0.4 mm thick cured thermoset film; (b) flexible film overextended on a round bottom flask; (c) dried sample; (d) under 240 g load; and its (e) magnified image [reproduced with permission from Zhao et al.; published by ACS, 2018] [49].

In addition, Feng et al. also synthesized the same imine bonds containing epoxy resin (Figure 3ii) as in a previous study, which was cured with aromatic diamine and developed a vitrimer with admirable mechanical properties and T_g values (tensile strength ~93 MPa; Young's modulus ~2196 MPa; T_g ~181 °C) [57]. These performances exceed the cured materials formulated with commercial bisphenol A epoxy resin and aromatic diamine as raw materials. This excellent performance is believed to be associated with the multiple aromatic rings and conjugated structures formed by the imine bond. Furthermore, the use of vanillin to formulate functional Schiff base vitrimers has also been reported; for example, the Schiff bond has antibacterial properties [57], has application prospects as an antibacterial coating, contains mono disperse polystyrene microspheres, and exhibits a color-changing function [63].

Nonetheless, the potential research goal is to retrieve carbon fiber (CF) from composite materials with excellent thermal, mechanical, and chemical characteristics while preserving the CF's properties in a profitable nondestructive manner [64,65]. Ma and coworkers prepared a recyclable thermoset with high performance and quick degradability through the dynamic spirodiacetal bond containing vanillin-modified epoxy monomer (Figure 3iii) and cyclohexanediamine (IPDA) [58]. Apart from excellent degradability, the cured spirodiacetal thermoset, its composite and coating had comparable or more promising thermomechanical properties than the cured bisphenol A thermoset. The CF-reinforced composite built on the spirodiacetal-containing resin is easily reclaimable under moderately acidic conditions that retain the characteristics of fresh CF, and the coating promptly detaches from the surface simultaneously.

Moreover, Zhu and coworkers produced a monoepoxide monomer from renewable vanillin and cured it with cyclicdiamine (PACM) to form an epoxy vitrimer, as illustrated in Figures 3iv and 5a [59]. During the curing process, aldehyde-amino reactions include a dynamic imine network, and the epoxy group of the molecule can simultaneously react with another amine group of hardeners. The resulting vitrimer has a tensile strength $\geq$ 81 MPa, Young's modulus $\geq$ 2112 MPa, and a $T_g \geq$ 172 °C, equivalent to commercial epoxy materials. After crushing and heat pressing, the mechanical properties and T_g of the vitrimer are identical to those of the original material. The author also studied the use of this curing system to prepare carbon fiber composite materials that are easily degradable and recyclable without deteriorating the properties of CF, as presented in Figure 5b,c.

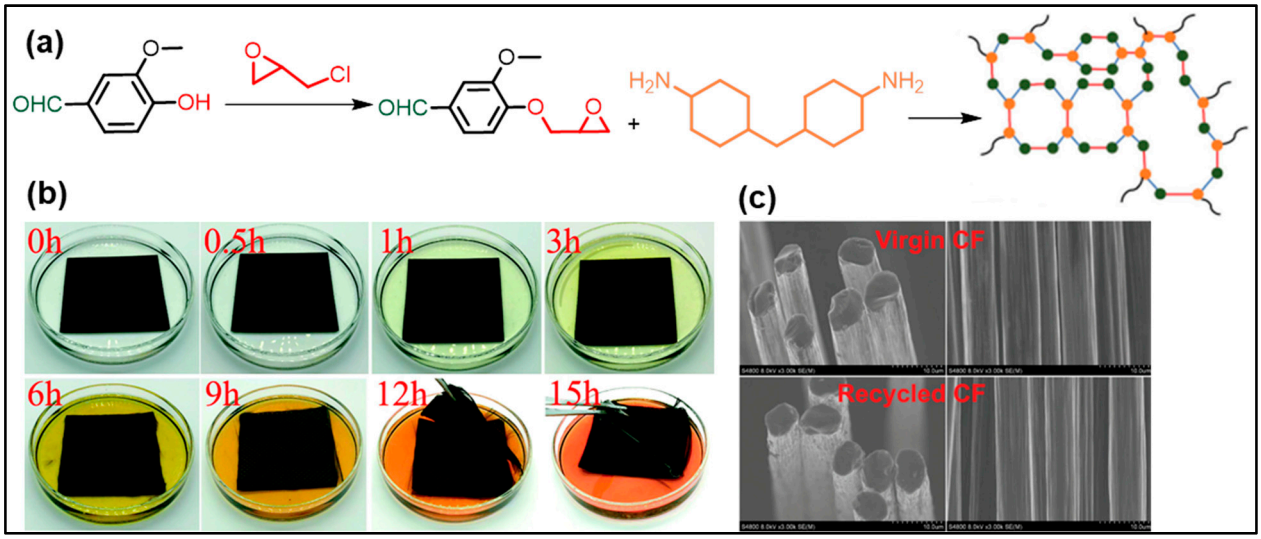

Figure 5. (**a**) Preparation way of epoxy vitrimer, (**b**) epoxy thermoset decomposition in 0.1 M HCl solution (methanol/H_2O = 8/2, V/V) at normal temperature for the recovery of carbon fibers from CFRCs, and its SEM images (**c**) [reproduced with permission from Wang et al.; published by RSC, 2019] [59].

By crosslinking the single glycidyl construction of vanillin (Van-Ep) along with isophoronediamine (IPDA) curing agent, Q. Yu et al. developed a vanillin-modified epoxy thermoset (Van-Ep/IPDA) with reversible imine linkages, which has outstanding reprocessability and acid degradability [50]. Van-Ep/IPDA thermosets (Young's modulus $\geq$ 2.30 GPa, elongation $\geq$ 4.4%, and tensile strength $\geq$ 65 MPa) and control samples (E51) have similar mechanical characteristics. Interestingly, even after three repetitions of hot pressing, all regenerated Van-Ep/IPDA thermosets have an identical degree of mechanical attributes as the original thermosets. In addition, it has a degradable property in acid solution due to its imine network.

W. Yuan et al. introduced a sustainable diepoxy monomer by acetalizing lignin-derived vanillin with the biomass polyolerythritol, which then reacted with sustainable epichlorohydrin, as shown in Figure 3iv [60]. The cured epoxy thermoset was easily degradable (totally liquefied in 1M HCl solution at 50 °C in 40 min) owing to the dynamic dicyclodiacetal bonds in the epoxy monomer. Even during a hot-humid ageing test, it remained stable under neutral and basic circumstances. Moreover, the rigidity of the dicyclodiacetal structure resulted in an extraordinary $T_g \geq 184$ °C, Young's modulus $\geq$ 4.7 GPa, and hardness $\geq$ 0.30 GPa, which are even more significant than those of traditional epoxy resins.

In another study, Ma and coworkers described a digestible, rigid and bioresources dynamic acetal bond-containing thermoset, as demonstrated in Figure 3v [61]. Under slightly acidic conditions, it was quickly destroyed into nonharmful vanillin and glycerol, resulting in the superior chemically degradable of its related epoxy thermosets, which is practical for reprocessing. Due to the aromatic structure, heterocycle, and methoxy group-related hydrogen bond in the thermoset has a more remarkable mechanical and identical thermal performance to a traditional counterpart. Most recently, Fang and coworkers developed a sustainable epoxy resin (Figure 3vi) originating from lignin derivatives vanillin via a simple oxidative coupling of vanillin to make divanillin in water under ambient conditions (80 °C) in only 30 min [66]. It was followed by a reaction of divanillin with biomass epichlorohydrin and finally treated with a green/commercial curing agent that showed outstanding thermal and mechanical performance and durability [66]. Since sustainable epoxy (EDV) possesses aldehyde and epoxy groups, mild acid can disintegrate the resin once it has served its purpose. Afterwards, X. Su et al. produced a biobased, high-performance vanillin-modified epoxy resin (DADE) (Figure 3vii), and the polyimine-epoxy crosslinked structure was created by forming the Schiff base bonds [62]. Treating with the identical primary amine (D230), the cured DADE exhibited better thermal ($T_g \geq 106$ °C) and mechanical characteristics (tensile stress $\geq$ 57.4 MPa, and elongation $\geq$ 3.1%) compared to the DGEBA ($T_g \geq 98$ °C, tensile stress $\geq$ 45.1 MPa, and elongation $\geq$ 4%, respectively). Furthermore, it could be recycled through thermal hot pressing, and the recycled specimens performed similarly to DGEBA. Nevertheless, most of the reported thermosets from vanillin exhibit low to moderate thermomechanical properties and require complicated reprocessing systems such as high temperature, pressure, catalysts, and high boiling point solvents, limiting their real-world applications.

Weng and coworkers recently published a greener Schiff-based epoxy monomer (GV-EP) from the naturally occurring 5-aminoguaiacol and vanillin, shown in Figures 3ii and 6a [52]. The green thermoset (GV-EP/DDM) using the identical hardener showed 33 °C, 38%, and 28% higher T_g, storage modulus, and Young's modulus than the control sample (DGEBA/DDM) owing to their stiff Schiff-base conjugated benzene ring. In addition, it can be mechanically recycled without sacrificing thermomechanical properties for triggerable imine linkages (refer, Figure 6b). Additionally, this product has remarkable shape retention abilities and degrades in acid solution at 90 °C (refer to Figure 6b). Meanwhile, the peak heat release rate (pHRR) and total heat release values (compared with the control sample) both showed decreases of 86.4% and 48.1%, respectively (Figure 6c), and the LOI value of GV-EP/DDM was 35.5%, which was significantly higher.

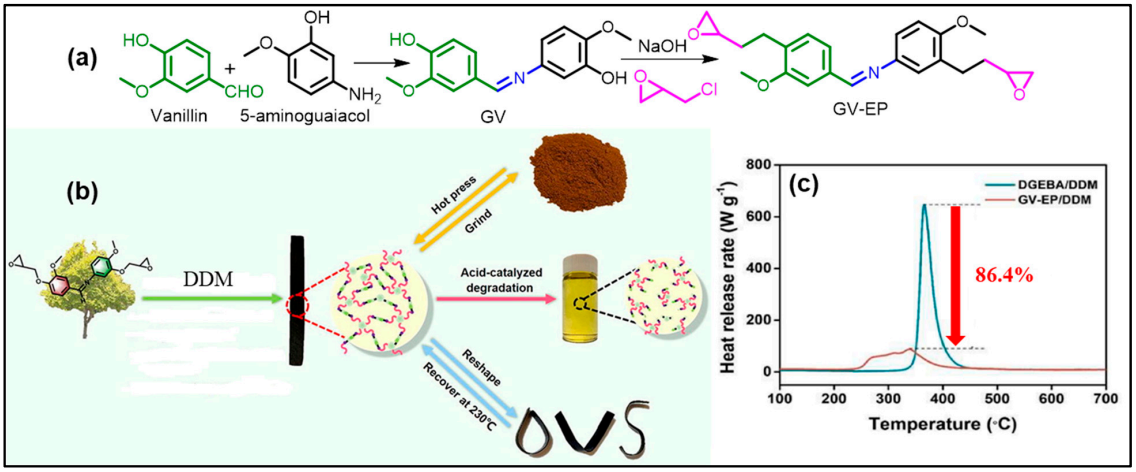

Figure 6. (**a**) Synthesized of greener Schiff-base epoxy monomer (GV-EP); (**b**) curing process and its physical reprocessing, chemical degrading and reshaping performance; (**c**) pHRR versus temperature curve for the developed and control thermosets from the cone calorimeter test [reproduced with permission from Li et al.; published by Elsevier, 2022] [52]. Red arrow used for the difference of heat release rate between two thermosets.

3. Vanillin-Modified Vitrimers

A species of plastic known as vitrimers was produced from thermosetting polymers. These are made of DCANs with thermally triggered bond-interchange systems that can change their structure. At elevated temperatures, the vitrimer can flow freely as a viscoelastic fluid. However, it performs like a typical thermoset and bond exchange systems are unimaginably delayed (frozen) at low temperatures. These are also glass formers with considerable strength. Their features unlock new prospects for thermoset product applications, for example, self-repairing or straightforward operation over a broad temperature span. The vitrimers produced from biomass vitrimer molecules or biobased recoverable hardening agents that are partially biobased inherently vitrimers will be the emphasis of this section. Over the past year, different methods of vanillin transformation for producing vitrimers have been suggested, as indicated in Figure 7. Their thermal and mechanical properties, as well as recycling conditions, are listed in Table 2.

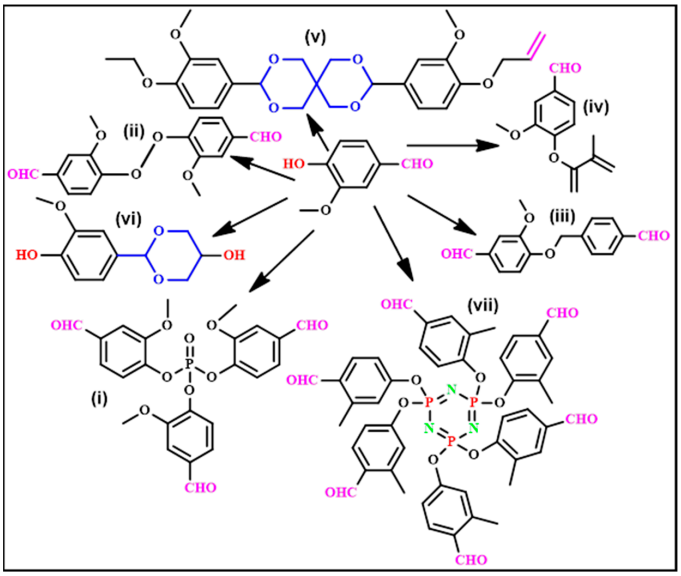

Figure 7. Vanillin modification methods for producing thermoset vitrimers.

Table 2. Thermal and mechanical properties as well as recycling conditions of vanillin-modified vitrimers.

Composition	Pristine Products		Recycling Conditions		Recycled Products		Ref.
	Strength (MPa)	T_g (°C)	Thermal	Chemical	Strength (MPa)	T_g (°C)	
TFMP + diamine	69	178	180 °C, 10 m	r.t., 24 h, acid	69	-	[67]
DAV + diamine	51	75	150 °C, 1 h	50 °C, 24 h, acid	52	-	[68]
VC + triamine + 4-AFD	17	43	60 °C, 20 m	50 °C, 24 h, acid	16	-	[69]
MVL + amine	22	75	200 °C, 10 m	r.t., 24 h, amine	21	-	[70]
HMDO + HDI trimer	68	130	-	50 °C, 40 m, acid	-	-	[71]
HVP + D230	58	98	120 °C, 5 m	r.t., 2 h, acid	56	-	[51]

Wang and coworkers developed recyclable flame-resistant vitrimers using phosphate ester bond-containing multi-aldehyde (Figure 7i) and diamine-based hardeners [67]. After repeated processing, the mechanical performances of the developed vitrimers are proximate to those of the pristine materials. They can be fully dissolved at normal temperature in an acid condition. However, Ye and coworkers used vanillin and dibromobutane as precursors to prepare binary polyaldehyde compounds (Figure 7ii) and then cured them with diamines and triamines to make a Schiff base vitrimer [68]. The performance of vitrimers is achievable and controllable by varying the ratio of diamine and triamine. Augmenting the ratio of ternary amines can boost the crosslinking density and improve the material's thermal (heat resistance, T_g) and mechanical properties. Similar authors prepared carbon fiber composite (CFRC) by using polyaldehyde compounds and diamine (aliphatic, cyclic, and aromatic) [72]. The maximum tensile strength and Young's modulus of two-layer CFRC are 505.4 MPa and 5.52 GPa, respectively, significantly lower than traditional thermosets due to their remarkably inferior interface. However, polyimine vitrimers can be quickly degraded in an acidic medium at 60 °C for 24 h without changing CF's surface morphology and chemical structure owing to reversible imine linkages. In addition, Z. Guo et al. produced vanillin vitrimers (VF_x) with several reversible covalent linkages (S-S and C=N) using dialdehyde (extracted from vanillin (VC)) and amine monomers that are auto-recovering, chemically deteriorating, and reprocessable, as indicated in Figures 7iii and 8a–d [69]. By reacting VC with tris (2-aminoethyl) amine and a small quantity of 4-AFD, VF_x with imine and disulfide linkages was created. More notably, VF_x might be destroyed in a hydrochloric acid (HCl) solution (p^H ~2) and reused to make thermosets again (Figure 8d). However, these thermosets exhibit lower thermomechanical properties. The mechanical characteristics of VF_{10}, which contains 10 mol % disulfide (S-S) linkages, were the most reasonable (T_g ~43 °C, tensile strength ~16.68 MPa), and almost similar mechanical characteristics were maintained after two recycling steps.

Chemical modifications of vanillin to an imine-containing vinyl ester resin ((Figure 7iv) using diamine or triamine at room temperature, Xu and coworkers produced green UV curable, thermally recyclable and chemically recoverable imine vitrimers [70]. After UV irradiation, the vinyl bond conferred photocurability, as evidenced by a substantial rise in storage modulus and a decrease in vinyl bonds. The cured epoxy resins had strong solvent resistance, excellent thermal stability (T_{d5} > 250 °C), and a high storage modulus (1.6~3.4 GPa) at ambient temperature. However, the thermosets might be thermally reproducible at 200 °C under 2 MPa pressure for 10 min. It can be chemically recovered in hexylamine at ambient temperature via the reversible imine exchange response. Likewise, the mechanical characteristics of the thermosets stayed intact even with two thermal recycling processes. In addition, Cortes-Guzman and coworkers produced a similar vitrimeric monomer as in the previous study and applied it to 3-D printing, which is recyclable, self-healable, and degradable [73].

Currently, M. Ge et al. invented an innovative acetal bond-containing green allyl ether monomer (BAMTU) (Figure 7v) derived from sustainable vanillin using green solvents [74]. Finally, it converted to the malleable transparent structure (BAMTU-SH) via thiol–ene "click" photopolymerization, as illustrated in Figure 9a,b [71]. The BAMTU-SH networks displayed good thermomechanical properties (T_g ~20 to 49 °C, tensile strength

~2.9–18.2 MPa, and elongation at break ~103.5–305.6%) in the combination of stiff aromatic portions of vanillin and flexible long aliphatic chains of thiols. Various capacities of thiols can control the features to fulfil specific conditions in application areas. BAMTU-SH4 had the best overall mechanical properties, with the highest toughness (14.5 MPa) and transparency (89.4–90.5% at 550 nm) (Figure 9b). Furthermore, the presence of acetal groups in BAMTU-SH causes it to decompose in a moderately acidic solution in 2.5–6 h (Figure 9c–d).

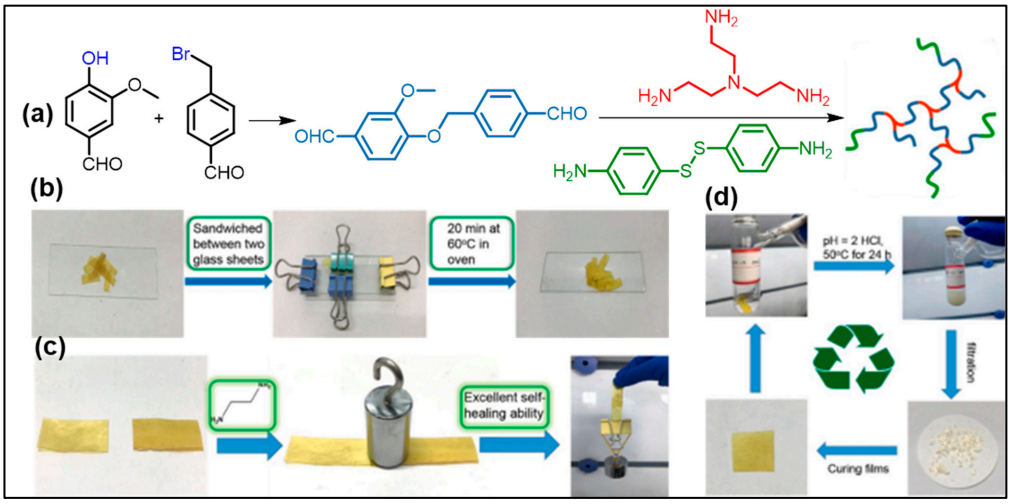

Figure 8. (**a**) Synthesis pathway of vanillin vitrimer; (**b**) mechanical regeneration of finely ground vitrimers; (**c**) self-healing performance of the cut samples that could sustain 500 g of load; and (**d**) chemical reprocessing of the cured vitrimers [reproduced with permission from Guo et al.; published by Elsevier, 2020] [69].

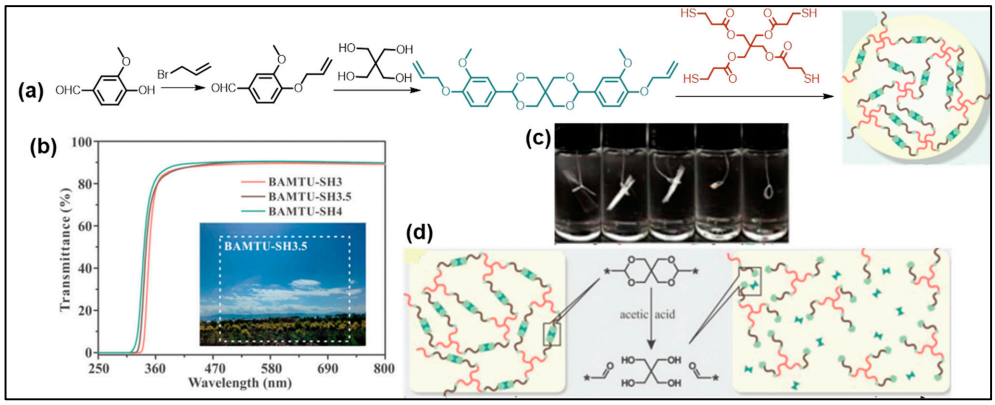

Figure 9. (**a**) Synthesis way of acetal bond-containing vanillin vitrimer; transparency (**b**), degradability (**c**) and its mechanism (**d**) of acetal bond-containing cured vitrimer [reproduced with permission from Ge et al.; published by RSC, 2021] [74].

In 2020, B. Wang et al. developed a biomass acetal diol, 2-(4-hydroxy-3-methoxyphenyl)-1,3-dioxan-5-ol (HMDO) (Figure 7vi), to make an easily recyclable CF-reinforced PU composite [71]. The acetal diol was formulated from vanillin (lignin derivative) and utilized to make the PU thermoset (PU-HMDO) by reacting through a hexamethylene diisocyanate trimer. Moreover, PU-HMDO might be fully dissolved in an acidic condition in 40 min for the cleavable acetal groups. Again, the heterocyclic arrangements of acetal and isocyanurate exhibited suitable mechanical (tensile strength-68 MPa, elongation-7.9%) and thermal (T_g-130 °C) characteristics for PU-HMDO, which are identical to those of a PU thermoset (PU-BPA) made from widely existing diol bisphenol A. Ultimately, the mechanical and physical properties of the PU-HMDO-based CF composite appeared comparable to those of the PU-BPA-based CF composite. CF could also be retrieved with preserved microstructure,

molecular structure, and physical characteristics under moderately acidic conditions, which could be used to make fresh CFRC.

Recently, a flame-resistant vanillin-derived cyclophosphazene (HVP) vitrimer was formed by coupling sustainable available vanillin and hexachlorocyclotriphosphazene with D230 as a hardening agent, followed by the use of the resulting material in CFRPs, as demonstrated in Figures 7vii and 10a [51]. The resultant composite (HVP/D230-CF) appeared to possess a considerable crosslinked intensity and a high P-N ratio, validating the composites' exceptional mechanical and flame retardancy performances. The non-deteriorated upcycling of CFs and HVP monomeric units from composite products is obtained under acidic conditions due to the degradable imine linkages, which are critical for preserving the stability of fresh CFs and HVP monomeric units, as indicated in Figure 10b. The reconstructed CFRPs executed similarly to raw CFRPs and can be quickly reprocessed and mended at normal temperatures. In addition, the mechanical properties of developed composite (HVP/D230-CF) were precisely equivalent to those of the control sample (E51/D230-CF). In addition, Luo and coworkers developed the identical vitrimeric monomer (HVP) by combining sustainable vanillin and hexachlorocyclotriphosphazene and crosslinked it with different aliphatic diamines to form vitrimers [75]. The resultant vitrimers have exceptional tensile strength (35–57 MPa) and thermal properties (T_g of 58–120 °C). Moreover, shortened carbon chain-containing diamine-cured vitrimers had a better mechanical and thermal performance. The innovative vitrimers displayed excellent solvent stability in water, alcohol, alkali, and salt but degraded in acid to reclaim 95% of their monomer (HVP). Remarkably, the diverse imine bonds allowed the vitrimers to be recycled under heating without destroying their functionality. According to the oxygen molecule in the polymer chain of the alkoxy-diamines, the vitrimers exhibited higher LOI values (about 28%) and V-0 ratings in the UL-94 test. Further, HVP and MDA were efficiently used to develop reusable, reconfigurable, recoverable, and fire-retardant carbon fiber composites (CFRPs) by Zabihi and coworkers [76]. The CFRC showed excellent mechanical and thermal properties, including tensile strength $\geq$ 461 MPa, flexural strength $\geq$ 455 MPa, $T_g \geq$ 129 °C and storage modulus $\geq$ 2.57 GPa. The nondeteriorated retrieving of CFs and HVP molecular units from the CFRC is obtained in an acidic solution, which preserves the stability of CFs and HVP molecules. The performance of the mechanically cracked CFRP in terms of repairability (70%) and reshapability is good. Furthermore, the LOI values of CFRP exceeded 33.2% and V-0 rating according to UL-94.

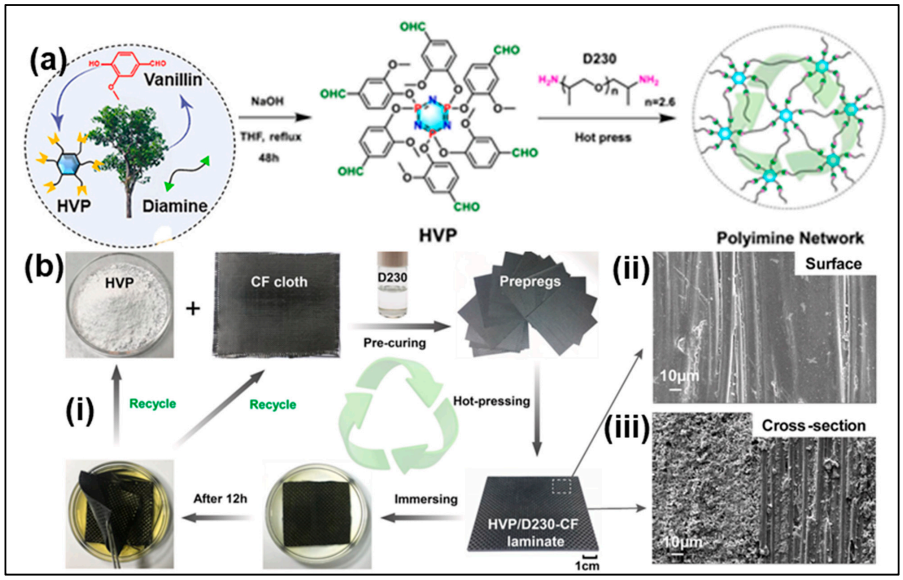

Figure 10. (**a**) Synthesis procedure of polyimine vitrimer; (**b**) formation of HVP/D230-CF composite and its upcycling (i), and SEM image (ii) surface and (iii) cross-section [reproduced with permission from Liu et al.; published by Elsevier, 2021] [51].

4. Vanillin-Modified Curing Agents

Some typical crosslinkers or hardeners for epoxy resins are amines, acids, amides, anhydrides, phenols, and polyphenols [77]. These crosslinkers have diverse operational groups, including amines, carboxylic acids, and hydroxyl groups, which interact with the epoxide groups of epoxy resin to generate 3-D crosslinking structures. Biobased inherently recyclable hardeners will be discussed in this section. However, only some investigations have been published on biobased recyclable curing agents. As shown in Figure 11, four main types of vanillin derivatives Schiff-base curing agents have been developed by researchers. Their thermal and mechanical properties, as well as recycling conditions, are listed in Table 3.

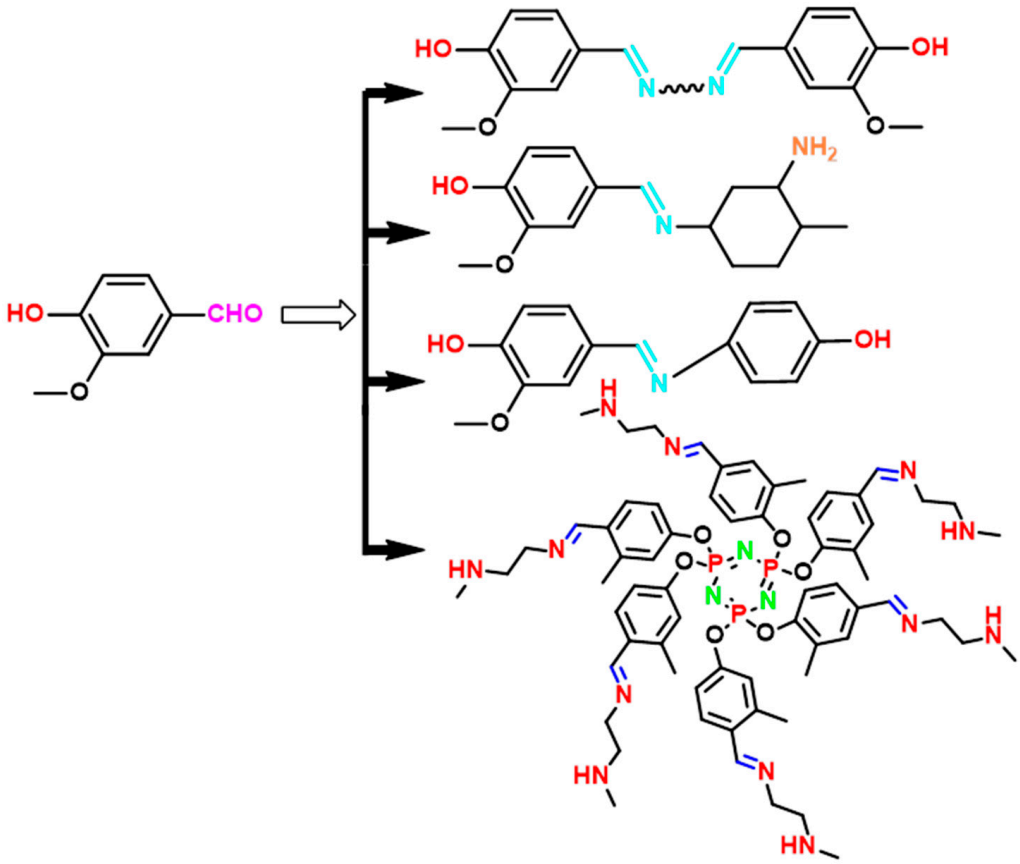

Figure 11. Possible formation of recyclable curing agents from biobased vanillin.

Table 3. Thermal and mechanical properties, as well as recycling conditions of vanillin-modified curing agents cured vitrimers.

Composition	Pristine Products		Recycling Conditions		Recycled Products		Ref.
	Strength (MPa)	T_g (°C)	Thermal	Chemical	Strength (MPa)	T_g (°C)	
DGEBA + Van2HMDA	85	78	110 °C, 15 m	70 °C, 8 h, acid	10	63	[54]
DGEBA + IH-VAN	60	120	170 °C, 30 m	60 °C, 3 h, IPDA	58	127	[18]
DGEBA + Van-OH	79	96	120 °C,12 h	50 °C, 2 h, acid	49	-	[11]
Gte + VA	62	70	140 °C, 10 m	50 °C, 2 h, EDA	63	70	[78]
GDE + HVPA	39	82	100 °C, 3 m	r.t., 45 m, acid	35	-	[79]

V. Mai et al. synthesized a bioderived curing agent (Van2HMDA) from naturally available vanillin (Van) and hexenediamine (HMDA), which subsequently cured the commercially available epoxy resin (DGEBA) incorporation of a catalyst to form recyclable epoxy thermosets, as illustrated in Figure 12 [54]. At elevated temperatures, the epoxy

vitrimer exhibited thermo-repairing capabilities and could be reconfigured by imine exchanges of the curing agents (Figure 12). Again, hydrolysis did not affect the imine linkages in the thermoset polymers while being immersed in water at normal temperature for more than seven days. Still, they may be rapidly degraded in acid due to imine bond hydrolysis, as shown in Figure 12.

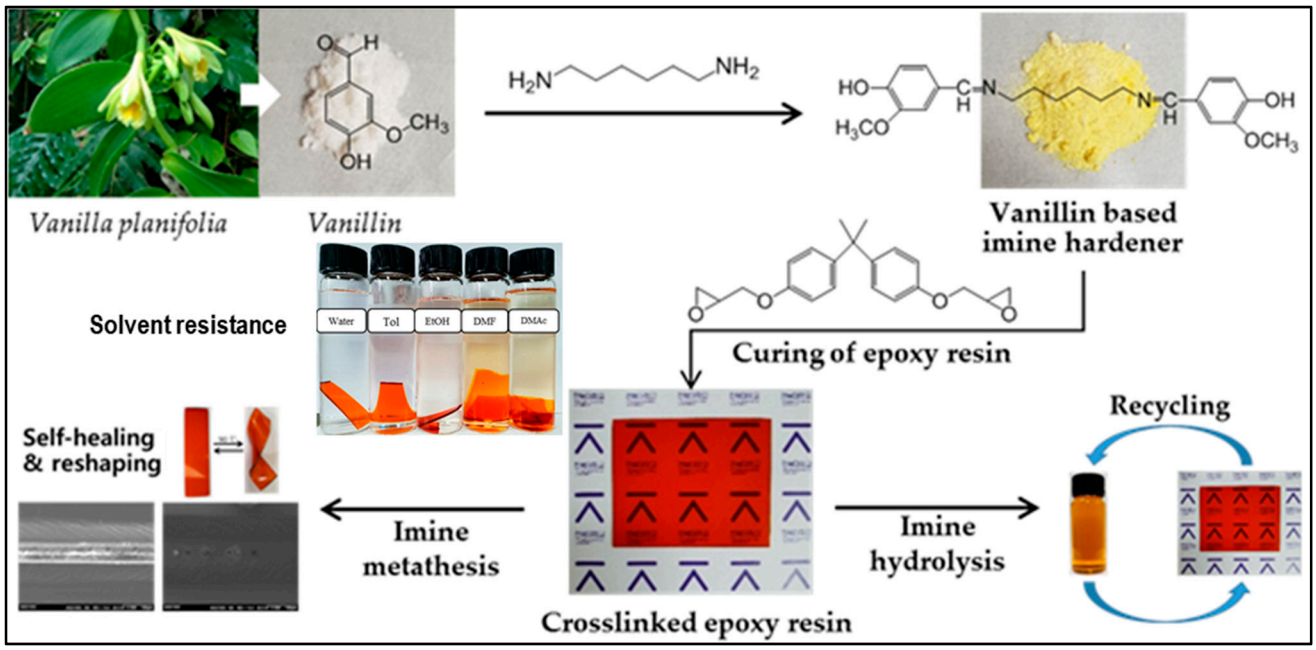

Figure 12. Synthesis pathway and properties of healable, reusable, and solvent-stable epoxy vitrimers from imine bonds-containing vanillin-modified curing agent and DGEBA [reproduced with permission from Mai et al.; published by MDPI, 2019] [54].

Interestingly, H. Memon et al. produced an imine bond-incorporated curing agent using biomass vanillin and fossil fuel-based p-hydroxybenzaldehyde, which was used to cure the commercially available DGEBA epoxy resin [18]. Thermomechanical properties, including T_g > 120 °C, tensile strength > 60 MPa, Young's modulus > 2500 MPa, and solvent resistivity, were all outstanding of these cured thermosets. Moreover, the cured thermosets are degradable and closed-loop reprocessable due to the introduction of an imine reversible covalent link (Figure 13a). In addition, mechanically reconstructed and chemically regenerated epoxy thermosets retain a significant proportion of thermomechanical attributes compared to cured epoxy thermosets with petroleum-based compounds (Figure 13a). According to the same authors, another curing agent was developed from the lignin abundant vanillin and petroleum methylcyclohexane diamine (HTDA) with reversible imine bonds that had sufficient thermal and mechanical properties (i.e., $T_g \geq 131$ °C, strength ~82 MP) as well as solvent resistance [80]. The epoxy thermoset is re-manufacturable and chemically degradable thanks to the included dynamic imine bonds, and it has almost identical T_g and mechanical characteristics as reprocessed thermosets. More importantly, the degraded products may be reusable to make new epoxy vitrimers, with no waste produced during reuse and recycling. CFRC made with this epoxy vitrimer has outstanding mechanical characteristics and can be repaired under hot-press conditions. After interlaminar shear failure, the repaired CFRCs regained a strength return of 92%. By decomposing the matrix resin in an amine solvent through dynamic amine–imine exchange processes, nondestructive carbon fibers may be extracted from CFRCs, as displayed in Figure 13b.

Moroever, X. Liu et al. produced a biobased curing agent (Van-OH) from lignin-based vanillin and m-xylylenediamine with dynamic imine bonds and further developed biobased vitrimers by curing commercially available DGEBA epoxy resin, as shown in Figure 14a [11]. The sustainable vitrimers showed fast stress relaxation behavior, self-

repairing, remoldability, and weldability, as displayed in Figure 14b–e, because of the reversible imine networks. Additionally, two fractured dog-bone-shaped specimens were joined together in the center at 120 °C and 10 N pressure for 12 h. The welded sample's fractured sections revealed tensile failure rather than cohesive failure (Figure 14b). In addition, the materials have adequate solvent stability (Figure 14f) and strong mechanical characteristics (79.1 MPa). Over 15 days in water, the substances seemingly showed a tensile strength of 70.5 Mpa, Young's modulus of 2.32 Gpa, and an elongation of 6.67%, nearly equal to the pristine one. The cured thermoset also exhibited hot-driven malleability. A 30 mm × 30 mm × 2 mm rectangular thermoset sheet was stretched over a circular glass mold after treatment at 120 °C for 10 min and then contracted (Figure 14g(i–iii)). Under a 500 g load, the curved sheet retained its unique shape (see Figure 14g(iv–v)). It was satisfying to notice that the substance could return to its former flat form after being heated to 120 °C for 10 min (Figure 14g(vi)). Simultaneously, the authors reheated the specimen at 120 °C for 10 min, as indicated in Figure 14h, it could be returned to its original form even after softening, half-folding, quenching, and reheating. Additionally, the substances exhibited deterioration and ecofriendly reprocessing abilities in slightly acidic environments with the hydrolysis of reversible imine networks (Figure 14c). The same researchers also synthesized and compared two reversible imine bond-containing curing agents using sustainable vanillin, aromatic diamine, and aliphatic diamine as precursors and then combined them with DGEBA [5]. Both thermosets have remarkable heat and chemical stability. Simultaneously, mechanical attributes such as stress, strain, and modulus were equivalent to or better than those of the standard DGEBA epoxy resin. Notably, the CFRPs made with these bioderived epoxy thermosets as the matrix could be solubilized at normal temperature under mild acidic environments, and the retrieved CFs reserved the surface configuration, chemical composition, morphology, and mechanical performance of the virgin CFs, allowing them to be used to make new CFRPs.

Most recently, Y. Liu et al. developed an imine bond-incorporated hardener (VA) from biobased vanillin and 4-aminophenol and finally cured it with glycerol triglycidyl ether (Gte) epoxy resin, as shown in Figure 15 [78]. The tensile strength of the biobased epoxy vitrimer is 62 MPa, which is comparable to that of amine-cured DGEBA. It also has good reprocessing, recycling, and UV shielding properties. It might be utilized as a matrix to make composite materials (CFRPs), exhibiting excellent tensile strength (449 MPa) and Young's modulus (12.9 GPa). Decomposition of the matrix in an appropriate amine solution results in the carbon fiber being reused without harming the composite material due to the amine-imine reversible exchange response of the imine linkages (Figure 15). Henceforth, the disintegrated epoxy monomers were recombined with retrieved CF fabric, a redeveloped CFRP with mechanical features similar to those of the pristine substances, permitting the carbon fiber-reinforced composite (CERP) to be recycled entirely (Figure 15). Although researchers claim that these thermosets are completely reusable, they have inferior thermomechanical and mechanical properties due to the aliphatic epoxy monomers. In addition, these epoxy resins are incredibly challenging to process and can only be operated at extremely high temperatures, limiting their application.

Liu and coworker successfully synthesized a bio-mass versatile hardener (HVPA) from vanillin-modified cyclophosphazene (HVP) and N-methylethylenediamine and formed vitrimer by curing epoxy monomers, as illustrated in Figure 16a [79]. This vitrimer revealed outstanding performances, including pressure-less quick healing, excellent shape memory, rapid recycling and dissolving in acidic solution owing to the even distribution of imine bonds in the polymer structure (Figure 16b–e). Additionally, with highly crosslinked density and N, P content in the polymer structure of thr vitrimer, it exhibited excellent mechanical properties, flame retardancy, and UV resistance.

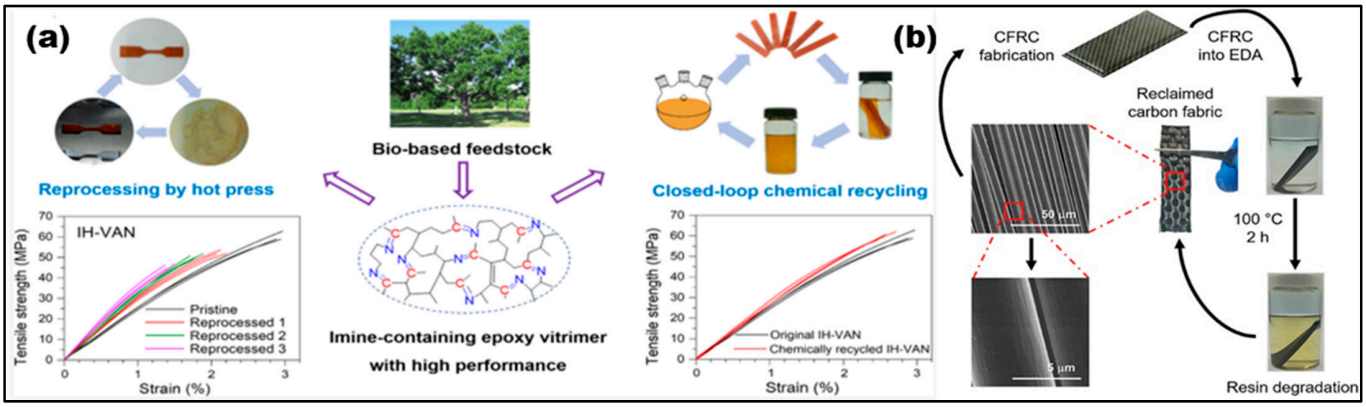

Figure 13. (**a**) Mechanically and chemically closed-loop recycling process and stress-strain curves of the cured biomass vanillin-modified themosets [18]; (**b**) schematic diagram of the complete reprocessing method of CFRCs and morphology of the surface of the recovered carbon fiber [reproduced with permission from Memon et al.; published by Elsevier, 2020] [80].

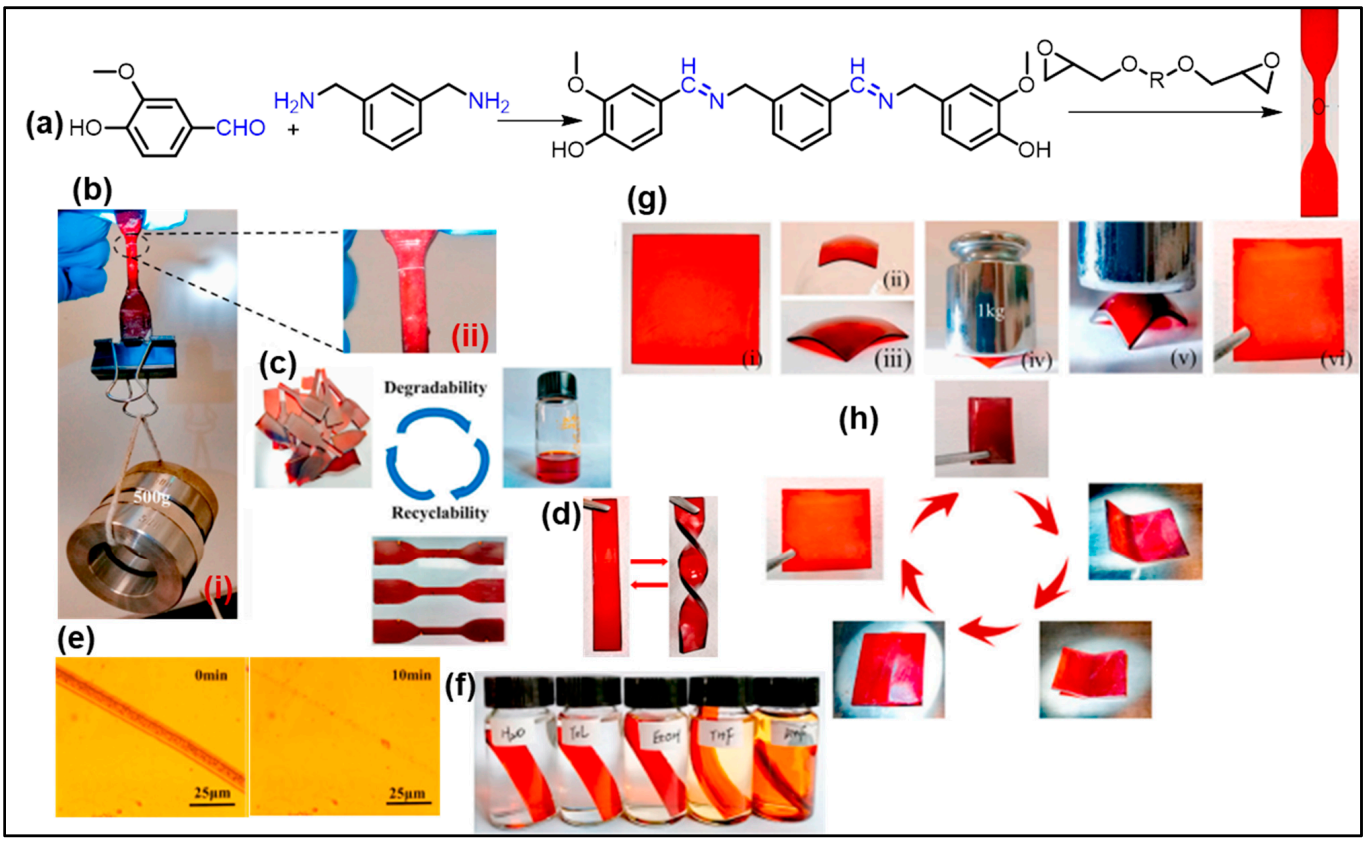

Figure 14. (**a**) Synthesis of vanillin-derived epoxy vitrimer; (**b**) weldability: (i) the specimen successfully adopted a 500 g load after welding, and (ii) partial magnification of the welding; chemical recyclability (**c**), malleability (**d**), repairability (**e**), solvents resistivity (**f**), hot-driven malleability (**g**): (i) cured vitrimer sheet; (ii) put the sheet on a round bottom flask and heat it at 120°C for 10 min; (iii) curved sheet in the cooled condition; (iv) remodelled specimen loaded 1 kg except remarkable deflection; (v) 1 kg loaded magnified image of the specimen; (vi) flat shape from the curved specimen after being heated; and (**h**) shape-memorability of the cured vanillin-derived vitrimer [reproduced with permission from Liu et al.; published by Elsevier, 2020] [11].

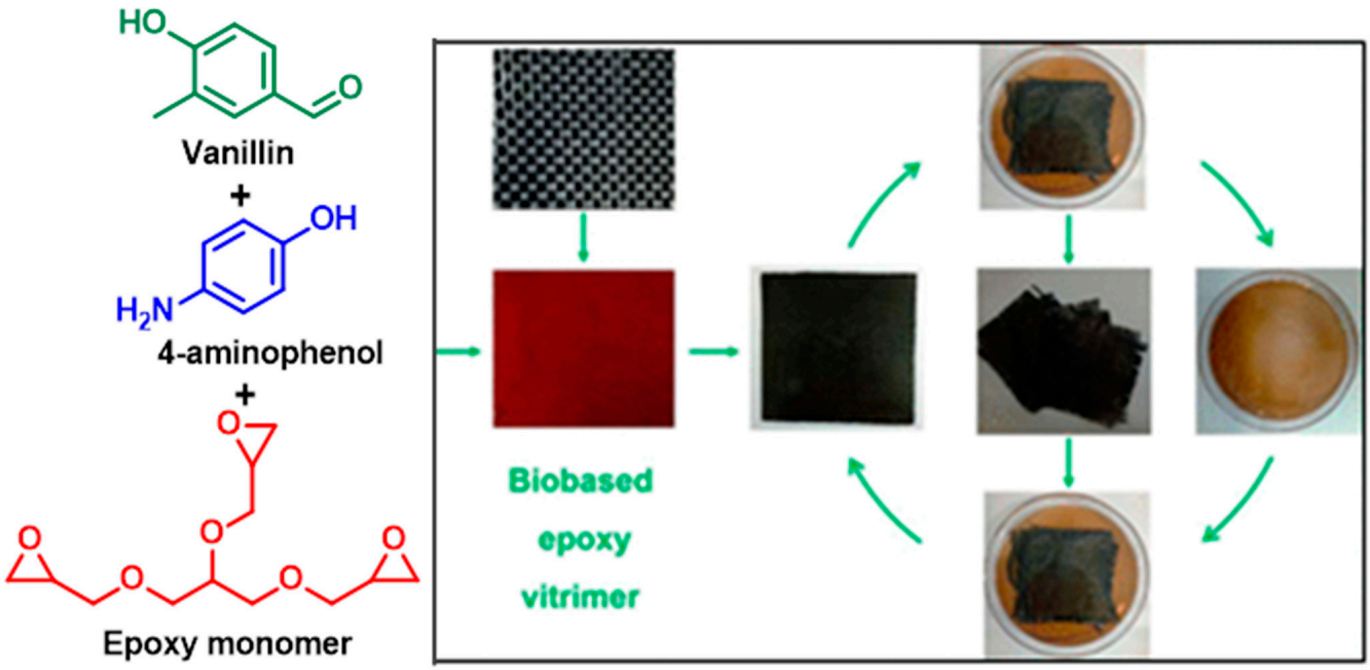

Figure 15. Synthesis way of vanillin-modified vitrimer and full recycling of carbon fiber reinforced composite (CFRP) [reproduced with permission from Liu et al.; published by ACS, 2021] [78].

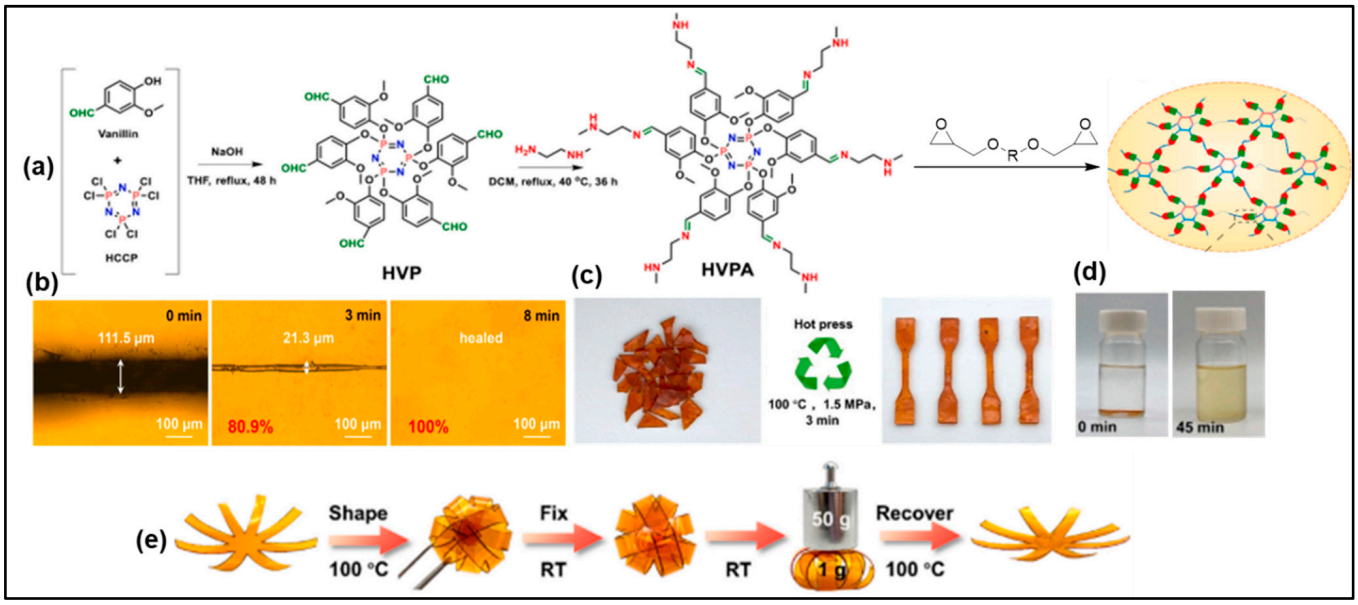

Figure 16. (**a**) Synthesized way of imine bond containing hardener (HVPA) from vanillin and its cured network; repairability (**b**), reprocessability (**c**), degradability (**d**), and reformability (**e**) of the cured thermoset [reproduced with permission from Peng et al.; published by Elsevier, 2022] [79].

5. Fully Biobased Vitrimers

Biobased epoxy monomers, whether they contain reversible bonds cured by biobased hardeners or biobased epoxy monomers cured by reversible bonds containing biobased hardeners, are classified as completely biobased recyclable epoxy thermosets in this investigation. Because of the growing concern regarding environmental sustainability, the biomass content of the products is supposed to be as high as possible. As a result, completely bio-based recyclable epoxy thermosets are attractive. The truly bio-based epoxy thermosets with inherent recyclability will be discussed in this section.

X.L. Zhao et al. created fully sustainable epoxy vitrimers using biomass epoxidized soybean oil (ESO) and vanillin modified (VSB) hardener (Figure 17) in the presence of 1,2-dimethylimidazole (DMI) as a catalyst at different ESO and VSB weight ratios (R = 0.5, 0.6, 0.7, 0.8, 0.9, or 1.0) [81]. Among them, R = 1.0 has more excellent thermo-mechanical properties than the other weight ratios of ESO and VSB. Recyclable thermosets have multiple functionalities, such as reproducibility, repairability, multiple configurability, and programmability, due to the dynamic Schiff base bonds that make it easier to fabricate.

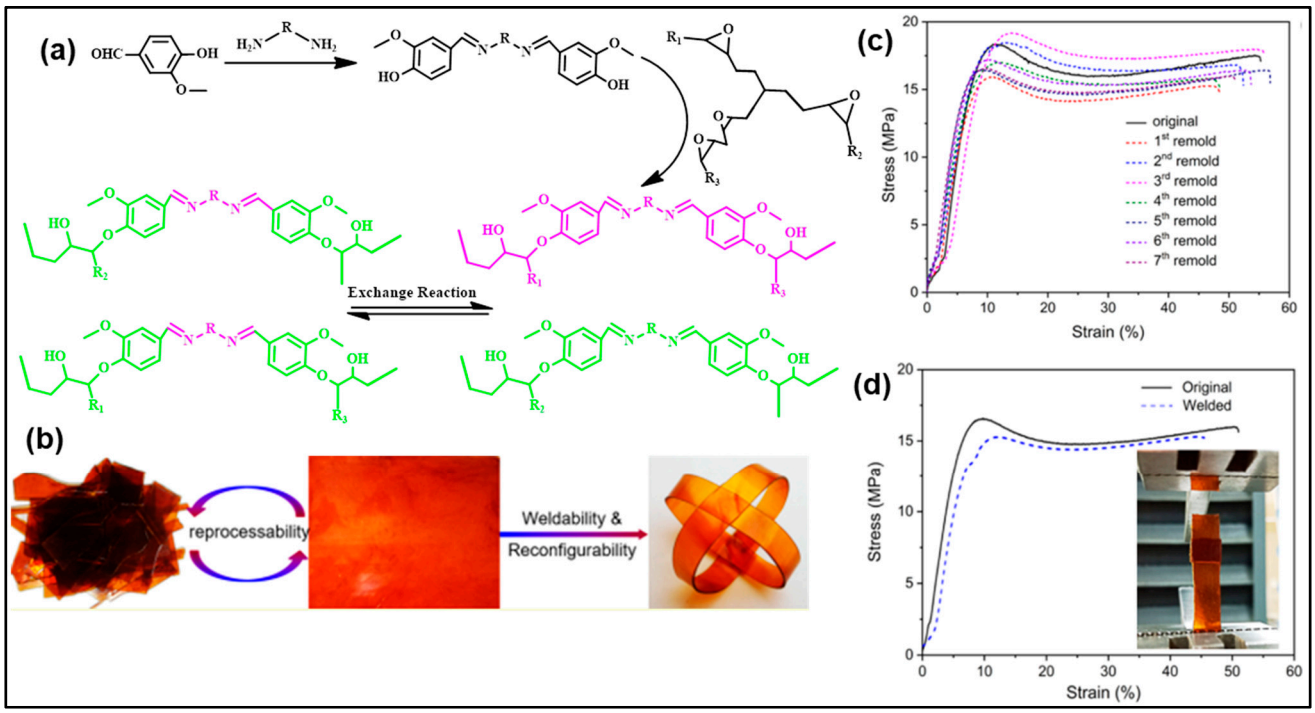

Figure 17. (**a**) Preparation of fully bio-based vitrimers from ESO and vanillin modified (VSB) hardener and its exchange reaction; (**b**) reprocessability and weldability, (**c**,**d**) mechanical strength of pristine and remolded or welded samples [reproduced with permission from Zhao et al.; published by ACS, 2020] [81].

Recently, Z. Zhou et al. developed completely bio-based polyimine vitrimers by combining a dialdehyde or trialdehyde produced from vanillin with a commercial bio-based amine in a condensation reaction (Figure 18) [13]. The polyimine vitrimers had exceptional ductility, with an elongation at break of 167–640%, making them suitable for usage as an elastomer. They also had decent pliability and reproducibility, despite having a high crosslinking density due to rapid imine metathesis. The aldehyde monomer was recovered after acid degradation (0.1 MHCl), which might be utilized to make a thermoset vitrimer to complete the closed-loop sequence. In addition, the original and regenerated polyimine vitrimers had almost equal tensile strength and elongation at break.

A degradable and flame-resistant green vitrimer (VTA-EP/DFA), displayed in Figure 19a, was successfully developed by Nabipour et al. from a fully bioresource vanillin-modified epoxy monomer (VTA-EP) and 5′-methylenedifurfurylamin (DFA) [82]. Due to the unsaturated linkages and benzene ring, the VTA-EP/DFA vitrimer has more excellent thermal ($T_g \geq 170$ °C) and mechanical properties such as tensile strength ≥ 60 MPa, storage modulus ≥ 3271 MPa, and elongation at break $\geq 2.8\%$ than the reference DGEBA/DDM thermosetting materials. The VTA-EP/DFA obtained a V-0 grade in the UL-94 test and had a more excellent LOI value ($\geq$38.5%) than the reference thermoset, except for the inclusion of flame-retardant molecules. Consequently, the green epoxy vitrimers demonstrated outstanding degradability in various solvents in an acidic environment due to the dynamic imine bonds, as shown in Figure 19b.

Du and coworkers developed a variety of fully biomass thermosets from vanillin-modified aldehydes and diamines, as illustrated in Figure 20a [83]. The mechanical and thermal characteristics could be optimized by regulating aldehyde and diamine content proportion. The biomass thermosets showed remarkable thermo-mechanical performance with a storage modulus varying from 0.80 to 3.07 GPa and a tensile strength ranging from 32.1 to 58.0 MPa, equivalent to conventional thermosets due to the addition of high rigid aromatic rings and crosslinked density. Notably, the fully biomass thermosets could be recycled several times without changing their properties owing to the inclusion of triggerable imine bonds in the molecular structure (Figure 20b). In addition, the weldability efficiency was more than 90.6% (Figure 20c). Besides, it was dissolvable in an acidic solution, allowing closed-cycle reprocessing through the reclaimed monomers, as shown in Figure 20d.

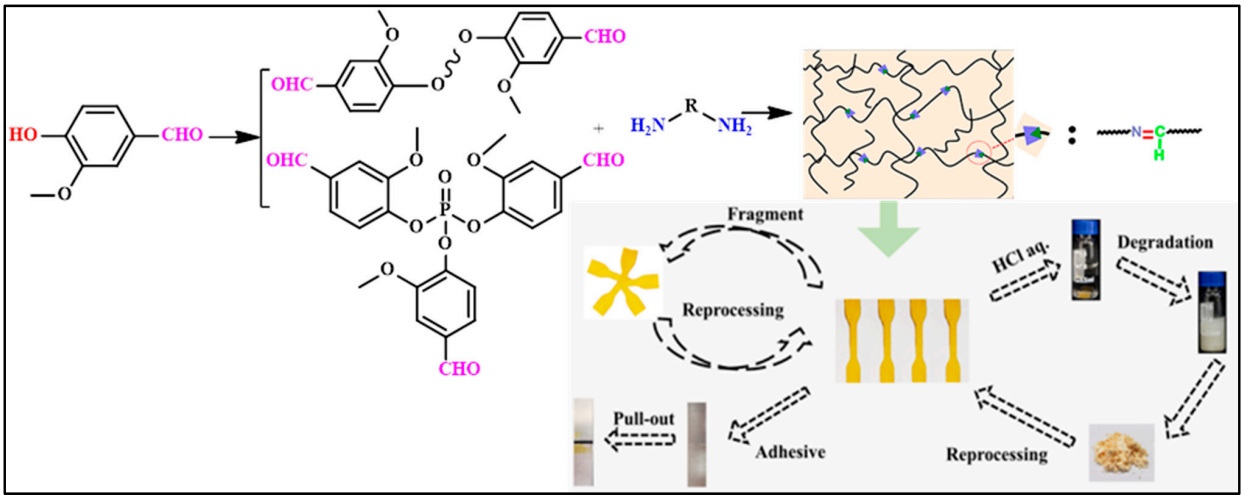

Figure 18. Synthesized routes of completely biobased reversible polyimine vitrimer from sustainable vanillin and amine, and its thermal and chemical recyclability [reproduced with permission from Zhou et al.; published by ACS, 2020] [13].

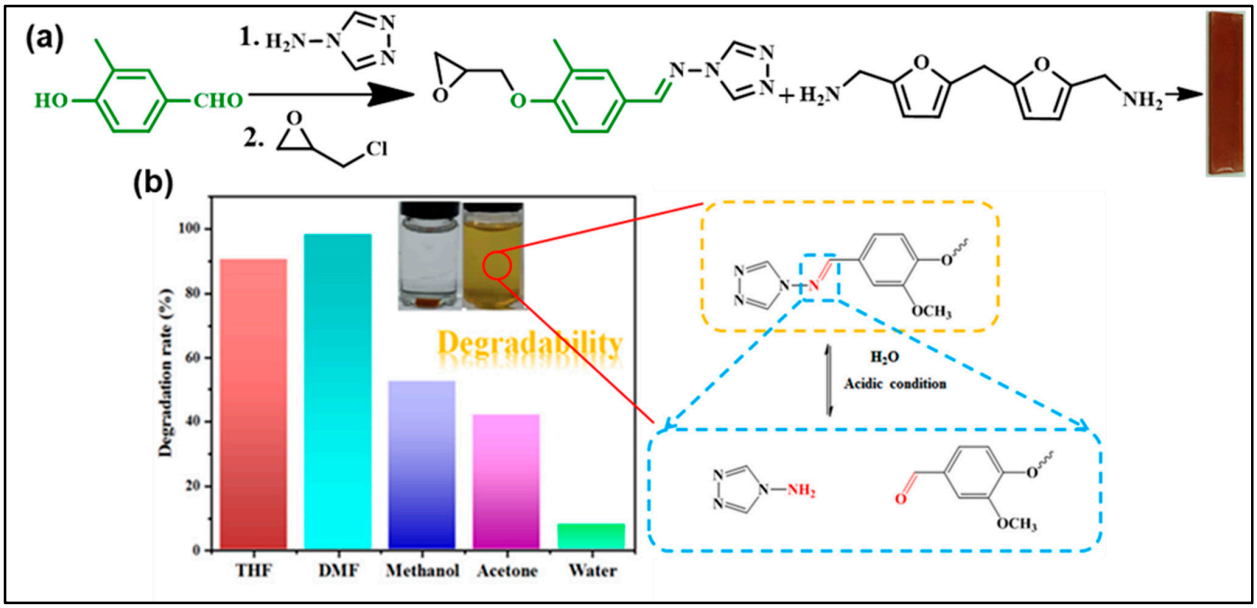

Figure 19. (**a**) Vanillin-modified epoxy monomer (VTA-EP) and its thermoset synthesis pathway, (**b**) degradability of fully green vitrimer (VTA-EP/DFA) at different solvents and its degradation mechanism [reproduced with permission from Nabipour et al.; published by Elsevier, 2021] [82].

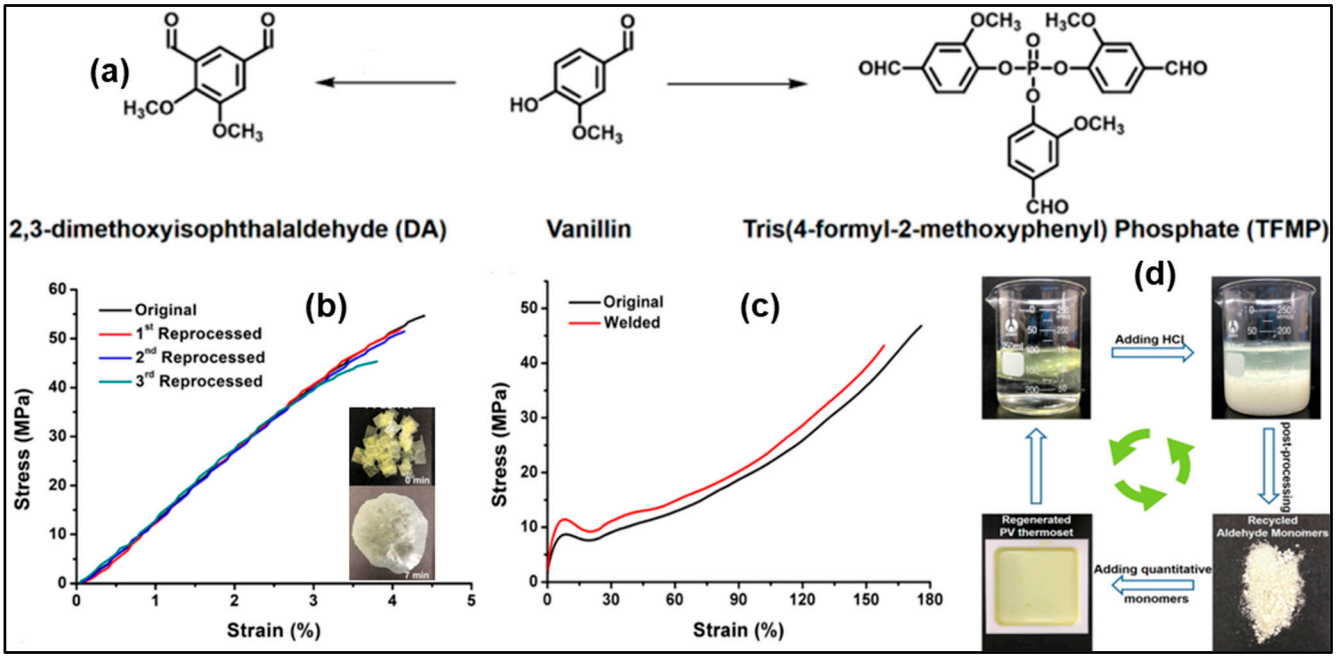

Figure 20. (**a**) Synthesized pathway of aldehyde from vanillin; mechanical recycling (**b**) and weldability (**c**) performance; and (**d**) closed-cycle chemical recycling [reproduced with permission from Hong et al.; published by ACS, 2022] [83].

6. Potential Applications of Vanillin-Modified Epoxy Vitrimers

Vanillin-modified epoxy vitrimers are developed from sustainable, nontoxic, and green materials which are reprocessable and self-healable. These fascinating properties of vanillin-modified epoxy vitrimers are usable in many applications, as demonstrated in Figure 21. The applications and illustrative schemes suggested by various studies are presented in this section.

6.1. Green Matrix for Composites

Vanillin-modified vitrimers can be utilized to form a recoverable fiber-based polymer composite. Memon and coworkers produced a carbon fiber-reinforced vanillin-modified composite [80]. The original composite exhibited superior flexural strength $\geq$1028 MPa and Young's modulus $\geq$ 56 GPa, retaining the performance of 74 and 80%, respectively. The reversible properties of Schiff base in vanillin-modified vitrimers allow the composite to be recovered and regenerated. It suggests that the deteriorated composite product can endure thermal reprocessing to reuse the repaired CFRCs. By dissolving the vanillin-modified vitrimer matrix via Schiff base degradation response using ethylene diamine (EDA), the CF can be recovered entirely by retaining its fresh properties and structure.

6.2. Curable and Regenerative Adhesives

Although commercialized adhesives are often used, they cannot be reworked, recycled, and they have poor bond strength and chemical stability [84,85]. DCAN-enabled degradable adhesives have demonstrated tremendous promise for solving the aforementioned problems [86,87]. Liu and coworkers described the properties of vanillin-modified vitrimers as an adhesive [12]. The iron plates were bonded by an epoxy vitrimer utilizing heat compression at 120 °C. The adhesive is still visible on both iron sheets after the testing, which suggests that cohesive failure rather than adhesive failure causes lap-shear damage at the iron sheet and epoxy vitrimer interfaces. Notably, the vanillin-modified vitrimer displayed near-identical adhesive performances alongside other biomass adhesives [88–90] and some petro-based adhesives [91,92].

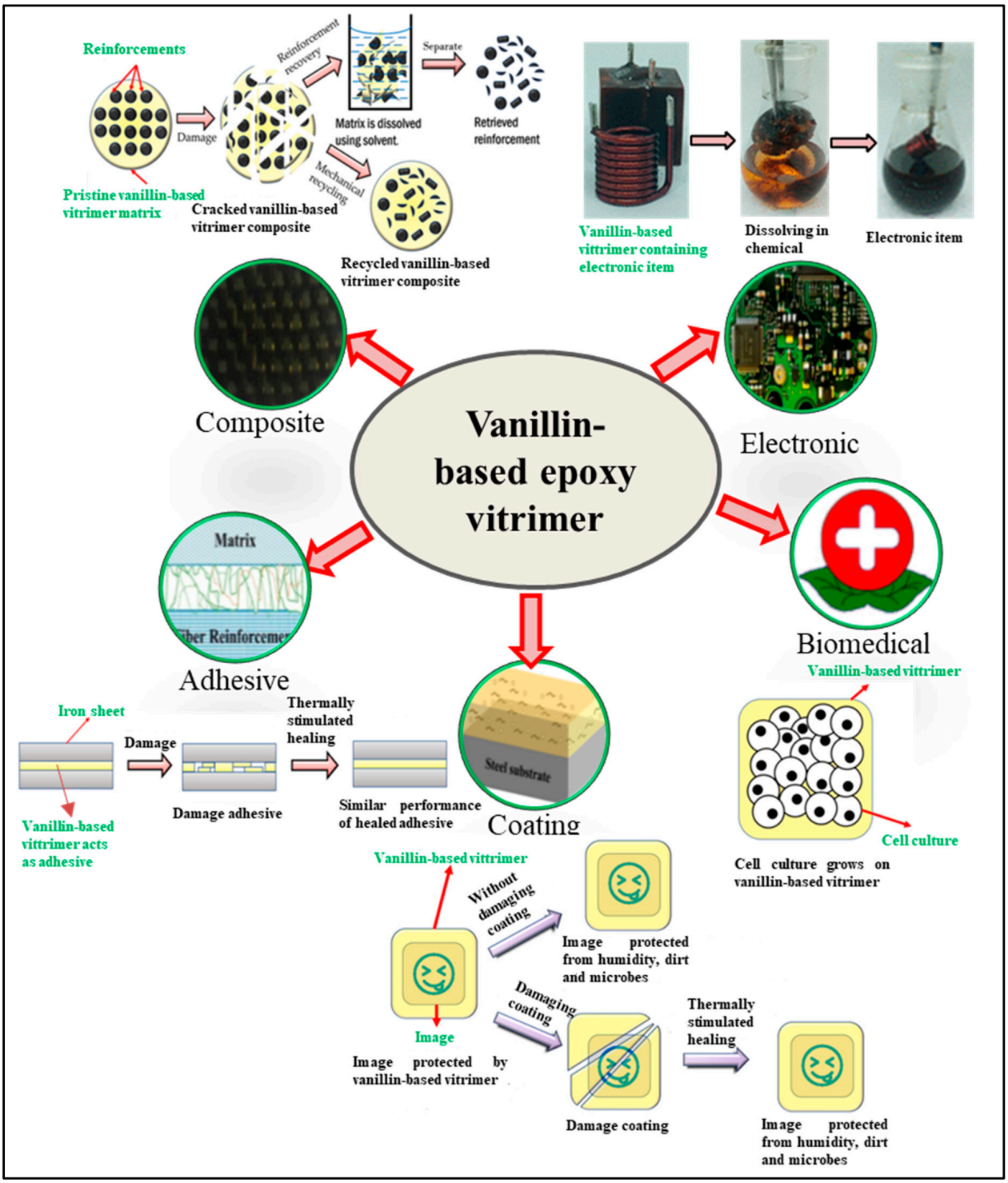

Figure 21. Potential applications of vanillin-modified epoxy vitrimers.

6.3. Curable Coating

Biomass polymer coatings are attractive since they are a more environmentally friendly alternative to coatings and laminates made of petrochemicals [93]. Kadam and coworkers evaluated the effectiveness of bio-based epoxy resin as a paper laminate for two years and noticed no impacts from humidity, dirt, or microbes on the coating [94]. After being exposed to a harsh environment, the coating might be recyclable and self-healing.

6.4. Biomedical Applications

Thermosets are being widely applied in medical research. For example, in tissue implant and alloplastic tissue rehabilitation by implementing transplanted biofactors (cells, genes, proteins) within porous and biodegradable scaffolds. Vascular grafts, aortic heart-valves, and dressing for wound repair are just a few of the significant medical applications for collagen-based polymers. In addition, epoxy thermosets show lower moisture absorption, higher biodegradation rates, antimicrobial, and outstanding mechanical features that can be utilized as drug carriers, extracellular matrix, or bone cement for medical applications and a variety of different products also utilized in the healthcare and cosmetics industries [11,57,95].

6.5. Electronic Devices

Electronic devices such as computers, smartphones, and wearable electronics have recently been pervasive. It is challenging and necessary to address end-of-life and defective e-waste in order to build a sustainable environment. Recoverable and malleable thermosets provide new opportunities for the recycling of electronic equipment [96]. For example, Zou and coworkers first developed a thermoset-based e-skin by adding conductive AgNPs into the DCANs containing thermosets [97–99]. The developed e-skin can be repaired and completely recovered and reused. It can sense moisture, stress, flow, and heat, repairing itself through mild pressure and temperature and fully recycling at normal temperature. The mechanical and electrical properties of repaired and recycled e-skin are comparable to the pristine one.

7. Difficulties and Future Perspectives

Nowadays, it is necessary to find a solution to the issue of plastic's impact on the environment, human health, and societal development. The aforementioned issues may be resolved by producing polymers with DCANs using renewable biomass feedstock. Moreover, research in this area is still at an early stage, and many difficulties and issues need to be resolved. In terms of production, collecting, and storing, vanillin sources are still more costly and operate on a smaller scale than fossil fuel sources. Many lignin derivatives of vanillin are widely found in nature. However, most of them have complex molecular structures, which limit their applicability and require molecules of a single structure. Using biobased feedstock to develop recyclable polymer materials is also one of the most popular research topics. Although there has been a lot of interest in related studies, most are still in the research stage. With the use and industrialization of vanillin-modified polymeric materials, a more high-quality study is required to develop materials that can replace current petroleum-based polymeric materials in terms of quality and profitability. The synthesis pathway is quite challenging for the reported vanillin-modified recyclable thermosets. Because of this, there are still obstacles in simplifying synthesis techniques to improve recyclability, nontoxicity, and biodegradability. The bond energy of DCANs is lower than conventional covalent networks, which will reduce the material's thermo-chemical performances. Most vitrimer products require challenging manufacturing conditions, including high curing temperatures (120–200 °C) and extended curing times (12–24 h), which limits the scope of uses for these biomaterials. To address the issue of material recycling and reuse, more research should be conducted on the chemical recycling method, which first decomposes the material via the vitrimer's network decomposition mechanism before recrosslinking it.

Regarding the difficulties faced by recycled vanillin-modified thermosets, the following are some possible future perspectives: The performance of vanillin-modified epoxy vitrimers may be enhanced by incorporating new methods into the synthesis process. For instance, using tri- and tetra-functionalized epoxy monomers based on vanillin with multifunctional curing agents that contain aromatic rings can improve mechanical performance. As vitrimer research develops quickly, functional vitrimers are an important topic of concern. By altering the molecular structure, their functionality might be added. For example,

a functional molecule could be introduced into a vitrimer to offer additional advantages. By simply including a functional group that bacteria can break down, biodegradable vitrimers could be produced. The molecular structure of vitrimers could also be altered to incorporate fire-resistant chemical molecules. There is also new scope to investigate the possibilities of using vanillin-modified epoxy vitrimers, for example, 3-D printing, solvent-assisted programming elements, soft actuators, and recoverable polymer-matrix in natural filler nanocomposites.

However, difficulties and prospects for the future coexist. It is expected that as research in this area expands and intensifies, industrialization of green and ecologically friendly materials, mainly recyclable materials based on vanillin, will be possible. It will enhance human beings and living organisms as well as support sustainable development.

8. Conclusions

In conclusion, this paper comprehensively reviews vanillin-modified epoxy vitrimer as a recently developed biomass vitrimer. Most thermoset products are prepared from non-sustainable fuel resources, which can contaminate the environment during production, usage, and disposal. One of the most important parts of solving the aforementioned problems is the implementation of green resources to form thermoset polymeric materials. Vanillin-based raw materials have been used in the industrial manufacturing of polymer materials because they are simple to modify structurally. Traditional thermosetting materials as a broad class of high-molecular-weight products, are tough to decompose, repair, and recover owing to their stable crosslinking networks. Once the products are harmed, recycling issues could arise, causing resource loss and environmental impact. By inserting DCAN into the crosslinking network, it is possible to develop reusable, recyclable, and degradable thermosetting products, essential for increasing product longevity and minimizing waste. In order to improve the attractiveness of these materials in the prospective market, it is important to underline that increasing product lifespan and reducing waste is equivalent to lessening the cost of utilizing resources. Difficulties and outlooks of vanillin-modified epoxy vitrimer are mentioned significantly in this paper.

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