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Perspective

Vitrimer as a Sustainable Alternative to Traditional Thermoset: Recent Progress and Future Prospective

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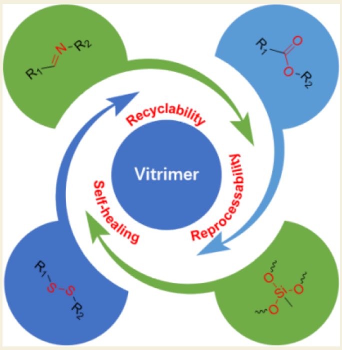
ABSTRACT: Thermosetting resins are widely applied thanks to their excellent comprehensive performance. However, their permanently cross-linked networks pose significant challenges for recyclability, raising serious concerns regarding human health and environmental impact. In recent years, vitrimer, a novel class of polymer that combines the properties of thermosets and thermoplastics, has emerged as a potential alternative to traditional thermosets. In this review, the origin, development, and network regulation strategies of vitrimer are briefly introduced. Common dynamic covalent bonds (DCBs) that can be applied to fabricate vitrimers include Schiff base, ester, disulfide, and silyl ether. This review highlights the recent development of vitrimers based on these DCBs. Finally, emerging development trends are discussed, and strategic recommendations are proposed to accelerate the commercial adoption of high-performance vitrimers.



KEYWORDS: *vitrimers, Schiff base, ester, disulfide, silyl ether*

1. INTRODUCTION

Thermoset resins are widely applied as matrices for fiber-reinforced polymer composites or adhesives owing to their excellent electrical insulation, mechanical strength, and chemical and physical durability. Their applications span the electronics, construction, aerospace, and other industries.[1−3] However, it is difficult to recycle thermosets due to their permanently cross-linked structure, and most end-of-life thermosets are often disposed of by incineration or landfill. It not only fails to meet the needs of carbon peaking and carbon neutrality, but it also has a serious impact on the global environment and human health.[4,5] Therefore, there is an urgent need to develop recyclable thermosets.

The concept of vitrimers emerged from the need to overcome the fundamental limitations of traditional polymers, specifically the permanent cross-linking in thermosets that prevented remelting, reprocessing, or dissolution, as well as the inadequate long-term stability and durability often associated with thermoplastics. The concept of a vitrimer was first proposed in 2011 by Ludwik Leibler and colleagues. It was demonstrated through the introduction of zinc acetate or zinc acetylacetonate catalysts into a bisphenol A glycidyl ether (DGEBA)/carboxylic acid system.[6] By catalyzing the transesterification between ester and hydroxyl groups within the matrix at elevated temperatures using these organometallic compounds, dynamic topological rearrangement of the cross-linked network was achieved, enabling the recycling of the vitrimer. This temperature is referred to as the topology-freezing transition temperature (T_v). Below T_v, the material exhibits high strength, dimensional stability, and thermal resistance, which is similar to conventional thermosets. Above this temperature, it becomes reprocessable like thermoplastics, thereby overcoming the fundamental limitation of irrecyclability inherent in traditional thermosets.[7−9] The bond exchange process that enables the reversible topological rearrangement of the cross-linked network follows Arrhenius kinetics, with viscosity decreasing exponentially as the temperature increases.

The dual characteristics of vitrimers arise from the incorporation of dynamic covalent bonds (DCBs) into their cross-linked networks.[10−12] These DCBs enable the network to undergo reconfiguration and rearrangement under external stimuli (e.g., light, heat, and pH) without compromising the material's structural integrity. This unique capability facilitates applications of thermoset-like materials in recycling, self-healing, controlled degradation, and biomimetic materials.[13−15] Before Leibler et. al conceptualized vitrimer, the research in dynamic chemistry could be traced back to the pioneering

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dynamer work conducted by Jean-Marie Lehn and his colleagues in the 1990s. Dynamers can alter their structure and properties through the reorganization and rearrangement of both covalent and noncovalent bonds: a mechanism that fundamentally resonates with the inherent characteristics of vitrimers.[16−18]

Subsequently, there was a surge of interest in the study of dynamic covalent chemistry and dynamic covalent polymers. Christopher N. Bowman et al. formally defined polymer networks incorporating DCBs as Covalent Adaptable Networks (CANs) in 2010.[19] Based on differences in the mechanisms of covalent bond exchange, CANs can be further classified into dissociative and associative types.[20−22] In dissociative CANs, covalent bonds are first broken and then formed under certain external stimuli. During chemical bond exchange, the number of cross-linking points first decreases and then increases again. Dissociative bond exchanges include the Diels−Alder adducts, aminal transamination, and Michael adduct exchange.[23−38] For example, in the reversible ring addition reaction based on furan and maleimide, the furan-maleimide adduct undergoes covalent bond dissociation when heated. As a result, furan and maleimide derivatives are formed, which reduces the polymer cross-link density and system viscosity. Once cooled, the furan and maleimide derivatives react again to reform new cross-linking points. During this process, the topological network structure is rearranged, and the original cross-link density is restored, thereby recovering the material's properties on a macroscopic level.[39−41] Dissociative CANs are promising in smart materials, green chemistry, and biomedicine.

By contrast, associative bond exchange involves the simultaneous breaking of original associative covalent bonds and the formation of new ones in response to certain stimuli. Therefore, under macroscopic conditions, the cross-link density of the polymer remains unchanged during the associative bond exchange. The representative examples of associative covalent bonds include ester, Schiff base, and silyl ether,[42−53] which generally have good mechanical properties and weather resistance.

The vitrimers belong to the category of associative CANs, wherein the cross-link density remains constant throughout the bond exchange. In addition to the characteristics of associative bond exchange, the viscoelastic behavior of the vitrimer during cross-linking network rearrangement complies with Arrhenius theory and exhibits a characteristic T_v. Furthermore, due to the nature of dynamic covalent cross-linking, vitrimers can perform functions such as recycling, self-repair, and chemical degradation.

In recent years, some studies have shown that the breaking and formation of bonds in dissociative CANs can occur rapidly and then the macroscopic properties, such as stress relaxation and flow behavior,[54] are similar to those of a vitrimer (e.g., disulfide bonds and biphenyl radicals). It further blurs the boundaries between dissociative and associative CANs, which is conducive to expanding their application scope. The vitrimer typically has good creep resistance and solvent resistance on a macroscopic scale, which is close to the application scope of traditional thermosets. Therefore, it would be beneficial for future advances in the practical application of vitrimers to review and summarize recent developments and applications.

2. STRATEGIES FOR REGULATING PERFORMANCE OF VITRIMERS

Initially, improving the recyclability of vitrimers usually results in a compromise of their mechanical properties, heat resistance, and other properties. The comprehensive properties of the vitrimer are closely related to the design of its dynamic covalent network. Consequently, researchers have developed various network control strategies to fine-tune the properties of vitrimers and enable them to be applicable in high-end usages.

2.1. Adjusting Catalyst Type and Amount

Catalysts can lower the barrier to bond exchange reactions, thereby enhancing the dynamic recovery capacity of the vitrimer. Leibler et al. found that using an external catalyst (zinc acetate) enabled the recycling of thermosets and increasing the catalyst content reduced the relaxation time of the obtained vitrimer. High concentrations of organometallic catalysts could damage the mechanical properties of the vitrimer and were difficult to disperse evenly within it. To address this issue, Zhang et al. synthesized an organic copolymer-modified catalyst (Zn-PAM) via the polymerization of acrylonitrile and zinc methacrylate.[55] The resulting Zn-PAM achieved higher catalytic efficiency than zinc acetate and triazabicyclodecene (TBD) while significantly improving the mechanical properties of the vitrimer, mainly due to the enhanced compatibility with the substrate caused by the saturated chain segments.

2.2. Regulating Cross-Link Density

A higher cross-link density increases the entropy of polymer chain segment disturbance, which can speed up bond exchange reactions. Hayashi et al. synthesized a series of transesterified vitrimers with an identical hydroxyl content and flexible chain segments by using a polyester possessing multiple COOH (PE-COOH), 1,4-butanediol diglycidyl ether, and butyl glycidyl ether.[56] The cross-link density of the system was controlled by adjusting the ratio of the two glycerol ethers. By adjusting the cross-link density, they found that the high cross-link density of the vitrimer accelerated the topological network rearrangement due to its high entropy value.

2.3. Adjusting Dynamic Covalent Bond Density

A higher density of dynamic covalent bonds means a higher reactant content, which increases the probability of bond exchange reactions. Chen et al. increased the density of DCBs in the vitrimer by simultaneously introducing disulfide bonds into the epoxy monomer and curing agent, thereby significantly reducing the bond exchange activation energy (E_a) of the obtained vitrimer.[57] Similarly, the rapid relaxation of the vitrimers can also be achieved by increasing the density of β-hydroxy ester and Schiff base in the dynamic covalent network.

2.4. Neighboring Group Participation Effect

The discovery of the neighboring group participation effect originated from research on catalyst-free dynamic covalent polymers. The neighboring group participation is associated with substituent effects that stabilize the transition state by bonding to the reaction center.[58] Additional hydroxyl or carboxyl groups in ester-based dynamic covalent networks activate carbonyl groups through hydrogen bonding, thereby enabling topological rearrangement.

2.5. Electronic Interaction

In addition to the neighboring group participation effect, tertiary amines, α-CF_3, β-carbonyl groups, and other functionalities can be introduced into the dynamic covalent network through covalent bonding. Furthermore, catalyst-free recovery can also be achieved through their electronic interaction with ester groups.[59−61] For instance, Altuna et al. introduced diethylamine into the DGEBA/citric acid/sebacic acid system, resulting in a tertiary amine-catalyzed transesterified vitrimer. The resulting vitrimer exhibited a relaxation time of approximately 500 s at 180 °C, allowing for rapid topological rearrangements of the ester-based dynamic covalent network.

2.6. Multiple Dynamic Covalent Bonds

Different dynamic covalent bonds have their unique structural and functional characteristics. For example, Schiff bases have antibacterial and flame-retardant properties, ester groups have high thermal stability, and silyl ether bonds have good thermal stability and water resistance. By reasonably combining the characteristics of the dynamic covalent bonds, high-performance and easily recyclable vitrimer can be prepared. Ma et al. synthesized a vitrimer based on ester and Schiff base by using levulinic acid, lysine, and N-(*p*-aminobenzoyl) glutamic acid as raw materials.[62] Due to the presence of tertiary amines and dual dynamic covalent bonds, the relaxation time of the resulting vitrimer at 180 °C was only 32 min, with an E_a of approximately 70 kJ/mol, enabling rapid recycling of the vitrimer.

2.7. Combined Strategies

In addition to the above, the design of dynamic covalent networks can apply the above strategies comprehensively, according to the needs of the application, to obtain a high-performance vitrimer. Chen et al. introduced ester groups (dynamic covalent bonds), phosphate esters (dynamic covalent bonds), tertiary amines (internal catalytic groups), and hydroxyl groups (internal catalytic groups) into the dynamic covalent network through rational molecular design, thereby achieving flame retardancy and toughening of the resulting vitrimer, as well as high physical recycling efficiency.[63] The vitrimer that has completed its service life can achieve nearly 100% flame retardancy recovery under 190 °C, 10 MPa, and 1 h of hot pressing.

3. RECENT DEVELOPMENT OF VITRIMERS

The development of recyclable polymers remains a key area of current research due to the nonrenewable nature of petroleum resources and the environmental issues associated with plastics. In recent years, the vitrimer has attracted widespread attention due to its strength, durability, and chemical resistance, which are comparable to those of traditional thermosets, as well as the excellent recyclability at the end of its service life. This phenomenon can be attributed to their distinctive DCBs. The common DCBs in vitrimers include ester, Schiff base, disulfide, and silyl ether. The chemical nature of dynamic covalent bonds determines the kinetics, stability, and application scenarios of vitrimers.

3.1. Vitrimers Based on Schiff Base

In general, Schiff bases (C = N) are formed by condensing amines and aldehydes or ketones, as shown in Figure 1. This process can occur without a catalyst, and the Schiff base can be hydrolyzed under acidic conditions to produce aldehydes or ketones and amines.[64−66] In addition, the Schiff base exhibits flame-retardant behavior, promoting carbonization and releasing nonflammable gases during combustion.[67−69] Furthermore, the Schiff base shows antibacterial properties. These features distinguish the Schiff base vitrimer from the others. Due to the fact that Schiff base exchange does not require a catalyst and has a relatively low E_a, the dynamic recovery properties of the vitrimer are excellent, offering potential for energy-efficient recycling.[70]

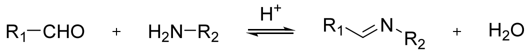

Figure 1. Classic synthetic method and dynamic covalent chemistry of Schiff bases.

In 2014, Zhang et al. synthesized a catalyst-free poly-Schiff base vitrimer (Figure 2a) via an amine-aldehyde condensation reaction involving 1,4-phthalaldehyde, diethylenetriamine, tri(2-aminoethyl)amine, and the vitrimer exhibits extensibility driven by either heat or water.[71] The obtained vitrimer exhibits stress relaxation behavior that is consistent with the Arrhenius equation. Its modulus can recover by up to 10% of its original value after 0.5 h of relaxation at 80 °C. In addition, the material exhibits excellent recycling properties. As shown in Figure 2b, the vitrimer powder can be remolded under hot pressing conditions of 80 °C, 90 kPa, and 45 min, resulting in a slight improvement to the mechanical properties of the recycled vitrimer. Notably, the resulting vitrimer exhibits water sensitivity that differs from that of traditional Schiff base vitrimers. It maintains consistent mechanical properties after high-temperature water-bath treatment and also relaxes in water (Figure 2c). Theoretically, this water-induced relaxation of the cross-linked network can mitigate material aging caused by traditional high-temperature processing, thereby extending the material's cycle and service life.

Since then, there has been a proliferation of vitrimer systems based on Schiff base, and their performance and application scenarios have been continuously optimized and improved. For example, in terms of the economy of ingredients, Liang et al. developed a series of vitrimer (EPCNs) based on dynamic Schiff base exchange using the commercial epoxy monomer DGEBA, 1,4-phthalaldehyde, and polyetheramine (D230), employing a one-pot method that did not require a catalyst.[72] The mechanical properties and recyclability of the resulting vitrimer can be controlled by adjusting the 1,4-phthalaldehyde content (i.e., the proportion of Schiff base functional groups). Among them, the EPCN-4 vitrimer had a tensile strength of 51.8 MPa and an elongation at break of 20.4%, which addressed the issue of poor toughness in traditional thermosets. Owing to its low cross-link density and high concentration of Schiff base functional groups, the E_a for dynamic covalent network (DCN) bond exchange in EPCN-4 vitrimer was 47.9 kJ/mol, and scratches can be rapidly self-repaired within 8 min at 150 °C. The carbon fiber reinforced polymer (CFRP) composites prepared by EPCN-4 as the resin matrix can be completely degraded under weakly acidic conditions, thereby enabling the rapid and nondestructive recovery of carbon fiber composites.

In order to enhance the mechanical and heat-resistant properties of Schiff base vitrimers, Zhang et al. synthesized polyimide-Schiff base hybrid vitrimers (PIIHs) using 1,2,4,5-cyclohexanetetracarboxylic dianhydride, 2-methyl-4,4'-diaminodiphenyl ether, 1,4-phthalaldehyde, and tri(2-aminoethyl)-amine as the initial materials.[73] The resulting vitrimer exhibited

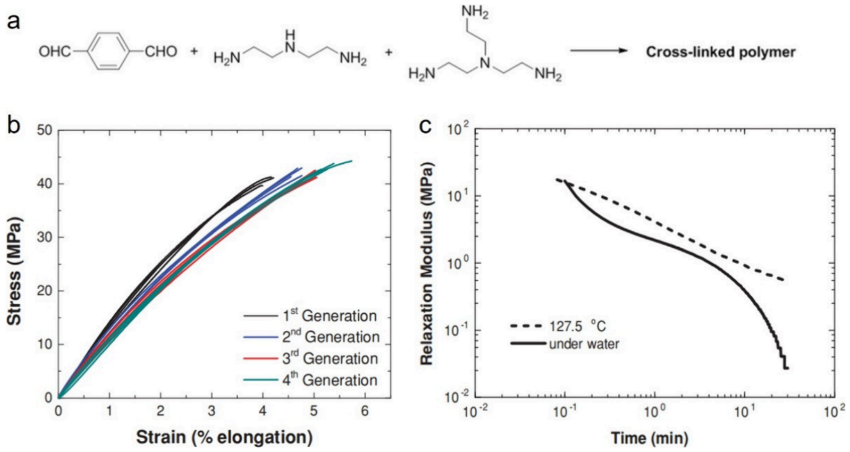

Figure 2. (a) Synthesis of poly-Schiff base vitrimer; (b) Stress−strain curves of vitrimer with different recycling times; (c) The stress-relaxation behavior of poly-Schiff base vitrimer discs under water vs heat.[71] Reproduced or adapted with permission from ref 71. Copyright (2014) John Wiley and Sons.

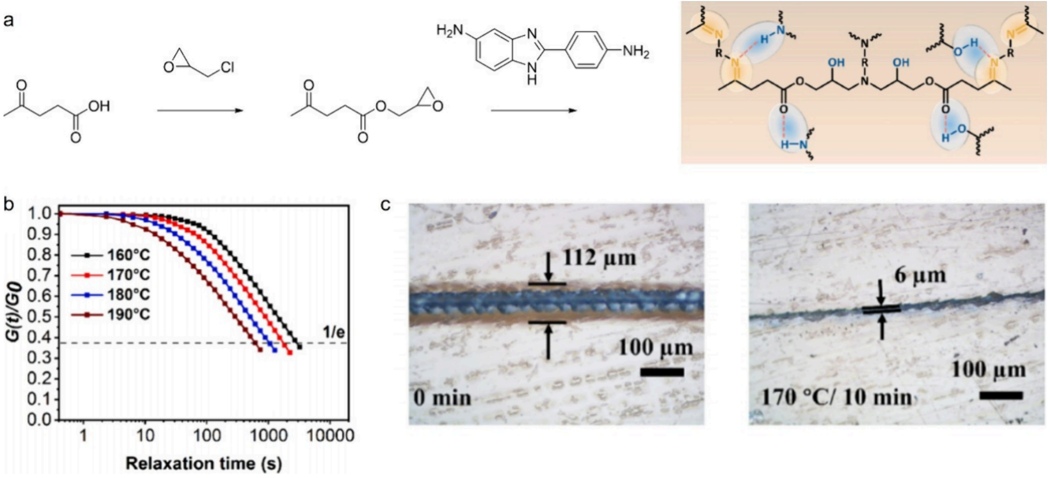

Figure 3. (a) Synthetic routes of ELA-BIA vitrimer; (b) modulus relaxation of ELA-BIA vitrimer at different temperatures; (c) optical micrographs of ELA-BIA vitrimer before and after being repaired at 170 °C for 10 min.[75] Reproduced or adapted with permission from ref 75. Copyright (2023) Elsevier.

a tensile strength and a tensile modulus of 97.0 MPa and 2.6 GPa, respectively, with a glass transition temperature (T_g) as high as 306 °C, making it suitable for specialized applications such as aerospace and aviation. Despite its high heat resistance, the E_a for bond exchange was moderate at 127.1 kJ/mol, and it still possessed welding, self-repairing, and chemical degradation properties.

Aiming to address the issues of brittleness and flammability associated with traditional thermosets, Wang et al. designed a Schiff base DCN that combined rigidity and flexibility using vanillin, 1,3-bis(aminopropyl)tetramethyldisiloxane, and 4,4′-methylenedianiline (DDM) as ingredients. The resulting vitrimer had an elongation at break of 13.2% and an impact strength of 61.8 kJ/m^2, exceeding those of some thermoplastics and demonstrating superior toughness.[74] In addition, the catalytic carbonization effect of Schiff bases and silicon-containing groups endowed the vitrimer with favorable flame retardancy, reducing the peak heat release rate by 51% compared to commercial DGEBA/DDM system. Moreover, the E_a of the DCN was 53.6 kJ/mol, enabling self-repair at 100 °C, while also exhibiting chemical degradability and nearly 100% mechanical recovery.

Taking into account the multifunctional nature of thermosets, as shown in Figure 3a, Tang et al. synthesized epoxy monomers (ELA) using levulinic acid as the ingredient. They then cured the monomers with 2-(4-aminophenyl)-1H-benzimidazol-5-amine (BIA) via epoxy ring opening and amine-aldehyde condensation, in order to formulate a vitrimer based on Schiff bases.[75] After curing, the hydroxyl groups, Schiff bases, and secondary amines in the cross-linked structure can form a high-content hydrogen bond network, endowing the vitrimer with a high T_g of 165 °C and superior mechanical properties. Its tensile strength and elongation at break are 67.1 MPa and 7.5%, respectively, close to those of commercial epoxy resin. The relaxation time of the obtained vitrimer at 190 °C was only around 10^3 s, and the E_a required for the bond exchange of DCN was 83 kJ/mol (Figure 3b). The low E_a allowed the material to self-repair at 170 °C for 10 min (Figure 3c). In addition, the excellent carbonization properties of the imidazole group and the Schiff base provided the vitrimer with good flame retardancy, including a V-0 rating in the vertical burning (UL-94) test and a limiting oxygen index (LOI) of 33.8%. The Schiff bases bonded in the network also provided 100% antibacterial activity against *Escherichia coli* and *Staph-*

ylococcus aureus. It offered a promising approach for the preparation of high-performance and multifunctional thermosets.

Considering the nonrenewable nature of petroleum resources, Zhu et al. synthesized a phosphorus-containing trialdehyde monomer (TFMP) from the biobased ingredient vanillin and used different commercial diamines to cure the monomer and develop a series of Schiff base vitrimers.[70] Notably, the vitrimer cured with DDM demonstrates outstanding applicability, with attributes including a T_g of 178 °C, a tensile strength of 69 MPa, a tensile modulus of 1.9 GPa, a UL-94 V-0 rating, and an LOI of 30.9%. The E_a required for DCN was 81 kJ/mol, which can achieve recycling at 180 °C for 10 min. The resulting vitrimer can be completely degraded into monomers under acidic conditions, with a yield of 76.6%. In addition, Hu et al. designed a fully biobased Schiff base vitrimer, using vanillin, 2-furfurylamine, and 4-amino-1,2,4-triazole as the reactants. The presence of numerous rigid groups resulted in T_g, tensile strength, and storage modulus of 170 °C, 60.8 MPa, and 3.3 GPa, respectively, which were higher than those of conventional thermosets. The presence of Schiff base enabled the vitrimer to achieve favorable chemical degradability. Despite the lengthy synthesis process and low yield of the biobased Schiff base vitrimer, it remains a feasible solution for developing fully biobased, high-performance thermosets.

3.2. Vitrimers Based on Ester

The vitrimer based on ester is a dynamic covalent polymer that is formed through transesterification between ester and hydroxyl groups. The bond exchange mechanism is illustrated in Figure 4. The ester groups are among the most widely applied functional groups in modern chemistry. There are many convenient synthetic routes for transesterified vitrimers, such as condensation reactions between carboxyl and hydroxyl groups, ring-opening reactions between epoxy groups and anhydrides or acid groups, and substitution reactions between acyl chloride groups and active hydroxyl groups, etc. There are also advantages to using multiple synthetic routes, such as access to a wide range of ingredients and low prices. The transesterified vitrimer has been the most studied and promising dynamic covalent polymer for industrial application since its development by Leibler et al.[54,76,77] First, there is a large market for traditional thermosets (e.g., epoxy/anhydride system), and the process and system formulations are well established, making it relatively easy to design and develop transesterified vitrimer and commercialize it. Specifically, the transesterified vitrimer can be prepared using a commercially available, mature EP system (DGEBA and acid/anhydride curing agent). This results in a hydroxyl-rich, covalently cross-linked network formed through ester cross-linking. Compared with other vitrimers, transesterified vitrimers have the following advantages: (1) ease of preparation and simplicity of the process; (2) commercial availability with a mature formulation; (3) good stability; and (4) widely available, low-cost raw materials.[78] However, it should be noted that transesterification requires a higher E_a than other dynamic bond exchanges due to its good stability, and catalysts are also required. This indicates that higher temperatures or catalyst contents are typically needed to achieve self-repair, recycling, and reshaping of transesterified vitrimers. Therefore, the focus of current research on transesterified vitrimers is on balancing their functional and dynamic properties, and various network control strategies have emerged as a result.

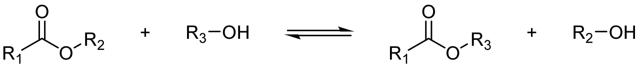

Figure 4. Schematic diagram of the transesterification mechanism.

In 2011, Leibler et al. prepared the first vitrimer, a dynamic covalent polymer that undergoes transesterification. As shown in Figure 5a, they introduced zinc acetate (5 ∼ 20 mol %) into the DGEBA/aliphatic carboxylic acid mixtures and observed significant stress relaxation behavior within the temperature range of 100 ∼ 280 °C.[6] It was found that the E_a of transesterification was approximately 80 kJ/mol in this work. The waste vitrimer can be reprocessed by hot pressing at 240 °C for 3 min (see Figure 5b), which was sufficient to produce recycled material that was essentially identical to the original material in terms of its mechanical properties and insolubility. At the same time, the resulting vitrimer can be hydrolyzed or alcoholized under high temperature and pressure, thereby breaking the ester chains and decomposing the cross-linked network to achieve chemical degradation. The vitrimers, first developed by Leibler et al., offer the high strength and stability of traditional thermosets, as well as the high-temperature resistance and reprocessability of thermoplastics (see Figure 5c), thereby overcoming the limitations of conventional

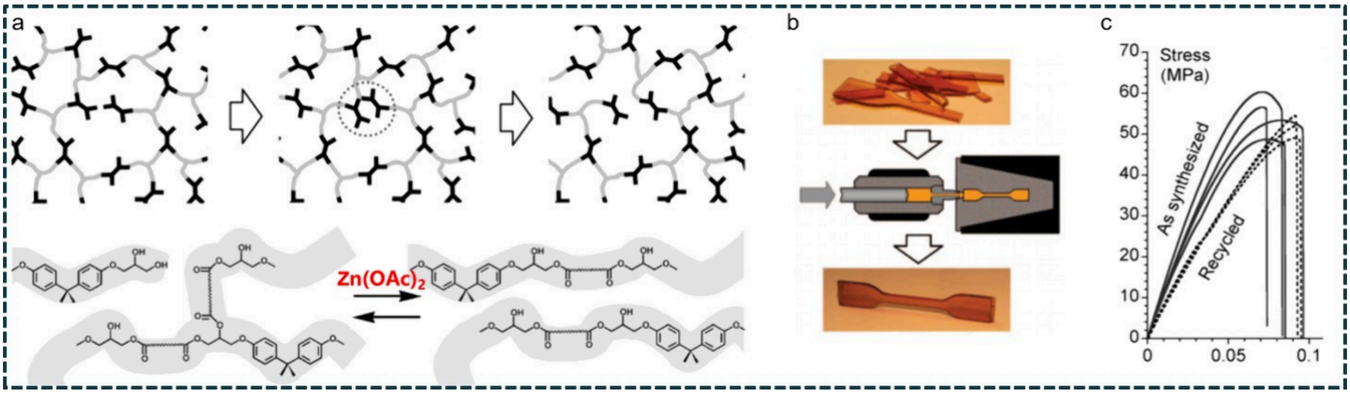

Figure 5. (a) Schematic diagram of the topological rearrangement of the epoxy/carboxylic acid system catalyzed by zinc acetate; (b) Recovery of waste vitrimer by hot pressing; (c) stress−strain curve of the vitrimer before and after recycling.[6] Reproduced or adapted with permission from ref 6. Copyright (2011) The American Association for the Advancement of Science.

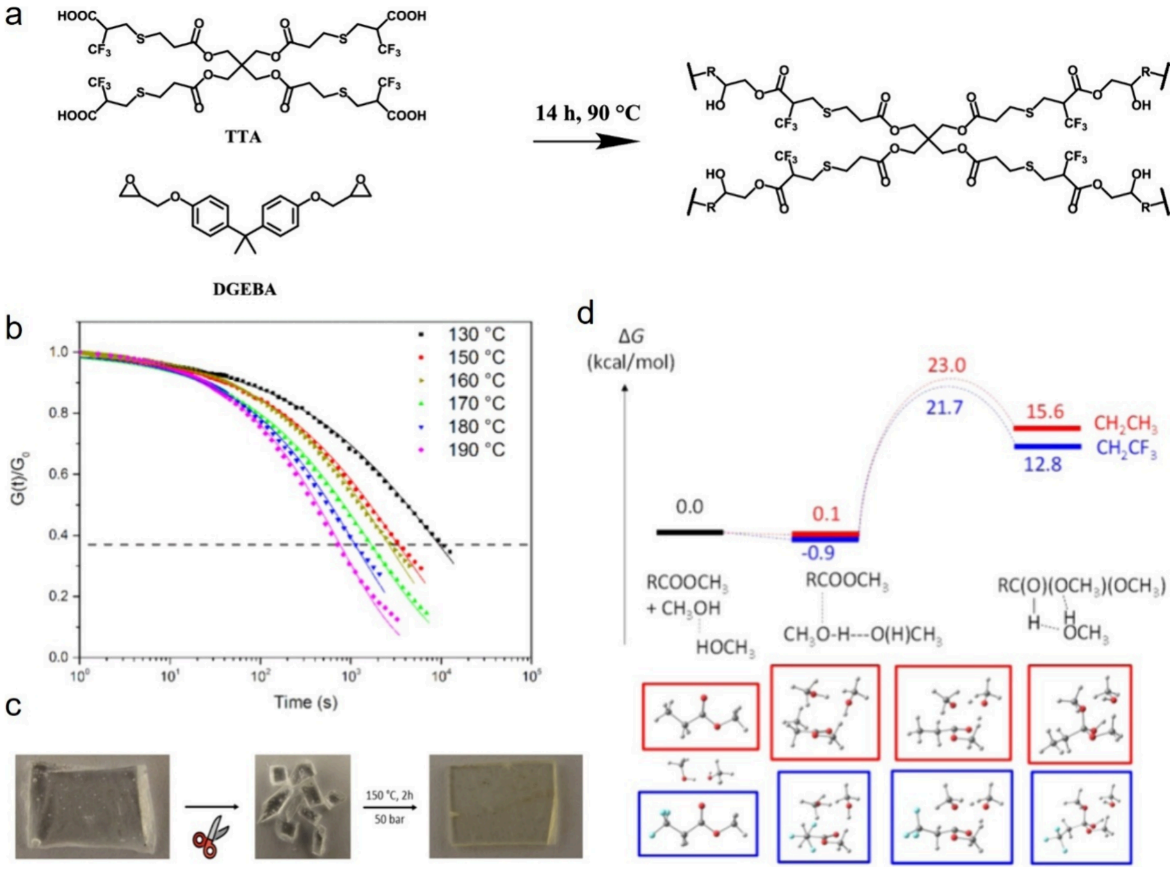

Figure 6. (a) Schematic diagram of preparation of α-CF_3 self-catalytic transesterification vitrimer; (b) Recovery of waste vitrimer by hot pressing; (c) stress−strain curve of the vitrimer before and after recycling.[79] Reproduced from ref 79. Copyright (2022) American Chemical Society.

thermosets. Although the high catalyst content can damage the mechanical properties of the substrate and cause the catalyst to leach out over time, posing a threat to the environment and human health, its development has nevertheless sparked a boom in vitrimer research among scholars.

The catalysts used for transesterification are primarily organometallic compounds. Prolonged use of these catalysts may result in the leaching of heavy metals or other chemicals, posing risks to human health and the natural environment.[80] This problem, caused by the addition of catalysts, has led to the gradual development of a catalyst-free transesterification vitrimer based on the internal activation of cross-linked networks. For example, the α-CF_3 self-catalyzed transesterification vitrimer, VD, which was designed by Vincent Ladmiral et al., is shown in Figure 6a. They synthesized an α-CF_3-containing tetracarboxylic acid curing agent via the thia-Michael addition reaction of pentaerythritol tetra(3-mercaptopropionate) and 2-(trifluoromethyl)acrylic acid. They then prepared a catalyst-free epoxy vitrimer by curing it with DGEBA.[79] The stress relaxation test revealed that the relaxation time (τ^*) at 190 °C was 708 s, and that the E_a of transesterification was 67 kJ/mol, which was much lower than those of the transesterified vitrimer prepared using additive catalysts (see Figure 6b). Furthermore, the catalytic effect of α-CF_3 on curing and transesterification was verified by density functional theory (DFT) calculations (see Figure 6d). The effect of the α-CF_3 neighboring group participation significantly reduces the temperature required for recycling. As shown in Figure 6c, the resulting vitrimer can be hot-pressed at 150 °C, 5 MPa, and for 2 h, and the recycled material exhibited similar mechanical and thermal properties to the original vitrimer. The scheme is based on click chemistry, which does not require a catalyst and has a low reaction temperature and high yield, thereby opening up new directions for the development of catalyst-free transesterified vitrimer. However, due to the large number of saturated flexible chains, its mechanical and heat resistance properties were relatively low. For example, the T_g was only 35 °C, and the temperature at 5% weight loss ($T_{5\%}$) was only 215 °C.

According to the theory of reversible reaction equilibrium, the hydroxyl groups in the vitrimer can also undergo self-catalyzed transesterification. Zhu et al. manufactured dynamic covalent polymers containing numerous hydroxyl and ester groups by curing itaconic acid-derived epoxy monomer using a mixture of glycerol and maleic anhydride.[81] It was reported that the hydroxyl accelerated the relaxation behavior of the vitrimer, enabling the relaxation modulus to return to 1/e of its original value within 3 h at 180 °C, even without the addition of a catalyst. The E_a was approximately 63 kJ/mol, and it enabled the vitrimer to be reshaped and recycled at 190 °C and 10 MPa under hot-pressing without compromising the mechanical properties. Similarly, Hu et al. developed a carboxylic self-catalyzed transesterification vitrimer. They synthesized the vitrimer, with a high T_g of up to 214 °C, from commercially available phthalic anhydride and diglycidyl ester of aliphatic cyclo (DGEAC).[82] The obtained vitrimer can be applied as a highly heat-resistant material. During transesterification, the formic acid group and the ester group at its neighboring position in the benzene ring tend to form a five-membered ring transition state, which can act as an

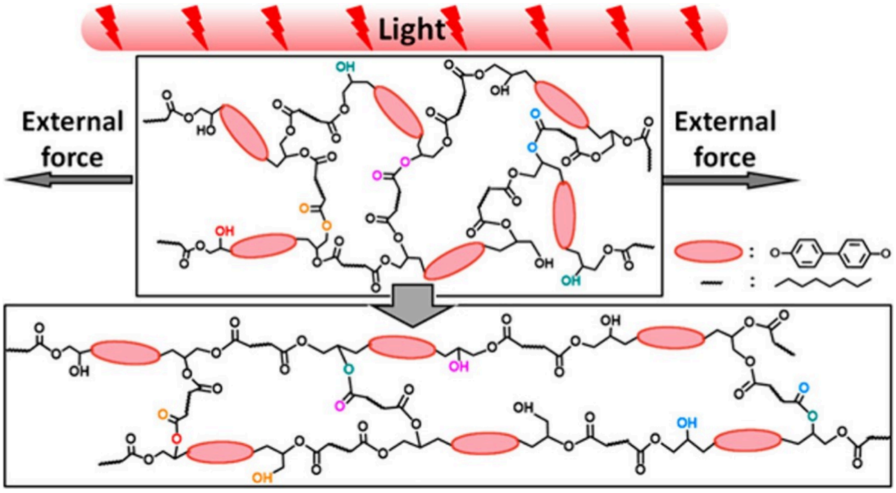

Figure 7. Mechanism of transesterification in carbon nanotube-doped vitrimer.[85] Reproduced from ref 85. Copyright (2016) American Chemical Society.

intrinsic nucleophilic catalyst to activate transesterification without the need for an external catalyst. Unfortunately, its stress relaxation was relatively slow compared with other vitrimers, making physical recycling difficult. However, the resulting CRFPs can be chemically degraded in an ethylene glycol solution for the recovery of carbon fibers. Subsequently, in order to address the difficulty of physical recycling of the above system, the team cocured glycerol with phthalic anhydride and DGEAC, achieving rapid relaxation of covalent cross-linked networks.[83] The τ^* of the resulting vitrimer at 180 °C was merely 205 s, primarily due to the presence of unreacted hydroxyl groups originating from glycerol. Although the rigidity of the cross-linked network was reduced, the vitrimer still maintained a high T_g of 140 °C and possessed excellent mechanical properties (tensile strength and modulus reaching 65 MPa and 3.2 GPa). Furthermore, due to the high content of hydroxyl groups in the network, the resulting resin exhibited enhanced adhesive properties with polymer substrates, achieving a shear strength of 20 MPa, much better than commercial adhesives.

Chen et al. incorporated hyperbranched structures into dynamic, cross-linked networks to enhance the mechanical and thermal properties of transesterified vitrimers.[59] They synthesized hyperbranched polyesters rich in hydroxyl groups using maleic anhydride and glycerol, and then cured them with rosin-derived fumaric acid and glycerol triglycidyl ether to prepare a series of hydroxyl-terminated, self-catalyzed transesterification dynamic covalent polymers. When the polyester content in the matrix was 15%, the resulting vitrimer exhibited high tensile strength and elongation at break (57.2 MPa and 21.5%) owing to the optimal cross-link density and hydrogen bonding of the terminal hydroxyl groups. The τ^* of the vitrimer at 220 °C was only 421 s, and its transesterification E_a was 101.7 kJ/mol, enabling crack self-healing within 1 h at 180 °C. Furthermore, the low viscosity of hyperbranched polyesters demonstrated that their epoxy premixes can be applied to CFRPs, resulting in composites with a tensile strength of 585 MPa.

In response to the issue of nonrenewable petroleum resources, Zhang et al. synthesized epoxy resins derived from ferulic acid and prepared a fully biobased, hyperbranched, transesterification vitrimer through curing with citric acid.[84] In contrast to conventional, fully biobased thermosets characterized by low mechanical strength and T_g, the ferulic acid-derived vitrimer had a hyperbranched topological structure. Through in situ reinforcement and toughening mechanisms, the vitrimer showed tensile strength, toughness, and T_g of 126.4 MPa, 5.29 MJ/m^3, and 94 °C, respectively. The abundance of hydroxyl groups accelerated the transesterification of the cross-linked network, while the hyperbranched topological structure reduced the distance between adjacent hydroxyl and ester groups, facilitating the reaction further. The resulting vitrimer had an E_a of only 58 kJ/mol. The E_a was significantly lower than those reported in previous studies (70 ∼ 150 kJ/mol). Unlike most strategies, this work can increase the cross-link density of the vitrimer, thereby improving the material's creep resistance.

To improve the economic efficiency of thermosets and address their flammability, Chen et al. applied the commercial flame retardant diethyl bis(2-hydroxyethyl)-aminomethylphosphonate (FRC-6) directly to the DGEBA/methyltetrahydrophthalic anhydride (MeTHPA) system to fabricate a catalyst-free transesterification vitrimer.[63] The FRC-6 can form covalent bonds with the matrix, thereby becoming part of the cross-linked network. The presence of ester and phosphate ester groups endowed the vitrimer with excellent flame retardancy, enabling it to pass the UL-94 V-0 rating and achieve an LOI of 28.3%, with a self-extinguishing effect. In addition, the peak heat release rate and total smoke production were reduced by 62.0% and 78.9% respectively, compared to DGEBA/MeTHPA, providing excellent flame retardancy and smoke suppression. DFT had verified that the Gibbs free energy of phosphate ester exchange was lower than that of traditional ester exchange. Due to the self-catalysis of tertiary amines and hydroxyl groups, a rapid formation of a covalent network can be achieved. Furthermore, the broken vitrimer can recover nearly 100% of its flame retardancy under conditions of 190 °C, 10 MPa, and 1 h of hot pressing.

In terms of triggering conditions, several studies have designed light-initiated transesterification vitrimers in addition to thermal-initiated ones. Ji et al. developed a light-induced transesterification vitrimer by incorporating carbon nanotubes into a polymer network.[85] As shown in Figure 7, the light was absorbed by carbon nanotubes and converted into heat, thereby achieving localized healing of the vitrimer. It can even

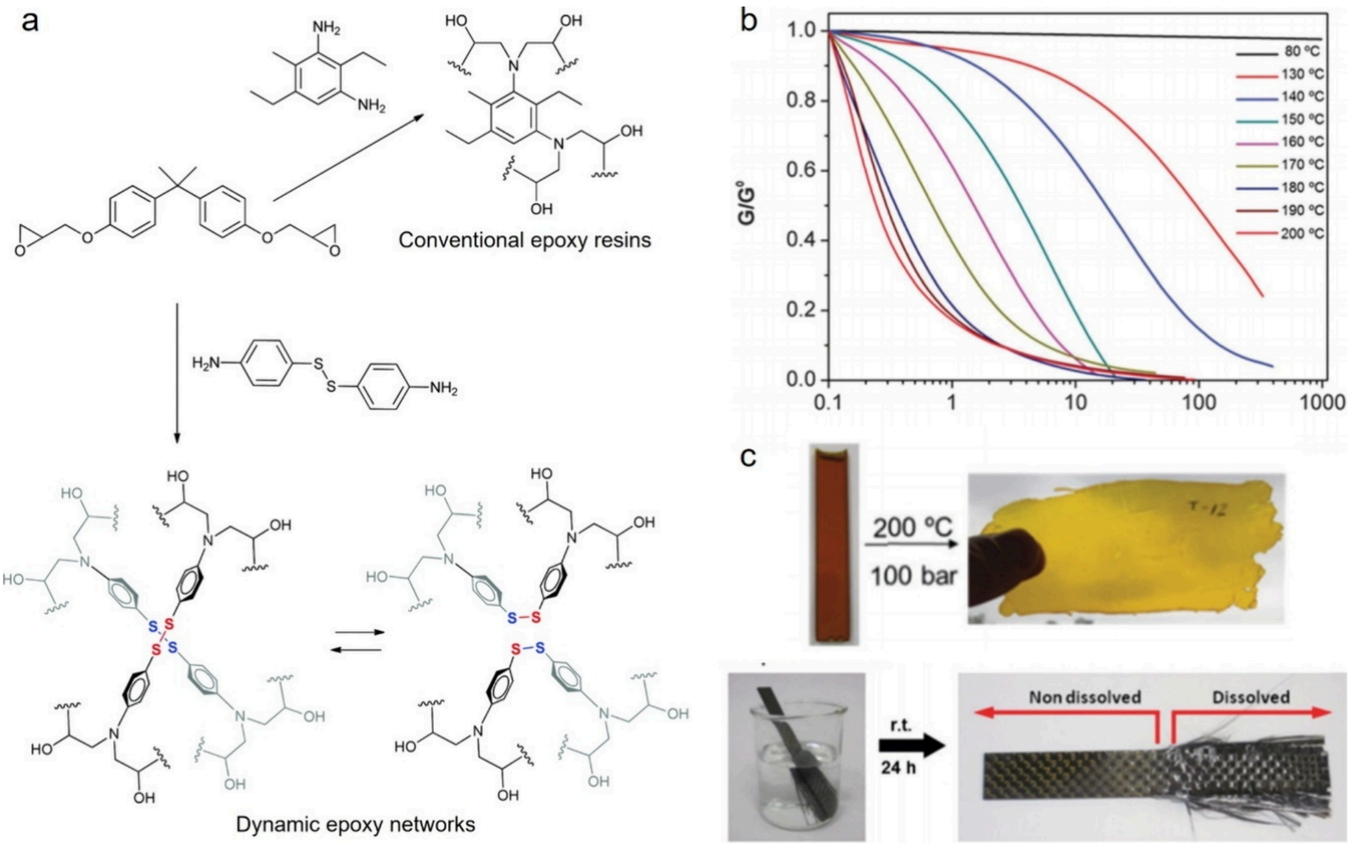

Figure 8. (a) The dynamic epoxy networks studied by Odriozola et al.; (b) normalized stress relaxation curves of the resulting vitrimer; (c) remodelling photo of the prepared vitrimer and degradation photos of the obtained CFRP composites.[88] Reproduced from ref 88. Available under a CC-BY 3.0 license. Copyright (2020) Alaitz Ruiz de Luzuriaga, Roberto Martin, Nerea Markaide, Alaitz Rekondo, Germán Cabañero, Javier Rodríguez and Ibon Odriozola.

achieve self-repair and healing of the material at low temperatures (e.g., −130 °C). It greatly expands the application field of the transesterification vitrimers, and the introduction of nanomaterials will inevitably bring more functionality to vitrimers.

3.3. Vitrimer Based on Disulfide

The discovery of disulfide bond exchange can be traced back to the research conducted by Tobolsky et al. on stress relaxation in sulfurized rubber in the 1950s. They found that the modulus of cross-linked sulfur-cured rubber could be reduced to 0, and they speculated that the disulfide bonds underwent bond exchange under the action of the catalyst.[86] However, due to technological limitations at the time, the mechanism could not be studied in detail. As verified by Jose′ M. Asua et al., the bond exchange of aromatic disulfides is based on radical-mediated processes, with the disulfide bond undergoing homolytic cleavage followed by the transfer of a sulfur-containing radical.[87] Although disulfide bonds undergo topological rearrangement by breaking and forming bonds, sulfur-containing free radicals have an extremely short lifespan and identical characteristics to associative dynamic covalent polymers. Therefore, scholars generally consider disulfide-based dynamic covalent polymers to be a vitrimer too. The E_a of disulfide bond exchange reaction is relatively low, enabling it to occur at lower temperatures than those required for transesterification. Due to their convenient preparation, a growing number of dynamic covalent polymers based on disulfide bonds have been developed.

Based on their findings, Odriozola et al. developed a dynamic covalent polymer system based on disulfide bond exchange using 4,4′-diaminodiphenyldisulfide (AFD) and DGEBA.[88] As shown in Figure 8, the AFD can react directly with the epoxy group, resulting in a simple and convenient process. The obtained vitrimer had a T_g of 130 °C, a tensile strength of 88 MPa, an elongation at break of 7.1%, and a $T_{5\%}$ of 300 °C. Its thermal and mechanical properties were similar to those of commonly used epoxy/amine systems on the market. Due to the presence of disulfide dynamic bonds, the E_a of the vitrimer was only 55 kJ/mol, with a τ^* of about 0.5 h (see Figure 8b). The resulting vitrimer can be reformed at 200 °C and 10 MPa, and it can be completely degraded in a mixture of thiol and N,N-dimethylformamide (DMF) at room temperature within 24 h (see Figure 8c), making it suitable for application in composite matrices.

Subsequently, Chen et al. designed a disulfide vitrimer with superior mechanical properties by increasing the content of disulfide bonds in the cross-linked network through a network regulation strategy. They synthesized thiol-containing epoxy monomers using bis(4-hydroxyphenyl) disulfide as the ingredient, curing them with AFD to obtain a vitrimer containing a high proportion of aromatic disulfide bonds.[57] Its T_g was 147 °C, and its tensile strength and Young's modulus were 63.0 MPa and 1.7 GPa, respectively. The tensile strength and Young's modulus of the prepared CFRP were 334.5 MPa and 10.5 GPa, respectively. Due to the presence of high-content disulfide bonds, the vitrimer can degrade more rapidly, achieving complete degradation in disulfide solution at

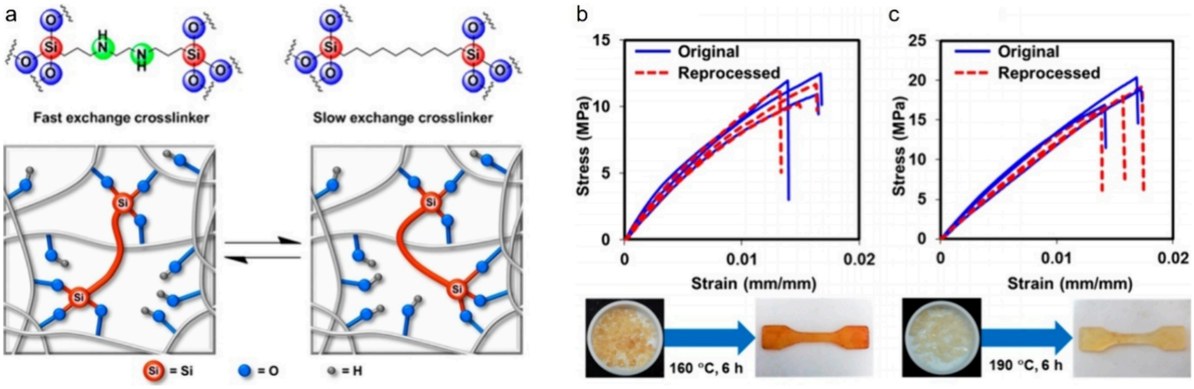

Figure 9. (a) Schematic diagram of silyl ether bond exchange vitrimer designed by Guan et al.; mechanical properties and reshaped recovery photos of silyl ether-based vitrimer containing (b) γ-NH and (c) γ-CH_2 groups.[47] Reproduced from ref 47. Copyright (2017) American Chemical Society.

90 °C within 1 h, thereby enabling the damage-free and rapid recovery of carbon fibers. In order to achieve the application of vitrimer in electronic devices, Chen et al. obtained epoxy resins with low dielectric constants by curing the same disulfide-containing epoxy monomer with the commercial curing agent tetraethylenepentamine, enabling its application in fields such as electronic packaging, while also achieving nondestructive repair and recycling of electronic devices.[89] The resulting vitrimer had a tensile strength of 71.9 MPa, a T_g of 115 °C, a resistivity equivalent to that of commercial epoxy resin, and a dielectric constant lower than that of commercial resin. Based on the bond exchange of disulfides, cracks in LED lamps encapsulated with the vitrimer can be quickly repaired at 150 °C, and they can also be degraded on demand in a disulfide solution, thereby reducing the generation of electronic waste and achieving environmentally friendly development in the field of electronic appliances.

Tomonori Saito et al. adopted a dual dynamic network control strategy involving disulfide and urea groups to cocure AFD and hexamethylene diisocyanate with DGEBA, resulting in the production of a vitrimer that was more easily recoverable.[90] Compared with the vitrimer formulated by Odriozola, the τ* was shortened from 17 to 3 min at 160 °C, and the reshaping temperature of the corresponding vitrimer was reduced from 200 to 160 °C. At the same pressure of 10 MPa, the reshaping time could be reduced to 1 min. The mechanical properties of the vitrimer remained essentially unchanged after six processing cycles, effectively reducing the aging behavior of conventional vitrimers during thermal processing.

To further expand the range of applications for disulfide-based vitrimers, Shan et al. obtained a nanomaterial (KH560-MoS_2) containing terminal epoxy groups by modifying MoS_2 with 3-glycidoxypropyltrimethoxysilane (KH560) and bonding it covalently with DGEBA/AFD.[91] The modified nanomaterials can act as energy converters, converting near-infrared light energy into thermal energy. When the density of the infrared laser is 2.4 W/cm^2, for example, the surface temperature of the obtained vitrimer reached 192 °C. The resulting vitrimer exhibited a scratch recovery rate of nearly 100% after being exposed to 808 nm near-infrared light for 60 s. It offered a wide range of potential applications for the research and development of light-responsive, self-healing thermosets.

Additionally, vitrimers based on disulfide bond exchange can provide a rapid alarm function in the event of material damage. Both Odriozola and Hu et al. observed the same phenomenon in a vitrimer that was prepared using AFD as a curing agent.[92,93] When the material was damaged (e.g., by impact or hammering), it turned a distinct shade of green. After heating, the material's performance and appearance were restored. It was caused by sulfonyl groups being generated when aromatic disulfide cross-links broke down, resulting in a distinctive green color. After heating, the sulfonyl groups in the cross-linked network sped up the exchange process, returning them to their original state before damage occurred. However, the high price of disulfides such as AFD, which costs over $150 per kilogram, limits the application of vitrimers based on disulfide bond exchange.

3.4. Vitrimers Based on Silyl Ether

The vitrimer based on silyl ether is formed by incorporating dynamic siloxane (Si−O) groups into a cross-linked network. These bonds can be exchanged under heating or catalytic conditions, reorganizing the network topology and endowing the material with intelligent properties such as self-healing, recyclability, and shape reconstruction.[94,95] In addition, the bond energy of silicon−oxygen single bonds (400 ∼ 500 kJ/mol) is much higher than that of carbon−oxygen single bonds (360 ∼ 385 kJ/mol).[96] This enables silicon-containing materials to exhibit high-temperature and oxidation resistance properties. Consequently, the vitrimer based on silyl ether bond exchange offers new possibilities for sustainable development in areas such as flexible electronics, green packaging, smart coatings, and high-temperature-resistant materials.

Guan et al. reported the first silyl ether-based vitrimer in 2017.[47] As shown in Figure 9, their systematic research found that the bond exchange rate of a vitrimer containing γ-NH groups was approximately 3 orders of magnitude higher than that of a vitrimer containing γ-CH_2 groups. In vitrimer form, the E_a for γ-NH siloxane bond exchange was 81 kJ/mol, which was much lower than that for γ-CH_2 substituted vitrimers. The corresponding T_v values were 47 and 125 °C, respectively; however, their T_g values were similar, both being around 125 °C. The adjustable silyl ether exchange, combined with the high thermal stability and reprocessability of silicone-based polymers, has made this series of materials widely applicable. Subsequently, in 2019, the team designed a silyl ether exchange vitrimer based on this system, which did not require hydroxyl groups to be present. The vitrimer was prepared by silanizing poly(ethylene-*co*-vinyl alcohol) with trimethylsilyl groups, followed by cross-linking with a bis-silyl ether cross-linker.[95] In the cross-linked network, there were essentially no active groups, such as hydroxyl or secondary amine groups, which prevented side reactions, such as dehydration, from occurring at high temperatures. Thus, the material exhibited high thermal stability, with a $T_{5\%}$ value above 400 °C. It can be reprocessed at least three times at 150 °C with no significant loss of mechanical properties, and it exhibited good creep resistance below its melting transition temperature.

Lu et al. introduced phenyl groups into the silyl ether bonds at the ortho positions, designing a benzimidazole resin with high-density dynamic Si−O−Ph cross-links, which exhibited a T_g of 301 °C and thermal stability up to 396 °C.[94] In addition, the resulting vitrimer can be reshaped under hot pressing at 220 °C and 10 MPa for 2 h. After three thermal cycles, the recovery rate of tensile strength was still greater than 75%. At the same time, the vitrimer exhibited favorable solvent resistance and remained structurally intact after 24 h of immersion in various solvents at 50 °C. The resin matrix allowed for the recovery of monomers in acidic solvents.

In order to enable the commercial application of silyl ether-based vitrimers, Zhang et al. developed silyl ether-cross-linked poly(ethylene-vinyl acetate) (EVA) vitrimers through the reactive blending of industrial-grade EVA and bis[3-(trimethoxysilyl)propyl]amine.[97] Notably, the resulting EVA-V0.8 vitrimer, which had the highest cross-linking density, exhibited the lowest activation energy (79.3 kJ/mol) of all the prepared vitrimers. In addition, the resulting vitrimer can be reprocessed under hot pressing at 210 °C and 10 MPa for 0.5 h. Following four heat recovery cycles, the elongation at break and tensile strength recovery rates of the vitrimer were both greater than 90%. The preparation of the vitrimer does not require the use of solvents, the process is simple, and the ingredients are readily available, making it cost-competitive, environmentally friendly, and easy to scale up for manufacturing.

Despite its relatively short development time, the vitrimer based on silyl ether has attracted increasing attention and research from scholars due to its reasonable price and potential applications in high-temperature scenarios. It is expected that the silyl ether-based vitrimer will be used in high-temperature applications, such as aerospace materials.

In addition to the aforementioned DCBs, many other DCBs have also been explored in the development of vitrimers, such as vinyl urea esters, diketene amines, borate esters, and phosphate esters.[47,48,53,95,98−100] Some of these vitrimers also exhibit high performance, but their relatively complex preparation processes pose challenges for industrial application.

4. FUTURE PERSPECTIVE

In recent years, with the continuous optimization of molecular design and DCN regulation methods for dynamic covalent polymers, the vitrimers has achieved multifunctionality, and the comprehensive performance of some reported vitrimers has superiority over traditional thermosets. However, there is still significant scope for innovation and exploration on the path to commercialization. The following points could be considered when developing vitrimer engineering applications in the future:

1. Introducing secondary sacrificial dynamic interaction forces that can dissipate energy into the dynamic cross-linked network enhances the toughness and strength of the vitrimers.
2. Cost control will be essential for large-scale industrial adoption of vitrimers, including optimization of raw material selection, simplification of synthesis routes, and design of scalable recycling procedure.
3. Introducing flame retardancy, thermal conductivity, and insulation regulation functions, while maintaining mechanical performance, to expand application scenarios.
4. Improving the creep resistance and solvent resistance of the vitrimer by introducing partial permanent cross-linked structures into dynamic cross-linked networks.
5. Developing fully bio- or carbon dioxide-based vitrimers systems to reduce dependence on petroleum resources and alleviate greenhouse gas emissions.

The multifunctionalisation of vitrimer is expected to become a critical trend for the next generation of high-performance thermosets. In the short term, the performance gap between vitrimers and traditional thermosets is expected to be closed, based on considerations of ingredient costs and manufacturing processes. In the medium to long-term, the focus will be on multifunctional integration and ingredient greening to provide better solutions for the safety and sustainable development of thermosets.

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CRediT: **Guofeng Ye** formal analysis, validation, visualization, writing - original draft; **Cheng Wang** visualization; **Yong Guo** resources; **Qingshan Yang** investigation; **Siqi Huo** funding acquisition, project administration, supervision, writing - review & editing.

Notes

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