

High-Performance Vitrimeric Benzoxazines for Sustainable Advanced Materials: Design, Synthesis, and Applications

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Polybenzoxazines are high-performance materials capable of replacing conventional thermosets such as phenolics, epoxies, and bismaleimides in composites manufacturing due to their excellent thermomechanical and chemical behavior. Their versatility and compatibility with biobased precursors make them an attractive option as composite matrices. Like other thermosets, polybenzoxazines are not recyclable and cannot be reprocessed. Incorporating dynamic bonds in benzoxazine monomers can produce vitrimeric polybenzoxazines, which can potentially overcome this limitation and can be tuned to exhibit smart functionalities such as self-healing and shape memory. Dynamic bond exchange mechanisms for vitrimer development such as transesterification, imine bond, disulfide exchange, transamination, transcarbamoylation, transalkylation, olefin metathesis, transcarbonation, siloxane-silanol exchange, boronic ester, silyl ether exchange, and dioxaborolane metathesis are potentially applicable to benzoxazine chemistry, with disulfide bond and transesterification having successfully vitrimerized benzoxazines with topological transitions at -8.5 and 88 °C, respectively. Benzoxazine vitrimers featuring glass transitions of 193 , 224 , and 222 – 236 °C are now known. These place polybenzoxazines at the forefront of the development of reprocessable and recyclable thermosetting polymers and composite matrices.

1. Introduction

Benzoxazine resins have drawn significant attention in recent years due to their potential to replace epoxies and other traditional thermosetting resins in the composites industry.^[1,2] This potential stems from their excellent thermomechanical and chemical properties, which are a result of polybenzoxazine's generally low free volume, nature of molecular chain interaction, and intermolecular packing.^[3] These properties are summarized in **Figure 1**. The significant shortcomings of benzoxazines are high cure temperatures (150 – 220 °C),^[4] due to the high activation energy needed to open the oxazine ring, low fracture toughness due to their brittle nature,^[5] low crosslinking density,^[1] resulting from the prevalence of intermolecular and intramolecular hydrogen bonding in polybenzoxazine systems which impedes network formation, thus limiting polymerization to low crosslinks.^[3,6] However, these drawbacks can be overcome by using catalysts, such as hydroxyl,^[7] carboxyl,^[8] and thiol,^[7] to reduce the curing temperature and by

blending benzoxazines with toughening agents and other resins to increase crosslink density and fracture toughness.^[1,9]

Benzoxazine systems combine the attractive properties of phenolics, such as high corrosion and temperature resistance, with high flame retardance and low dielectric constant. In addition, benzoxazine resins have a long out-life, high char yield, and very low cure shrinkage leading to outstanding dimensional stability.^[2,5,10,11] Upon heating to curing temperatures, benzoxazine monomers undergo a thermally induced autocatalytic ring-opening homopolymerization, often from a viscous oligomeric material to a glassy solid. Benzoxazine polymerization does not release toxic volatiles^[12] and does not yield water, unlike condensation polymerization of traditional phenolics. Also, benzoxazines can be copolymerized with other resin systems such as epoxies to obtain hybrid resins with intermediate properties, as illustrated in **Figure 2**. The forces of hydrogen bonding in polybenzoxazines are sufficiently strong as to limit segmental mobility, thereby contributing to high glassy state rigidity that would normally be expected from a much denser crosslink.^[3] Therefore, polybenzoxazines feature high glass transition temperature (T_g), much greater than their curing temperature and typically higher than that of phenolics (170 – 340 °C),^[13] fast development of mechanical properties as a function of conversion (exemplified

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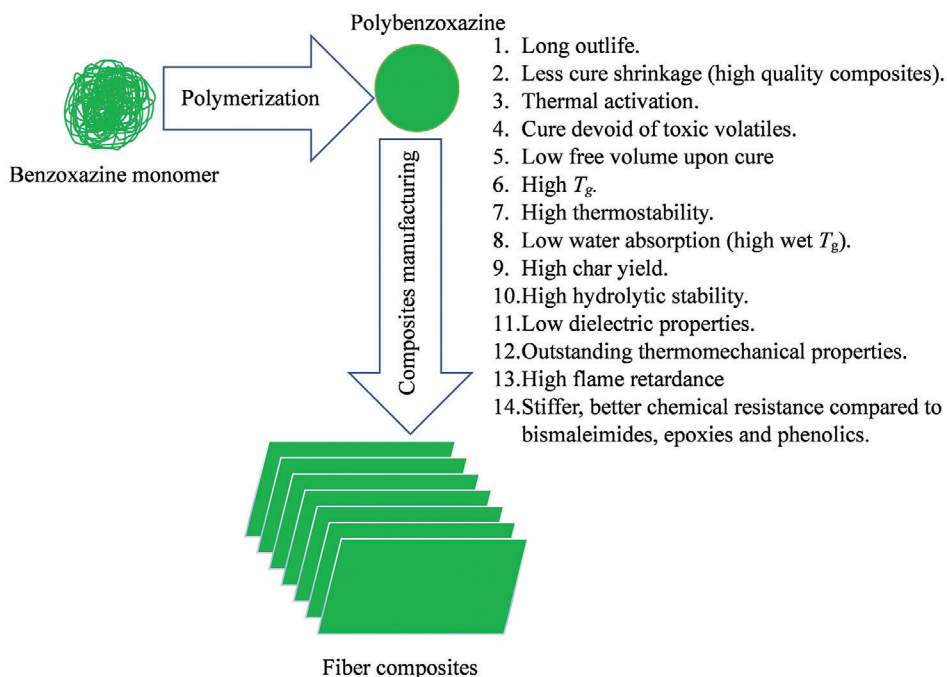


Figure 1. Schematic presentation of benzoxazine properties.

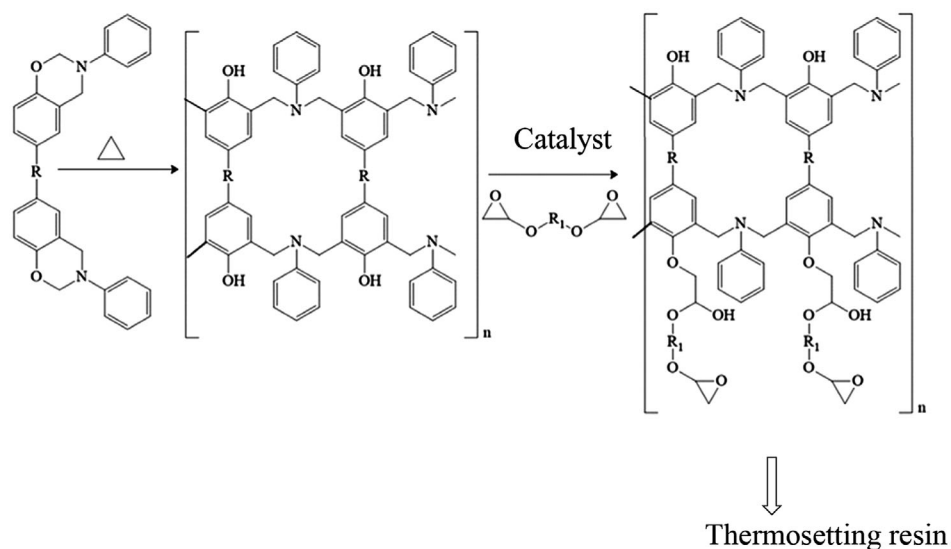


Figure 2. Reaction scheme of benzoxazines with epoxy resins.^[9]

by tensile strength and modulus in the range 100–125 MPa and 3.8–4.5 GPa, respectively),^[13] resistance to acids and bases^[10,13–23] and are generally hydrophobic despite having many hydrophilic groups. Due to high hydrophobicity, benzoxazines generally exhibit wet T_g not far lower than their dry T_g , thus making them attractive for the manufacture of components for wet environment operation, such as in aerospace applications. Benzoxazines are currently employed in various industrial applications, including coatings, adhesives, halogen-free laminates for printed circuit boards, encapsulants, and composites for fire-retardant applications.^[9]

Polybenzoxazine performance goes beyond that of traditional phenolics, epoxies, and bismaleimides, rendering them an attractive alternative to these matrices.^[2] Average performance benzoxazine polymers, such as commercially available bisphenol A-based polybenzoxazine, compare favorably with traditional phenolics and advanced epoxy systems,^[2,7] while high-performance benzoxazine polymers can be compared to bismaleimides with the advantage of lower cost in terms of raw materials.^[2] Benzoxazine resins offer a high flexibility of manufacture due to the versatility of their phenolic and amine precursors,^[10,11,24] low cost of raw materials, and ease of formulation. The superior resistance to

chemical corrosion, flame retardance, and excellent thermal stability renders benzoxazines a good candidate as a matrix for advanced composites manufacturing applicable in the fabrication of products exposed to high temperature, loads, and corrosive environments such as oil and gas exploration and civil engineering. The intrinsic flame-retardant behavior of benzoxazines has attracted the interest of the aerospace industry, which uses large amounts of phenolic prepreps to manufacture semistructural interior parts subject to fire smoke toxicity (FST) regulations.^[9] Benzoxazine chemistry is equally applicable to the electronics industry for the fabrication of halogen-free laminates used in printed circuit boards. Benzoxazine-based prepreps and infusion systems for advanced composites manufacturing are currently commercially available.^[9]

Despite the potential of benzoxazines to take over certain areas from epoxies,^[25] the prospect of developing high-performance benzoxazine vitrimers is rarely reported in the literature. A vitrimer is an associative covalent adaptable network (CAN) which, though retaining the excellent mechanical properties and solvent resistance of a typical thermoset at service temperatures, features the reprocessability and recyclability of thermoplastics by undergoing thermally activated bond exchange reactions without compromising network structural integrity in terms of the total number and average functionality of crosslinks. From rheological viewpoint, the viscosity of vitrimers follows Arrhenius temperature dependence. Vitrimers are distinct from dissociative CANs, which also undergo thermally activated bond exchange reactions. However, unlike vitrimers, network topology rearrangement in dissociative CANs involves depolymerization, and the material significantly loses its mechanical properties in the process. The relationship between viscosity and temperature in dissociative CANs follows the Williams–Landel–Ferry law. It is important to note that some dissociative CANs exhibit vitrimeric behavior by maintaining their network integrity while exchanging dynamic bonds via the dissociative mechanism.^[26,27] Like vitrimers, their viscosity follows Arrhenius temperature dependence to some extent. Such CANs are not true vitrimers due to the dissociative nature of their dynamic bond exchange. They are sometimes called vitrimer-like materials to distinguish them from true vitrimers.

Since the discovery of the first vitrimer in 2011,^[28] many resin systems are successfully targeted and reported as precursors for high-performance vitrimeric materials. The first known vitrimer is based on an epoxy thermoset with zinc-catalyzed transesterification exchange chemistry.^[28] Many epoxy vitrimers have since been reported, featuring excellent properties.^[29–77] Other reported vitrimers are based on polybutadienes,^[78–82] polyurethanes,^[83–99] polyhydroxyurethanes,^[100,101] polyurethane urea,^[102,103] polyesters,^[104–115] polycarbonates,^[116] and polyimides.^[117,118] These materials have low-to-medium-to-high glass transition temperatures, with polyimide vitrimer achieving T_g of 274 °C and a 5% weight loss temperature of 429 °C.^[117]

The development of biobased high-performance vitrimeric benzoxazine resins can result in significant progress as it has the potential of delivering a new, improved matrix for composites combining high performance, sustainability, ease, and low cost of manufacture. The molecular design flexibility of benzoxazines renders their chemistry compatible with biobased resources^[119] such as cashew nut shell oil, urushiol, terpene, levulinic acid, cel-

lulose, and glycerin.^[120] These natural renewable resources usually contain reactive functional groups that may remain unconsumed during synthesis, thus providing additional functionality to the synthesized benzoxazine monomer.^[121,122] Such functionalities permit the monomer to be further crosslinked with a wide range of materials to customize the resulting polybenzoxazine for specialized industrial applications.^[1,123–131]

The first known biobased benzoxazine resin with shape memory (**Figure 3**) is formulated by crosslinking a vanillin-derived benzoxazine monomer (coded VFA) with a diamine-terminated polyether (coded atpe) resulting in a high glass transition temperature (280 °C), highest storage modulus (4.2 GPa), and the highest tensile strength (90.4 MPa) among biobased benzoxazine resins.^[132] This material incorporates a dynamic imine bond that enables material malleability. Although this material exhibits shape memory due to the presence of the imine bond, it has no vitrimeric behavior.

Among biobased benzoxazines, there is increased interest in those based on lignin-derived vanillin.^[133–141] Lignin, a natural biopolymer used as a blend component of polybenzoxazine,^[142,143] is found in wood, aquatic plants, grasses, and other plant substances.^[144–146] Vanillin occurs naturally in vanilla plants but can be produced from lignin and other renewable resources.^[4] It has one free ortho position adjacent to the hydroxyl group, qualifying vanillin as a candidate for the synthesis of 1,3-benzoxazines, which are the only isomers of benzoxazines known to form polybenzoxazines.^[4,7,23] The aldehyde group of vanillin may remain available for further crosslinking after the benzoxazine synthesis is completed. Crosslinking vanillin-based benzoxazine at the aldehyde positions leads to a higher glass transition^[132] and prevents decarboxylation^[139] associated with polymerization of vanillin-based benzoxazines,^[147,148] which leads to early degradation during the polymerization process.^[139] This has made vanillin one of the most attractive precursors for benzoxazine synthesis. Many benzoxazines based on vanillin have been synthesized and characterized.^[4,132,147–154]

Other widely used biobased benzoxazine precursors include eugenol,^[149,150,153–157] obtained from clove oil, nutmeg, cinnamon, basil and bay leaf,^[157] cardanol,^[10,11,123,129,149,156,158–161] which can be obtained from cashew nut shell,^[10,123,158,159] and guaiacol^[153,154,162,163] obtained from pyrolysis of biomass.^[162,163] Apart from benzoxazines synthesized from the most widely used biobased phenols, other sustainable benzoxazines are reported, including those derived from rosin, obtained from the exudation of pines and conifers,^[164] resveratrol (a triphenol compound extracted from grapes, pines, legumes, and other plants),^[165] and chavicol^[166] (derived from bay oil, sweet basil, or betel oil).^[167,168] Other reported sustainable benzoxazines are based on daidzein,^[169] sesamol,^[170] p-cresol,^[171] arbutin,^[172] ferulic acid,^[173] urushiol,^[174] bakuchiol,^[175] diphenolic acid,^[176] coumarin,^[177] and terpene diphenol.^[178] The diversity of biobased phenolic systems and amines is an indication of the abundance of high-performance, sustainable benzoxazine resins that can be synthesized. These potential prepolymers can incorporate exchangeable dynamic covalent bonds, opening the possibility of developing high-performance sustainable benzoxazine vitrimers and furthering the frontiers of sustainable advanced materials. Incorporating biobased precursors is one

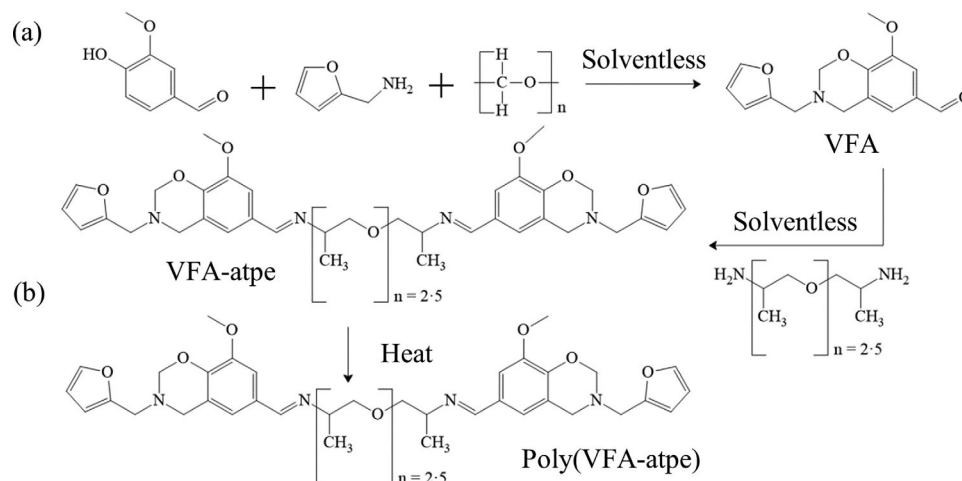


Figure 3. High-performance polybenzoxazine incorporating imine bond. a) Synthesis of benzoxazine monomer from vanillin, paraformaldehyde, and furfuryl amine coupled with crosslinking with poly(propylene glycol) bis(2-aminopropyl ether) to form VFA-atpe. b) Ring-opening polymerization of VFA-atpe.^[132]

of the attractions of benzoxazines because such systems do not pose environmental problems at the end of product life.

There are many review articles and viewpoints on the subject of vitrimer.^[26,179–190] However, the literature on benzoxazine vitrimers has not been reviewed. Therefore, it is highly relevant to review the state of the art in this area, as the literature on sustainable benzoxazine-based high-performance vitrimers is expected to grow soon. This article summarizes benzoxazine chemistry, vitrimer chemistry, and strategies for vitrimerizing benzoxazines to improve their functionalities, reprocessability, and applications. It presents empirical evidence suggesting that the design of high-performance vitrimers based on benzoxazine resin systems is a feasible direction for future development.

2. Benzoxazine Polymers

In this section, the chemistry of the formulation of benzoxazines and their polymerization is reviewed. The classification of benzoxazines is presented, together with the historical development of benzoxazine resins. Finally, the section highlights the various industrial applications of benzoxazines based on their very attractive properties.

2.1. Benzoxazine Chemistry

Benzoxazines are bicyclic heterocyclic organic compounds that contain oxygen and nitrogen in an unsaturated six-member ring fused with a benzene ring. They are normally synthesized by the Mannich condensation reaction involving a phenol, paraformaldehyde (i.e., formaldehyde polymer), and primary amine, as shown in **Figure 4**. Depending on the precursors' physical state and chemical reactivities at typical reaction temperatures (60–100 °C), the reaction may require the addition of a solvent or may proceed without a solvent.^[12,191] As noted earlier, if additional functional groups are attached to benzoxazine precursors, they may not be consumed during synthesis. Rather, they

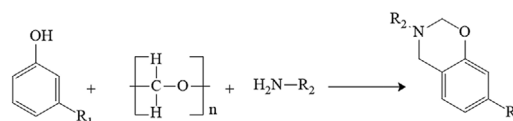


Figure 4. Scheme representing synthetic pathway of benzoxazine monomers.

may remain available for further crosslinking, permitting the tailoring of benzoxazine monomers and polymers to specialized functionalities.^[4] The diversity of phenols and amines implies that many benzoxazines can be synthesized, endowing the final product with a wide range of chemical and thermomechanical properties.

Pure benzoxazine monomers may crystallize depending on the molecular structure, exhibiting a completely amorphous structure once polymerized due to crosslinking.^[2] The ring-opening polymerization is driven by ring strain in the irregular chair structure of the six-membered heterocycle. Heating provides additional energy to the ring strain to bring about polymerization. The monomer usually contains some impurities, such as benzoxazine oligomers and unreacted phenolic raw materials. Such impurities, acting as cationic initiators, readily induce, or initiate, the polymerization of the monomer. Another factor that influences the polymerization of benzoxazines is the basicity of nitrogen and oxygen atoms in the oxazine ring. The stronger the basicity of the nitrogen and oxygen atoms, the more suitable for cationic opening the ring becomes.^[192]

The polymerization of benzoxazines is considered to occur by a two-step mechanism: the ring-opening step involving a heterolytic splitting of the N,O-acetal moiety into an intermediate zwitterion bearing iminium cation and phenoxide, followed by intramolecular electrophilic substitution that involves hydroxyl group and the iminium cation.^[193–196] The final product may be a phenolic or a phenoxy structure, depending on the conditions of the reaction.^[195] The polymerization of a benzoxazine monomer is illustrated in **Figure 5**.

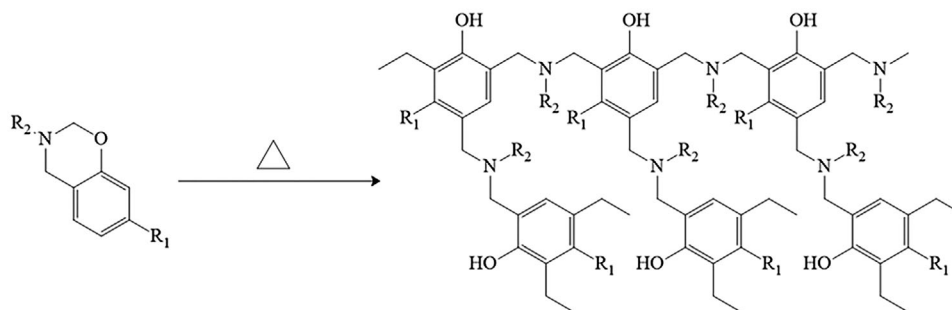


Figure 5. Thermally activated ring-opening polymerization of benzoxazines.

The enthalpy of polymerization per unit mass, often measured by differential scanning calorimetry (DSC),^[151,166,169,192,197–204] depends on two key factors: the concentration of preopened cycles in the monomer due to high synthesis temperature^[192] and the mass of the monomer.^[192,198,205] If there is a high concentration of preopened cycles in the monomer, the material is prepolymerized; thus, fewer cycles will be available for thermal opening, and the enthalpy tends to be reduced.^[192] Conversely, a low concentration of already opened cycles in the monomer implies that more cycles are available for thermal ring-opening, which results in a high polymerization enthalpy. Also, the higher the molecular mass of the monomer, the lower the enthalpy of ring-opening per unit mass and vice versa.^[192,198] The molecular mass of a benzoxazine monomer depends on the number of oxazine moieties in the monomer and the mass of other chemical groups attached to the benzoxazine cycle(s). Since the reaction is essentially ring-opening and crosslinking, the heat of reaction is a function of the amount of the oxazine ring available in the monomer and given no preopened oxazine cycle ahead of polymerization, the heat of reaction per unit oxazine ring is constant, $\approx 73.0 \text{ kJ mol}^{-1}$.^[166,199]

Suppose the benzoxazine monomer contains another reactive group that participates in the curing reaction, such as a functional group or an unsaturated double bond, in addition to the oxazine ring. In that case, the overall polymerization enthalpy increases over the range generally observed for oxazine ring-opening polymerization.^[151,166,200]

Various methods in the literature are used to determine the activation energy of benzoxazine polymerization. From the available evidence, these activation energies range between 70 and 130 kJ mol^{-1} ^[132,170,205–207] depending on the molecular weight distribution of the benzoxazine monomer.^[205] Apart from information from spectroscopic studies, which normally confirms successful synthesis of a new chemical, comparing the enthalpy of polymerization of a novel benzoxazine vitrimer with those of nonvitrimer benzoxazines from literature could aid in understanding whether or not a novel benzoxazine vitrimer polymerizes.

2.2. Classification of Benzoxazines

Benzoxazine classification can be summarized under three major classes: class A, B, and C.^[2] Class A benzoxazines are made from monoamine and phenols and could be functional or nonfunctional depending on whether there are functional groups attached to the monomer. The polymer shown in Figure 5 is

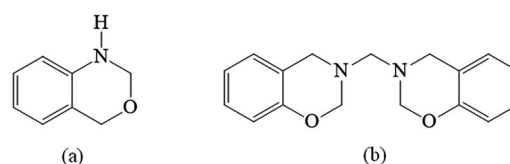


Figure 6. First known benzoxazine monomers.^[208] a) 2-substituted-1,2-dihydro-3,4-benzoxazine. b) Methylene-bis-(3,4-dihydro-1,3,2-benzoxazine).

obtained from a nonfunctional benzoxazine monomer. Class B benzoxazines are made from diamines and monofunctional phenols. They can be functional or nonfunctional. Functional class B benzoxazines may contain polymerizable groups such as epoxy, methacrylate, nitrile, acetylene, allyl, glycidyl, maleimide, norbornene, oxazoline, phthalonitrile, propargyl, or vinyl ester or potentially polymerizable groups with a suitable partner such as carboxyl, hydroxyethyl ether, phenol, methylol, or primary amine. Class C benzoxazines are linear polymers having oxazine rings in the main chain due to the reaction between diphenols and diamines. These polymers can further crosslink by the ring-opening polymerization of the oxazine rings. They are highly reactive polybenzoxazines, sometimes called thermoplastic/thermosetting crossover molecules. There are three subcategories of this class: the main-chain type, where the oxazine group is either the only reactive group in the main chain or the main chain contains the oxazine group and secondary reactive group; side-chain type, which incorporates reactive groups, such as polystyrene, polyvinyl chloride, polyvinylidene fluoride, polyvinyl phenol, or polyvinyl alcohol as side chains; and telechelic type, which are prepolymers with functional terminal groups capable of additional chemical reactivity, such as further polymerization or crosslinking to modify the structure while maintaining the properties of the main chain.

2.3. Historical Development of Benzoxazine Resins

The synthesis of benzoxazine dates to 1944, when the first benzoxazines were produced from the condensation reaction of aldehydes and ketones with ortho-amino benzyl alcohol (Figure 6a) and ortho-hydroxy benzylamine (Figure 6b).^[208] Further works between 1949 and 1965 developed the basic understanding of the chemistry of small molecular weight benzoxazines.^[209–216] Oligomeric benzoxazines used to modify

epoxy systems were reported in 1973 patents.^[217,218] The first crosslinked polybenzoxazines based on multifunctional benzoxazine systems were formulated in 1985, aiming to develop coating systems.^[219–221] Although these developments provided an insight into the versatility of polybenzoxazines, they did not focus on relevant material properties.

The first report on polybenzoxazine properties was published in 1994.^[222] There are currently several review articles and book chapters on advances in polybenzoxazine research.^[153,223–239] Benzoxazines are investigated for improved thermomechanical performance with much focus on smart functionalities, such as self-healing^[240] which can occur by the Friedel–Craft reaction,^[241] photo-induced coumarin dimerization,^[242] supramolecular hydrogen bonding,^[243,244] ketene chemistry,^[245] metal–ligand interactions,^[246] or dynamic sulfide linkages;^[13] shape memory;^[132,150,152,243,246–253] as well as antifouling protection,^[254] and reprocessability.^[13,159,255,256] Polybenzoxazines were reprocessed by simple dynamic sulfide linkages enabled by chopping into pieces and thermal treatment^[13] and by mussel-inspired catechol-Fe³⁺ coordination bonds.^[256] There are now a few reprocessable polybenzoxazines whose reprocessability is enabled by dynamic bond exchange without depolymerization. These are discussed in Section 4.

2.4. Properties and Applications of Benzoxazines

The excellent properties of benzoxazines, highlighted in this review, make them appropriate for a wide range of industrial applications. Due to the molecular chain rigidity of polybenzoxazines, coupled with interactions of hydrogen bonding, they exhibit a high mechanical strength-to-weight ratio making them attractive for high strength lightweight structural applications. Also, they exhibit high thermal resistance, rendering them suitable for insulation applications. Nonrelease of toxic volatiles and near-zero shrinkage during cure make benzoxazines an attractive option for composites manufacturing.

Benzoxazines are used as matrices for composites and nanocomposites. Apart from benzoxazine's aromaticity, which generally endows fire resistance, nitrogen atoms forming linkages between monomer units of the polybenzoxazine greatly enhance flame retardancy, thus making benzoxazine resins suitable for the manufacture of fire-retardant composites.^[257] Benzoxazine resins are compatible with laying up/autoclaving,^[258] resin transfer molding (RTM),^[257,259,260] vacuum-assisted resin transfer molding (vaRTM),^[259] vacuum transfer process (VAP),^[259] filament winding,^[257,260] and press molding.^[257,260] Polybenzoxazine composites can be applied in ablative materials,^[261] including heat protection in rockets and engine nozzles.^[257]

Benzoxazine matrices are used in the manufacture of carbon fiber composites.^[258,262–268] A comparison of the fire smoke toxicity (FST) properties of selected benzoxazine prepregs to an aerospace-qualified phenolic prepreg indicates that high-performance benzoxazine prepregs are a promising alternative for aerospace interior applications.^[9] Thus, benzoxazines are likely to replace phenolic resins for interior applications (such as seating and storage) because of their excellent fire smoke toxicity rating;^[269] furthermore, phenolic resin composite parts normally have surface voids resulting from outgassing of water

from the curing reaction. Repair of such voids increases the overall manufacturing cost. This shortcoming of phenolic resins is overcome by benzoxazine matrices whose polymerization does not yield water. Carbon fiber-benzoxazine tooling prepregs designed for aerospace tooling applications are now commercially available.^[270,271] Benzoxazine-based composites are qualified for the auxiliary power unit (APU) housing of Airbus A380, thus replacing the traditional bismaleimide, while Airbus A350's in-board and outboard wing flaps carbon fiber T-stingers are produced using benzoxazine based tooling.^[270] Benzoxazine is also applied in aerospace in the form of adhesives for bonding large bismaleimide tooling assemblies.^[270]

Glass fiber-reinforced polybenzoxazine composites are successfully manufactured,^[272,273] while a low-density moderate-strength silica fiber-reinforced polybenzoxazine has been developed and put forward for thermostructural applications.^[274] Also, benzoxazines are compatible with cellulose fibers due to the similarity of the molecular structure of polybenzoxazines to lignin, leading to the development of cellulose fiber-reinforced benzoxazine composites.^[260,275–279]

Nanocomposites based on benzoxazine resins have been investigated with promising outcomes. The incorporation of clay nanofillers improves the ultimate thermomechanical properties of the benzoxazine matrix.^[280–292] Carbon nanotube-reinforced polybenzoxazine composites have also been developed in which the nanoparticles are well-dispersed in the benzoxazine matrix with good adhesion, leading to increased storage modulus and glass transition temperature of the composite^[293] as well as enhanced toughness, flexural, and fracture strength of the composite.^[294] Polybenzoxazines have also been used in nanocomposites based on polyhedral oligomeric silsesquioxane (POSS) to enhance flame retardance, thermal stability, crosslink density, glass transition temperature, and char yield,^[295–305] while silicon-carbide (SiC) whiskers are incorporated into benzoxazine systems to reduce curing time and enhance flexural modulus of the composite.^[306–308] Other nanocomposites based on polybenzoxazines include graphene oxide-cardanol-based polybenzoxazine for electrical applications,^[160] cyclophosphazene nanotube (PZT)-reinforced poly(benzoxazine-co-ε-caprolactam) (P(BZ-co-CPL)) nanocomposites developed for fire-retardant applications,^[309] polybenzoxazines incorporating titanium oxide^[310] or barium titanate used for dielectric property enhancement,^[311] silica nanoparticles used for alkali metal and alkali earth metal ion extraction,^[312] thermal and mechanical property improvement,^[313] and controllable wettability application;^[314] expanded graphite nanoplatelets applied for their low gas permeability, electrical conductivity, and mechanical properties in polymer electrolyte fuel cell (PEFC) bipolar plates.^[315] Other formulations include nickel-zinc ferrite-reinforced benzoxazine nanocomposites endowed with magnetic behavior^[316,317] and boron nitride-based polybenzoxazine nanocomposites proposed for applications in aerospace and electronic packaging due to their good thermal and dielectric properties.^[318] Moreover, silver phosphate-benzoxazine soft gel nanocomposites were developed and found to exhibit photocatalytic performance.^[319] The prospect of benzoxazine nanocomposites for advanced industrial applications has led to various research efforts devoted to the understanding of polymerization kinetics of benzoxazine nanocomposites.^[320,321]

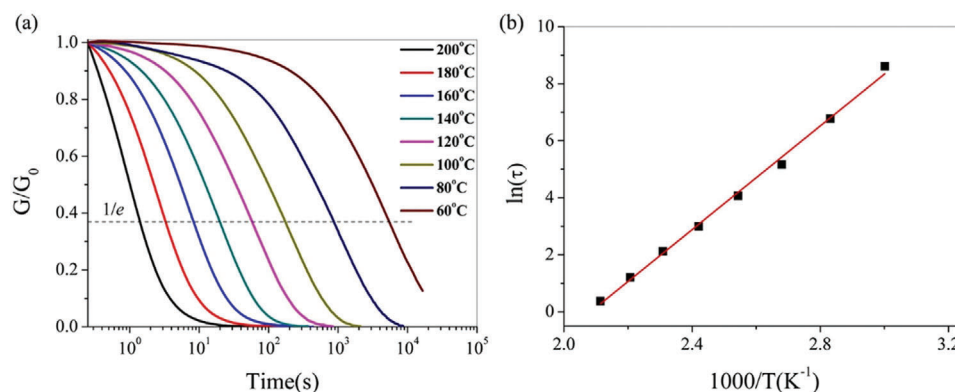


Figure 7. T_v detection from stress relaxation experiment. a) Normalized stress relaxation as a function of temperature. b) Arrhenius temperature dependence of stress relaxation. Reproduced with permission.^[188] Copyright 2019, American Chemical Society.

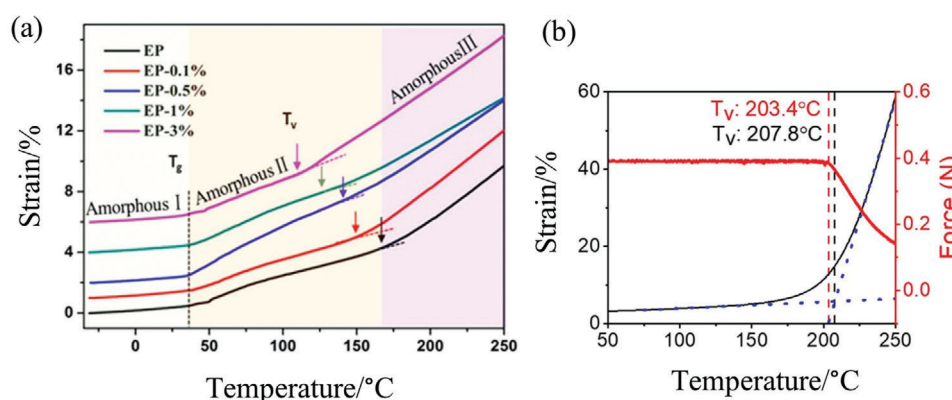


Figure 8. T_v detection by dilatometry a) T_v as a point of initial deviation from approximately linear strain curve. Reproduced with permission.^[332] Copyright 2016, American Chemical Society. b) Both strain and force curves as indicators of T_v , which is taken as the onset of plastic flow rather than an initial deviation from an approximately linear strain curve. Reproduced with permission.^[339] Copyright 2021, American Chemical Society.

3. Vitrimeric Systems

3.1. Properties and Advantages of Vitrimers

The introduction of the term “vitriimer” by the French physicist Ludwik Leibler and his co-workers,^[28] came with a contemporaneous introduction of the term “topology freezing transition” (topology freezing transition temperature), T_v , which has since become a subject of interest to the polymer community due to the nature of this transition. It relates to the chemical phenomenon of bond exchange rather than a physical phenomenon. Unlike physical phenomena such as glass transition and melting, which DSC can easily measure, T_v cannot be measured by the DSC. If a vitriimer is heated above its T_g , molecular segments gradually become mobile, leading to observable macroscopic flow, while bond exchanges are initially negligible due to high viscosity. On further increase in temperature, the viscosity decreases following an Arrhenius temperature dependence until a certain “upper limit” viscosity is attained, when segmental mobility becomes significant, and bond exchanges become pronounced. The upper limit viscosity for bond exchange is arbitrarily chosen as 10^{12} Pa s. The temperature corresponding to this viscosity is the T_v .

As noted, T_v has elicited a lot of interest within the polymer. Its measurement is not direct. Four methods are applied in the literature to probe vitriimer T_v :

- Stress relaxation (**Figure 7**), by measuring viscosity-dependent relaxation time as a function of temperature, using the time at which the initial modulus decreases to $1/e$ (i.e., 37%), the viscosity of 10^{12} Pa s, and Maxwell’s relation: $\eta = G\tau^*$ where η is viscosity, G is the plateau complex modulus in the rubbery region (typically measured using dynamic mechanical analysis), and τ^* is the relaxation time.^[35,47,159,322–329] The stress relaxation of vitrimers can also be analyzed using Kohlrausch–Williams–Watts (KWW) function to estimate the average relaxation time.^[330,331]
- Dilatometry (**Figure 8**), by observing the point at which vitriimer entropic elasticity contraction—normally observed as linear dependence of rubbery modulus on temperature—deviates from linearity and becomes irreversible plastic extension due to heating under load. The T_v appears on a dilatometry strain-temperature curve as the point of transition between the elastomeric region and the plastic

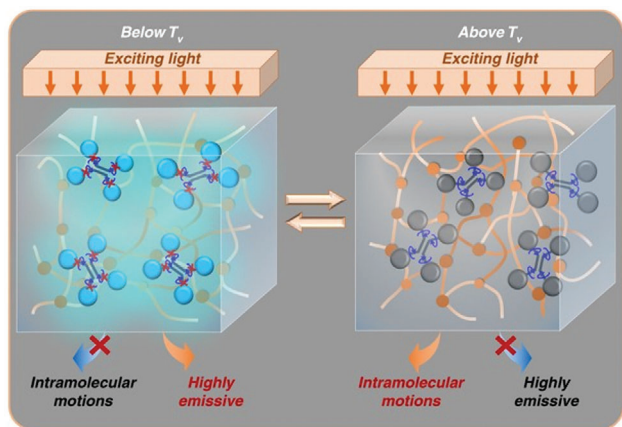


Figure 9. Fluorescence emission of AIE molecules as a function of temperature. Below T_v , emissivity is high. Above T_v , emissivity is weak. Reproduced with permission.^[341] Copyright 2019, Springer Nature.

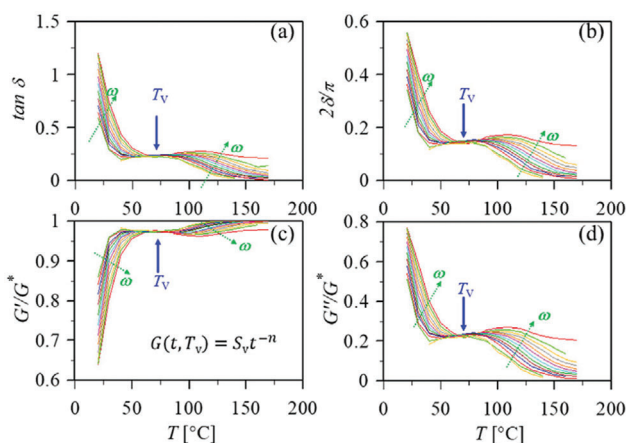


Figure 10. T_v as an expression of a power-law relaxation modulus where the point of coalescence of lines of constant frequency: $\tan \delta$, $2\delta/\pi$, G''/G' , and G''/G' at an intermediate temperature indicates T_v , temperature being the independent variable. Reproduced with permission.^[342] Copyright 2020, American Chemical Society.

region.^[28,45,106,115,332–340] This method is sometimes called nonisothermal elongational creep measurement.^[339,340]

- iii. Aggregation-induced-emissions (AIE) luminogens (**Figure 9**), by doping vitrimer with AIE as a fluorescent probe and observing the turning point as the fluorescence intensity function—which decreases with temperature—transitions to a new slope.^[341]
- iv. Multifrequency oscillatory scan Rheometry (**Figure 10**), by observing the point of coalescence of vitrimer functional lines of constant frequency.^[184,185,342]

Two classes of vitrimers are distinguishable, depending on the position of the vitrimer's T_v on the thermogram relative to its T_g ,^[343] which determines the thermomechanical and rheological properties of the vitrimer.^[344]

- (a) Vitrimers having T_v greater than T_g . If T_v is above T_g and the material is heated up to its glass transition temperature, it

undergoes a transition from a glassy state to a rubbery state. As heating is continued between T_g and T_v , the material behaves like an elastomeric solid unable to flow since the bond exchange reactions are slow, making the material topology frozen. On reaching T_v , the bond exchange reactions become fast, permitting macroscopic flow, and the material becomes a viscoelastic liquid. At this point, the material viscosity gradually decreases following an Arrhenius temperature dependence. This behavior is illustrated in **Figure 11a** in which the relative volume of the vitrimer and the logarithm of its viscosity are plotted against temperature for an amorphous vitrimer.

- (b) Vitrimers having T_v lower than T_g . Based on the definition of vitrimer's T_v which relies on the attainment of viscosity of 10^{12} Pa s, it is unimaginable for T_v of a material to practically occur below the T_g . This line of argument is supported by elongational creep measurement, where the softening (occurrence of T_v) cannot happen in the glassy state. Also, the coalescence of functional lines of constant frequency in multifrequency oscillatory scan Rheometry cannot happen in the glassy state since this phenomenon relates to softening (occurrence of T_v). However, the measurement of T_v using Maxwell's relation in stress relaxation, described in this review to distinguish between the rheology of the two categories of vitrimer, leads to a T_v below T_g for the metathesis-type bond exchange, which appears theoretically convincing with the explanation thereof. Therefore, the T_v of metathesis-type vitrimers remains a subject not yet fully understood. The current understanding of this subject, which may be modified with future studies, is explained in the next paragraph.

If T_v is below T_g and the vitrimer is heated, when the material reaches the topological transition temperature, it is potentially ready to flow. However, flow is restricted by a frozen segmental motion of the material in the glassy state. As soon as the T_g is reached, segmental motion is triggered, translating to a rapid bond exchange, initially following William–Landel–Ferry (WLF) behavior, and then adjusting to Arrhenius behavior in quick succession, as shown in **Figure 11b**. The type of behavior can be tuned to an extent, as T_v can be controlled by the catalyst type and concentration, while T_g is controlled by polymer composition.^[106] For high- T_g vitrimers, T_v is of little practical interest since the bond exchange is frozen by slow segmental motion below T_g ,^[187] and thermal reprocessing requires a very high temperature to achieve.

Vitrimerization is an attractive route for thermoset reprocessing. This is because apart from the simplicity of reprocessing, dynamic bond transfer of vitrimers ensures the preservation of network topology integrity, translating to mechanical property recovery, while the material undergoes a thermally activated stress relaxation. The concept enables thermoset recycling which is of great importance in the manufacturing and application of polymers to mitigate the environmental impact of disposal. The advantages of vitrimer over conventional thermosets, thermoplastics, and dissociative CANs are summarized in **Table 1**.

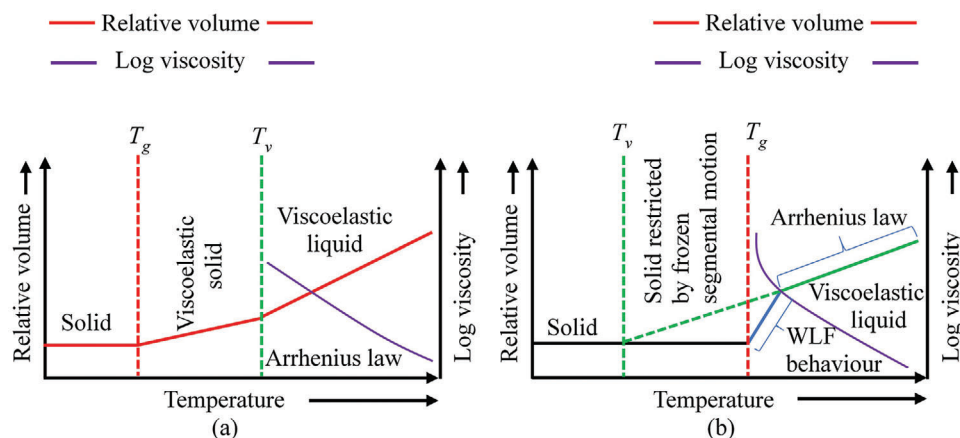


Figure 11. Plots of vitrimer's relative volume and Log viscosity versus temperature: a) $T_v > T_g$. b) $T_v < T_g$.

Table 1. Summary of advantages of vitrimer over other classes of polymers.

S/N	Characteristics	Thermoset	Thermoplastic	Vitrimer	Dissociative CAN
1	Mechanical properties	Stable	Unstable	Stable	Unstable
2	Solvent	Resistant	Soluble	Resistant	Soluble
3	High temperature	Resistant	Flows	Flows	Flows
4	Recyclability	Nonrecyclable	Recyclable	Recyclable	Recyclable
5	Repairability	Unrepairable	Repairable	Repairable	Repairable
6	Reshapability	Unreshapable	Reshapable	Reshapable	Reshapable
7	Weldability	Nonweldable	Weldable	Weldable	Weldable
8	Crosslink density	Constant	No crosslink	Constant	Compromizable

3.2. Dynamic Bond Exchange Mechanisms in Vitrimer Systems

Various chemistries can produce associative CANs, including transesterification, imine bond, disulfide exchange, transamination of vinylogous urethanes, diketoenamine transamination, transcarbamylation, transalkylation of sulfonium salts, siloxane-silanol exchange, olefin metathesis, transcarbonation, and silyl ether exchange. Each of these bond transfer mechanisms is reviewed in the following sections with examples of their applications to the vitrimerization of resin systems. This aims at uncovering potential reactions relevant to benzoxazines, with an established mechanism leading to dynamic topological transitions. These can serve as the basis for future research on benzoxazine-based vitrimeric systems.

3.2.1. Transesterification Exchange Chemistry

Transesterification is an equilibrium isodesmic exchange reaction in which an ester and alcohol are transformed into another ester and another alcohol via an alkoxy chain interchange. Various catalysts—such as organic bases, inorganic salts, acid catalysts, amine catalysts, Lewis acids, alkoxide catalysts, titanium tetraalkoxide catalysts, and organotin catalysts—are used to control transesterification reactions.^[345,346] The transesterification exchange mechanism is shown in **Figure 12**.

Transesterification is employed to synthesize the first known vitrimer, utilizing a Lewis acid catalyst—zinc acetate—in an

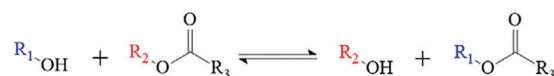


Figure 12. Transesterification exchange mechanism.

epoxy system involving diglycidyl ether of bisphenol A (DGEBA) and a mixture of fatty dicarboxylic and tricarboxylic acids.^[28] Transesterification is widely applied in various resin systems for matrix vitrimerization.^[41,45,51,115,188,255,332,336,346–356] Since benzoxazine polymerization is autocatalyzed, exchange chemistry not requiring catalysis may well be the best strategy for its vitrimerization. In this regard, catalyst-free transesterification-enabled polybenzoxazine vitrimers with moderate T_g (79–125 °C), depending on the combining ratio of the precursors, are developed, incorporating tertiary amines and hydroxyl groups in the polymer chain since tertiary amines can catalyze transesterification reactions.^[255]

3.2.2. Imine Bond Exchange Chemistry

Imines contain a nitrogen-carbon double bond in which the nitrogen has a lone pair of electrons and is bonded to either an organic group, in which case the molecule is a Schiff base or to a hydrogen atom resulting in a non-Schiff base imine. Imine bonds—usually formed from the condensation reaction of aldehydes and amines—participate in dynamic exchange reactions

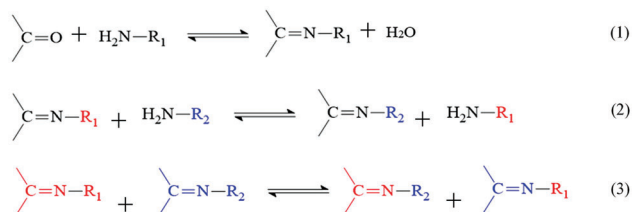


Figure 13. Equilibrium processes of imine bond chemistry.

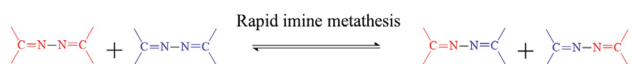


Figure 14. Mechanism of transimination (imine metathesis) using 1,2-di(propan-2-ylidene) hydrazine moiety of a polyimine network.

in one of three equilibrium processes: dissociative imine hydrolysis/condensation (reaction with water), associative imine-amine transamination, and associative imine-imine exchange (imine metathesis or transimination).^[46,47,50,186,357–359] The three equilibrium processes are represented in **Figure 13**.

Imine dynamic chemistry is mainly exploited using dissociative imine hydrolysis.^[186] This is the case with a chemically degradable vitrimer-like polyurethane network with good antibacterial ability exploiting imine bond exchange for its reprocessability.^[360] However, for true vitrimers involving imine bonds, imine-amine transamination or imine-imine exchange

dominate, since vitrimers undergo associative network topology rearrangement. The application of imine chemistry in vitrimeric systems is attractive, partly due to the versatility of potential imine-containing CANs made possible by the diversity of commercially available aldehydes and amines,^[46] and partly because, unlike transesterification reactions, imine bonds do not require the use of catalysts to undergo intermolecular exchange, as they are weak covalent bonds.^[43,46,50,326,344,357,361–373] The mechanism of transimination is illustrated in **Figure 14**. The associative dynamic imine chemistry—through one or both of imine-amine transamination and imine metathesis—is applied to develop a broad range of vitrimeric systems for industrial application.

A Schiff base precursor, Tris(4-formyl-2-methoxyphenyl) phosphate, is synthesized through a typical condensation reaction between lignin-derived vanillin and phosphorus oxychloride and cured with 4,4-diaminodiphenylmethane (MDA), 4,4-diaminodicyclohexylmethane (PACM), or hexamethylenediamine (HMD) to produce malleable thermosets (Schiff base CANs) as shown in **Figure 15**. The thermosetting material exhibits rapid processability and high monomer recovery upon treatment with a solution of tetrahydrofuran, hydrochloric acid, and deionized water. The material also exhibits permanent shape changeability and outstanding fire retardance.^[359] Other material properties include activation energy of bond exchange ranging from 49 to 81 kJ mol^{−1}, high *T_g* of about 180 °C, tensile strength of about 70 MPa, and tensile modulus close to 1.9 GPa. Stress relaxation for this material is completed within 2–10 min at 180 °C.

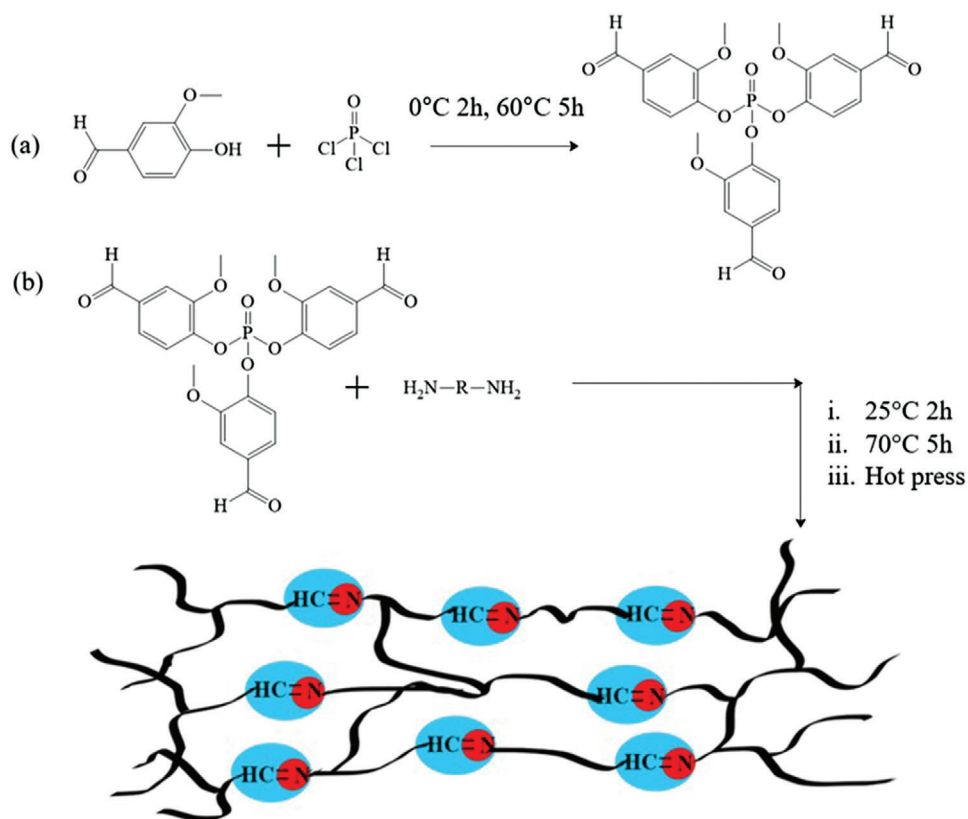


Figure 15. Schematic for the synthesis of a renewable Schiff base CAN. a) Synthesis of Tris(4-formyl-2-methoxyphenyl) phosphate. b) Preparation of Schiff base CAN.^[359]

Dynamic self-healing imine bond vitrimers exhibit tensile strength and elongation at break recovery up to 71–73%, through imine metathesis after three hot-pressing cycles,^[368] elongations at break ranging from 21% to 24% with Young's modulus from 4.4 to 5.1 MPa, and strength ranging from 0.69 to 0.73 MPa, after successive recycling,^[326] high T_g (172 °C) with a tensile strength of 81 MPa, modulus of 2.1 GPa, high thermal stability ($T_{d5\%} = 323$ °C) and elongation at break of 15%,^[43] T_g exceeding 120 °C with tensile strength and Young's modulus above 60 and 250 MPa, respectively,^[46] and T_g of 56 °C with fast bond exchange at 80 °C.^[364] Other vitrimers based on imine bond include biobased polyimine elastomeric vitrimers exploiting the reaction between di- and trifunctional polyether amines and a furan-based dialdehyde,^[358] and an aldehyde group-terminated polybutadiene rubber (APB) with different molecular weights crosslinked with tris(2-aminoethyl) amine via imine bond linkages.^[373]

3.2.3. Disulfide Metathesis

Polymer networks endowed with disulfide bonds normally undergo catalyst-free reversible disulfide metathesis when exposed to an appropriate stimulus such as heat or light,^[39,374–382] due to the low energy barrier needed to achieve reversible simultaneous breaking and formation of S–S bonds.^[383] The process may involve either of or both dissociative and associative pathways, depending on the prevailing conditions and patterns of substitution involved.^[186] The network is a vitrimer only when the bond exchange is solely associative. The disulfide bond is suitable for the design of materials exhibiting good shape-memory^[325] and self-healing at moderate temperatures,^[375] as well as recyclability with the retention of mechanical properties.^[384,385]

The effects of network crosslinking density and chain rigidity, and mobility on the self-healing characteristics of an adhesive epoxy polysulfide thermoset material (EPS25 and EPS70) were demonstrated,^[386] indicating that apart from being deployable for self-healing applications, disulfides do not significantly affect the thermal stability of resins,^[376] neither do they have a deleterious effect on mechanical properties,^[37] as the material exhibits full recovery of mechanical integrity by re-establishing cohesive as well as adhesive properties after 10 cycles of healing involving thermal treatment at 100 °C.

An isosorbide-derived epoxy (IS-EPO) reacts with 4,4'-disulfanedioldianiline (MDS) to yield MDS-EPO vitrimer, which shows fast stress relaxation, good recycling, reprocessing, and controllable shape memory, unlike another IS-EPO cured with 4,4'-methylenedianiline (MDA), a traditional curing agent for epoxy.^[34] The glass transition temperature of the MDS-EPO vitrimer is 41.4 °C, and its tensile strength is 11 MPa. The vitrimer (Figure 16) exhibits thermal stability with an onset degradation temperature of 270 °C, which is far above the reprocessing temperature of 100 °C.

The dynamic character of the disulfide bond is further demonstrated by comparing two similar monomers of polyurethane networks consisting of castor oil, isosorbide, and hexamethylene diisocyanate with a poly(urethane urea) composed of castor oil, isosorbide, hexamethylene diisocyanate, and 4-aminophenyl disulfide prepared under the same experimental conditions.^[102]

The difference between the two prepolymers is that the latter contains 4-aminophenyl disulfide, while the former does not. The permanently crosslinked polyurethane cannot be reprocessed, while poly(urethane urea) can be reprocessed with full recovery of mechanical properties due to the network topology rearrangement resulting from associative dynamic disulfide exchange. In a related study, it is demonstrated that upon the withdrawal of isosorbide from the reaction system, the mechanical properties of the poly(urethane urea) can be controlled by varying the 4-aminophenyl disulfide content and by manipulating molar ratios of relevant functional groups.^[103] Therefore, the tensile strength, Young's modulus, and elongation at break of poly(urethane urea)—composed of castor oil/4-aminophenyl disulfide at a weight ratio of 7:3—increased by 11.7, 2.7, and 5.2 times, respectively, compared to the control, castor oil-based poly(urethane) without 4-aminophenyl disulfide. The higher the disulfide content, the faster the stress relaxation is due to the increase in exchangeable disulfide linkage. Thus, the disulfide bond transfer mechanism is a promising chemistry for the synthesis of advanced benzoxazines.

A self-healing bis-disulfide bond-enabled vitrimeric epoxy resin ($T_g = 133$ °C) is successfully synthesized by the reaction of a difunctional epoxy monomer containing disulfide bonds and 4-aminophenyl disulfide.^[35] The self-healing matrix (Figure 17) can be doped with recoverable conductive carbon nanotube-polypyrrole fillers to enhance the mechanical properties of the epoxy vitrimer resin, giving rise to a nanocomposite material reprocessable at 180 °C.^[35] The stress relaxation time decreases from 3 h at 130 °C to 9 s at 200 °C without a catalyst, following an Arrhenius temperature dependence of viscosity with low activation energy. The stress relaxation time is lowered by increasing the density of disulfide bonds in the epoxy resin while the thermomechanical properties of the dynamic epoxy network remain unaffected. The dynamic bond results in unique self-healing and processing properties of the epoxy. Thiols can degrade the dynamic epoxy network by reducing disulfide bonds. This reaction is exploited in recovering the nanofillers. The composite material can be dissolved in dimethylformamide solution of dithiothreitol at 50 °C for 24 h to recover the filler. The material has thermal stability with a degradation temperature of 275 °C, which is 95 °C above the reprocessing temperature. A similar study that employed disulfide bond-enabled epoxy vitrimer to develop a graphene oxide epoxy vitrimer nanocomposite reported a catalyst-free strategy where the nanofillers enhance self-healing properties, including the shape memory and flexural strength of the materials.^[325] From these results, it is envisioned that potential high-performance disulfide-enabled polybenzoxazine vitrimers would feature highly attractive characteristics.

Added to the advantage of operating catalyst-free, dynamic disulfide exchange is preferred over transesterification for faster stress relaxation, as evidenced by a self-healing recyclable dual dynamic exchange epoxy vitrimer exploiting the synergistic effect of disulfide metathesis and carboxylate transesterification to achieve rapid stress relaxation and moderate malleability.^[188] Vitrimeric systems governed solely by dynamic disulfide metathesis exhibit topology transitions below their glass transition.^[34,39,159,188,325,376,387] This allows fast stress relaxation and ease of reprocessability of thermosets, thus underscoring

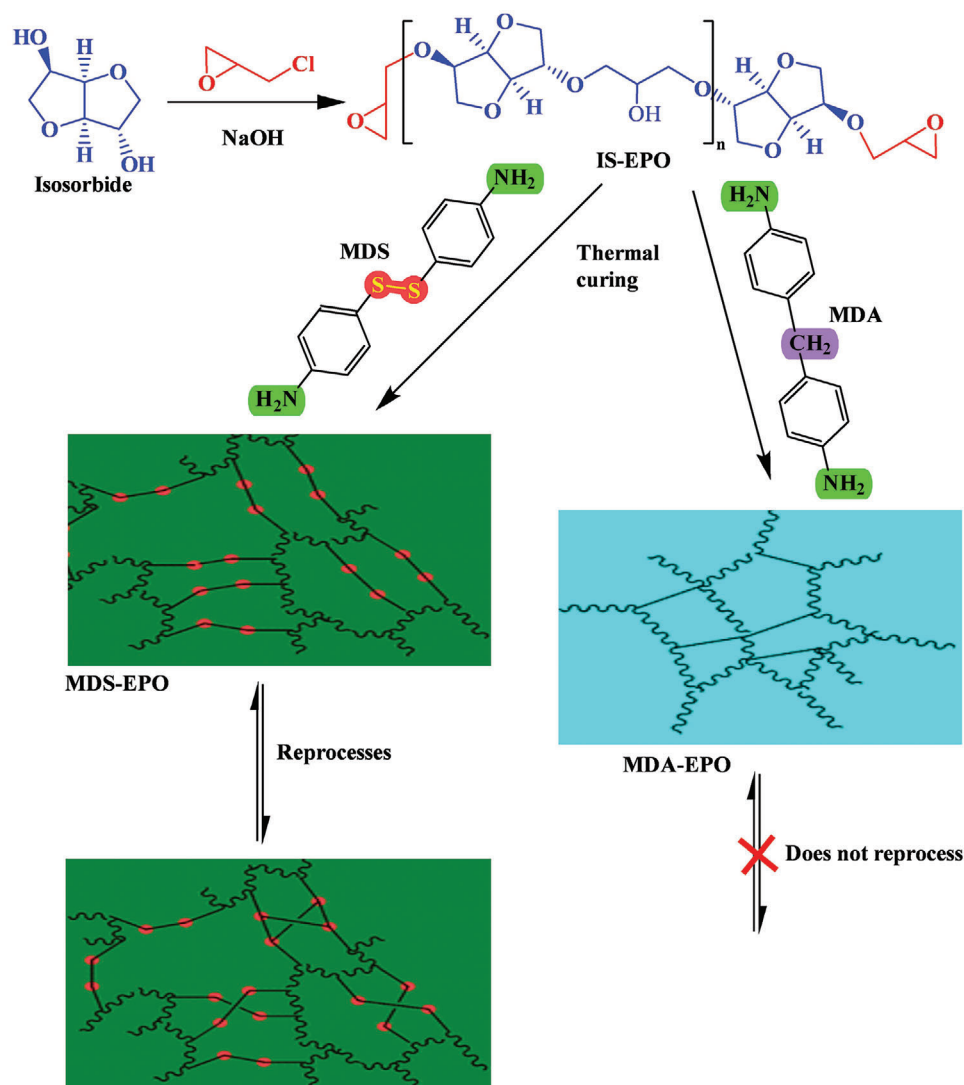


Figure 16. Synthetic route of isosorbide-derived epoxy (IS-EPO).^[34]

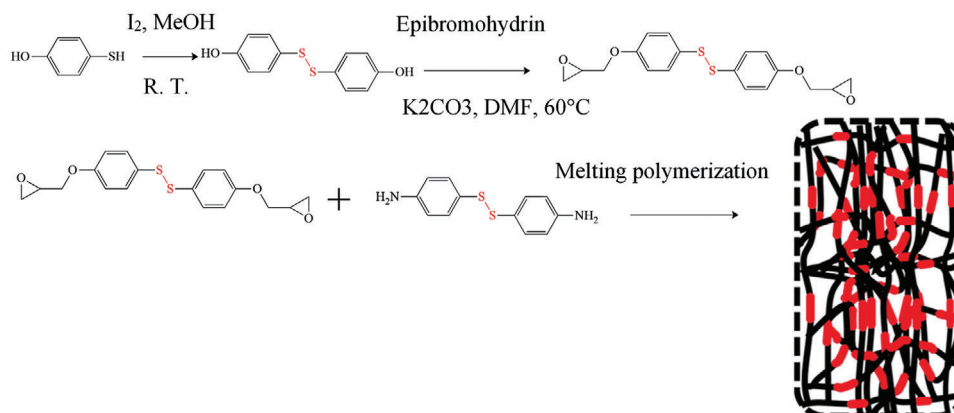


Figure 17. Schemes for the synthesis of bis-disulfide bond dynamic epoxy resin.^[35]

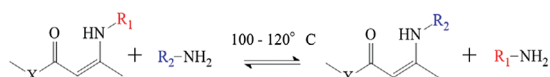


Figure 18. Transamination exchange of vinylogous urethanes and amides.^[388]

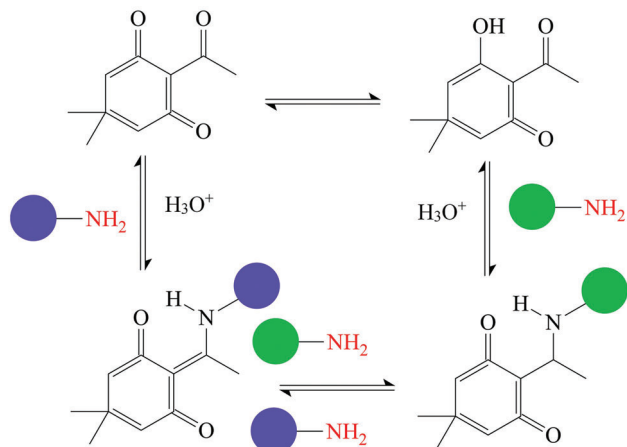


Figure 19. Transamination involving reversible dynamic covalent diketoenamine bonds.^[390]

dynamic disulfide metathesis as a simple and efficient catalyst-free bond transfer mechanism for vitrimers.^[343] The application of dynamic disulfide exchange reaction in benzoxazine vitrimerization is very attractive due to the disulfide bond catalyst-free fast exchange reaction on one side and its self-healing and shape memory properties on the other side.

3.2.4. Transamination

Amine-amine exchange reactions are applied in vitrimeric systems. One such formulation, the first catalyst-free vitrimer, exploits the condensation reaction between acetoacetates and amines to yield poly(vinylogous urethanes) capable of reshuffling their network topology via an associative transamination.^[388] The transamination reaction is shown in **Figure 18**. The group labeled X represents either a vinylogous urethane (X = O) or a vinylogous amide (X = CH₂). Both vinylogous urethanes and vinylogous amides can undergo catalyst-free associative dynamic transamination at elevated temperatures.^[388] Other vitrimers based on transamination of vinylogous urethanes can be synthesized.^[84,389] Transamination exchange chemistry has also been applied to diketoenamine bonds, yielding closed-loop recycling of processable thermosets adaptable for high-performance dynamic covalent polymers involving both aliphatic and aromatic amine monomers.^[390] This is illustrated in **Figure 19**. Apart from the amine-amine exchange and diketoenamine bond transfer, transamination also manifests as one of the three equilibrium processes of imine bond exchange known as imine-amine transamination. In general, transamination is an appropriate exchange chemistry for the vitrimerization of benzoxazines due to the amine functional group derivable from amine and phenolic precursors of potential benzoxazines.

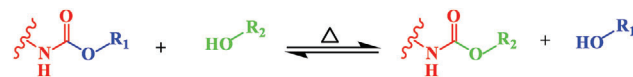


Figure 20. Transcarbamoylation in polyhydroxyurethanes.^[100,399]

3.2.5. Transcarbamoylation Exchange

Transcarbamoylation is the transfer of the carbamoyl moiety from one molecule to another, arising from the carbamate-only bond exchange which is generally applicable to polyurethanes.^[391] The mechanism for carbamate bond exchange depends on the nature of the polymer network^[100] and the presence of a catalyst.^[392] Some transcarbamoylation occurring in polyurethane CANs operate via the dissociative mechanism,^[393–396] due to the dissociative reaction of urethane bonds which normally requires a catalyst,^[392] while others operate via the associative mechanism^[101,397,398] often requiring no catalyst. Concurrent associative and dissociative dynamic chemistry due to the synergistic effect of associative transcarbamoylation and dissociative reversible cyclic carbonate aminolysis has been reported for polyhydroxyurethane networks.^[399] Such a network is not a true vitrimer due to the dissociative component of the dynamic chemistry.

A recently reported polybenzoxazine-polyurethane vitrimer featuring transcarbamoylation undergoes catalyst-free associative bond exchange.^[400] For a polybenzoxazine incorporating carbamate chemistry to be categorized as a vitrimer, the dynamic bond exchange must strictly follow the associative mechanism. The potential of transcarbamoylation for the design of new functional polymers has not been fully exploited. The excellent properties and molecular design flexibility of benzoxazines, already highlighted, place them at the forefront of all candidates in this regard. Transcarbamoylation exchange is shown in **Figure 20**.

3.2.6. Transalkylation Exchange Chemistry

Transalkylation exchange chemistry is applied to polymer science for the design of vitrimers and dissociative CANs. Of the four reported transalkylation types,^[27] only the catalyst-free S_N2-type transalkylation between trialkyl sulfonium salts and thioethers (sulfides) proceed through the associative pathway. Such transalkylation is sub-grouped as transalkylation of sulfonium salts and is implemented for poly(thioether) networks^[401] with appreciably higher bond exchange activation energy (108–113 kJ mol^{−1}) compared to catalyst-free transamination of vinylogous acyl compounds (59 kJ mol^{−1}).^[388] Transalkylation of sulfonium salts is proposed as a useful strategy for the recycling of industrial scrap rubber cured with sulfur.^[402] Other subgroups of transalkylation, namely trans-N-alkylation of pyridiniums,^[335,403] trans-N-alkylation of anilinium salts, and trans-N-alkylation of 1,2,3-triazolium salts,^[404] all proceed via the dissociative pathway. Therefore, materials incorporating these types of transalkylation are not vitrimers. In fact, 1,2,3-triazolium-based poly(ionic liquid) is viewed as the missing link between vitrimers and dissociative CANs due to their versatility which enables their tunability between completely depolymerizable dissociative CANs to CANs whose rheological characteristics are indistinguishable from vitrimers.^[404]

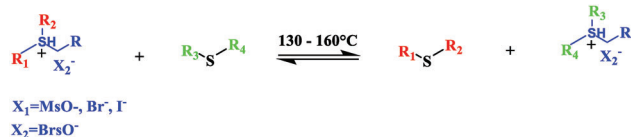


Figure 21. S_N2 transalkylation between trialkyl sulfonium salts and thioethers used for the design of poly(thioether) vitrimer networks.^[401]

An exchange chemistry capable of fast stress relaxation in the absence of a catalyst, transalkylation can be extended to a variety of thermosets, including benzoxazines to achieve functional vitrimers. To achieve a benzoxazine vitrimer design through transalkylation, systems capable of yielding dissociative CANs as detailed herein, should be avoided. The mechanisms for the transalkylation of sulfonium salts and trans-*N*-alkylation of 1,2,3-triazolium salts are shown in **Figures 21** and **22**, respectively.

3.2.7. Olefin Metathesis

Olefin metathesis is widely used in ring-opening metathesis polymerization due to the ease with which it forms carbon-carbon bonds.^[405–408] It is rarely applied to polymer synthesis because cross-metathesis lacks internal driving force. However, no driving force is required for network topology rearrangements involving functional group equilibria. Thus, olefin metathesis is an attractive method for thermoset vitrimerisation,^[186] as demonstrated using cross-linked polybutadiene networks incorporating second-generation Grubbs catalyst.^[78,79] The selection of Grubbs catalysts in preference to the more common metathesis catalysts is supported by the fact that they exhibit superior air and moisture stability and are generally functional group-compatible.^[409] The ambient temperature exchange reaction of olefin bonds can be exploited for possible self-healing applications.

Furthermore, olefin bonds can be used to increase the crosslinking density of polybenzoxazines, as they participate in coreaction with the benzoxazine functionality.^[156] However, compared to more straightforward imine, amine, or disulfide chemistry, applying olefin metathesis toward benzoxazine vitrimerization may be hindered by cost, dependence on catalyst, and creep associated with olefin-enabled networks.^[186] These facts are summarized in **Table 2**.

Table 2. Advantages and disadvantages of olefin metathesis^[156,186].

S/N	Advantages	Disadvantages
1	Ambient temperature bond exchange	Cost: Expensive
2	Self-healing application	Catalytic, risk of catalyst toxicity
3	Compatible with benzoxazine chemistry	Network prone to creep

3.2.8. Transcarbonation Exchange

Polycarbonates, which are organic compounds containing the carbonate functional group, generally undergo catalytic transcarbonation exchange reactions with free hydroxyl groups at elevated temperatures, similar to transesterification exchange.^[410–414] This concept is extended to polycarbonate vitrimers exhibiting titanium (IV) alkoxide-catalyzed stress relaxation at elevated temperatures.^[116] The associated chemically recyclable and acid-degradable vitrimer show full reprocessability without compromising material chemical and mechanical integrity, confirming the occurrence of topology rearrangement without depolymerization. The topology of the crosslinked polymer and the transcarbonation exchange is shown in **Figure 23**. This exchange chemistry may not be optimal for benzoxazine vitrimerization since it relies on catalysis to achieve stress relaxation in the vitrimer.

3.2.9. Siloxane-Silanol Exchange

Polydimethylsiloxanes are capable of dynamic siloxane rearrangement via acid or base-catalyzed stress relaxation.^[415] This is the basis of siloxane equilibration as a self-healing mechanism for polymers. The siloxane-silanol bond exchange has been demonstrated in a material formulated by ring-opening copolymerization of octamethylcyclotetrasiloxane and bis(heptamethyl cyclotetrasiloxanyl)ethane initiated by tetramethylammonium silanolate, which yields cross-linked polydimethylsiloxane (PDMS) networks with ethylene bridges and highly reactive anionic species of silanolate end groups.^[416] The material heals by siloxane equilibration, and the original mechanical strength of the silicone sample is fully restored. Polydimethylsiloxane-based vitrimers incorporating ex-

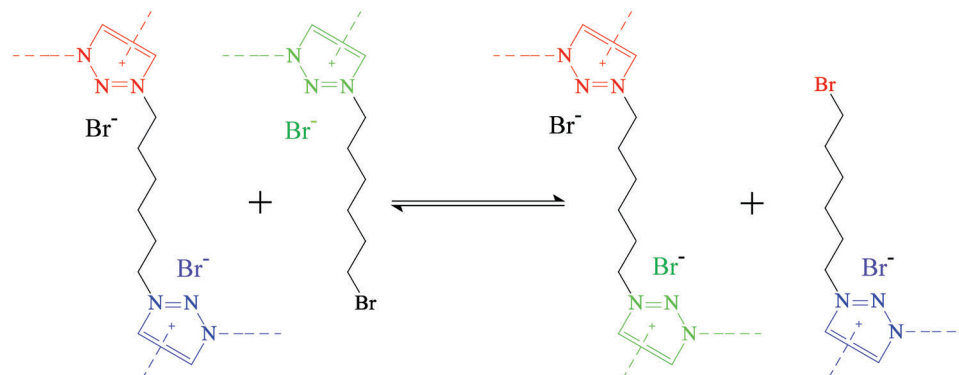


Figure 22. Transalkylation reaction mechanism of triazolium bond.^[404]

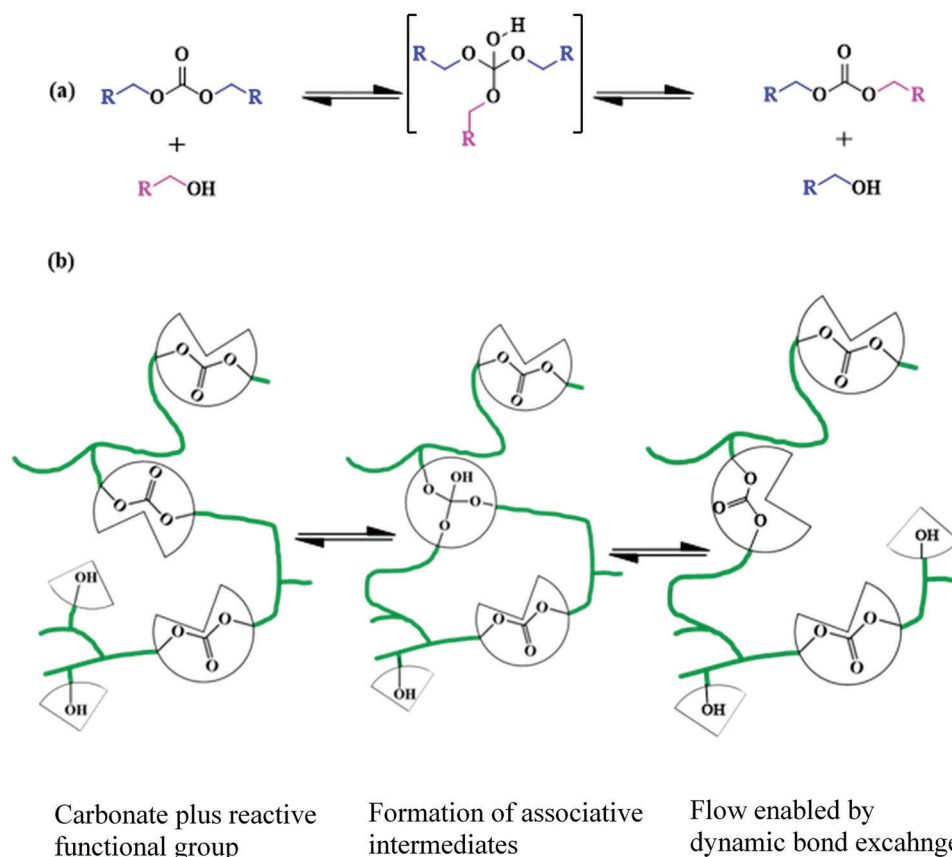


Figure 23. a) Transcarbonation exchange reaction between a hydroxyl nucleophile and a carbonate by the formation of an associative intermediate and the release of the exchanged carbonate and hydroxyl group. b) The topology of a cross-linked polymer network containing carbonates and hydroxyls is adjustable via transcarbonation exchange reactions.^[116]

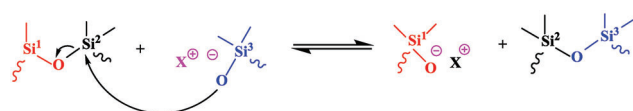


Figure 24. Siloxane-silanol exchange through addition and elimination of silanolate anion.^[186]

cellent performance can be synthesized.^[322,417–419] The siloxane-silanol exchange reaction is shown in **Figure 24**.

Siloxane-silanol exchange can be incorporated in benzoxazine synthesis with obvious cost implications since it involves catalysis for the polymer to relax stress. The major issue with silanolate anion systems is that they are susceptible to thermal degradation at 150 °C.^[186] However, incorporating siloxane-silanol exchange into thermostable benzoxazine systems needs to be explored as this may provide a good compromise between the high temperature needed for high-performance benzoxazine malleability on the one side and thermal degradation of the silanol system on the other side.

3.2.10. Silyl Ether Exchange

Bis-silyl ethers are identified as appropriate crosslinkers in vitrimer chemistry. They are used for crosslinking pendant

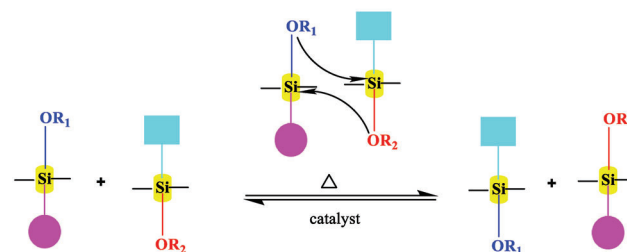


Figure 25. Schematic representation of silyl ether metathesis.^[421]

hydroxyl group-functionalized polystyrene vitrimer, thermally stable up to 350 °C,^[420] and for the development of thermostable polyethylene-co-vinyl alcohol vitrimers based on silyl ether metathesis, with degradation temperature of 427 °C and increased creep resistance^[421] (**Figure 25**). Silyl ethers have also been used in the synthesis of crosslinked vinylogous urethane polyethylene in reactive extrusion, yielding thermosets that exhibit stress relaxation by a heat-induced topological transition which enhances their reprocessability, recyclability, and hydrolytic stability.^[323,329] An extension of silyl ether metathesis to the vitrimerization of benzoxazines, is possible and would potentially yield a thermally and mechanically robust polybenzoxazine for high-temperature applications.

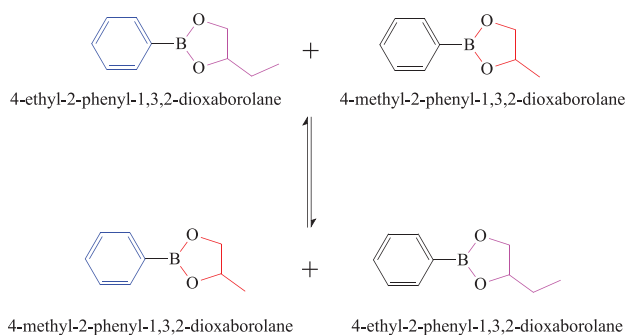


Figure 26. Schematic representation of dioxaborolane metathesis.

3.2.11. Dioxaborolane Metathesis

The reversible interchange of moieties connected by the strong boron–oxygen (B–O) bonds of boronic ester groups (**Figure 26**) is exploited to formulate vitrimers from polymers containing carbon–carbon single bonds in their backbone.^[422] The vitrimer can undergo catalyst-free dioxaborolane metathesis at low temperature (60 °C). Such exchange has recently been employed in polydioxaborolane vitrimer networks^[423] with topology freezing transition estimated to be below the glass transition, enabling fast dioxaborolane metathesis immediately above the glass transition.

In an earlier study to synthesize some dioxaborolane-enabled polybutadiene vitrimers, topology transitions have also been found to occur below glass transitions.^[80] Such chemistry yields vitrimers that exhibit improved creep resistance at service temperatures and desirable flow properties at processing temperatures,^[80] as well as outstanding thermomechanical and chemical resistance, and can be applied to poly(methyl methacrylate), polystyrene,^[422] and high-density polyethylene.^[422,424]

4. Vitrimerization of Benzoxazines

The versatility of benzoxazines implies the possibility of sustainable, low-cost, low-to-moderate-to-high glass transition vitrimeric formulations. To the best of our knowledge, **Table 3** summarizes the literature on benzoxazine vitrimer to date.

Self-healable, malleable, and reprocessable vitrimeric polybenzoxazines were pioneered by using cardanol, a cashew nut shell oil bio-phenolic component, and 4-aminophenyl disulfide

to formulate main-chain benzoxazine monomer.^[159] The synthesis route, polymerization, and reprocessability of the material by thermally activated topological rearrangement are illustrated in **Figure 27**. The use of a bifunctional amine with a disulfide group has the advantage of directly introducing dynamic exchange into the polybenzoxazine without requiring an extraneous vitrimerizer. Thus, the disulfide diamine moiety of the benzoxazine monomer performs two functions: i) the amine group of the monomer forms a new chemical bond with the phenolic group of a neighboring monomer upon oxazine ring-opening, retaining the chemical identity of its other two bonds; and ii) the disulfide bond is responsible for the disulfide metathesis that confers vitrimeric character on the material.

The polybenzoxazine vitrimer formulated from cardanol and 4-aminophenyl disulfide is not relevant to high-temperature applications as its glass transition temperature is 40 °C. The low T_g is due to the decreased crosslink density attributed to the dilution effects of cardanol resulting from the C_{15} alkyl side chain. Using other phenolic precursors with shorter or no side chains in the place of cardanol could potentially yield disulfide-based polybenzoxazine vitrimer systems with robust thermomechanical properties. The dynamic bond exchange is indicated by a fast stress relaxation of 18 s at 120 °C and low activation energy (64.5 kJ mol^{−1}). Due to its healable adhesive properties, this polybenzoxazine vitrimer is proposed as a potential 3D printing ink. Other properties of this benzoxazine system include monomer melt temperature of 83 °C, polymer topological transition at −8.5 °C, and polymer initial degradation temperature of 252 °C.

Reacting 4,4 Bis(hydroxyphenyl) valeric acid with polyethylene glycol in the presence of para-toluene (p-TSA) sulfonic acid monohydrate as a catalyst, a quadri-telechelic phenol-terminated polyethylene glycol diphenolic acid (PEG-DPA) is synthesized via a solvent-free Fischer esterification and Mannich-like closure. The PEG-DPA is reacted with paraformaldehyde, monoethanolamine and furfurylamine to yield a quadri-telechelic benzoxazine-terminated polyethylene glycol monomer containing ester bonds and aliphatic hydroxyl groups.^[255] Various formulations based on the PEG-DPA system range from monoethanolamine-only-containing monomers (**Figure 28**) to prepolymers containing various weight fractions of monoethanolamine (mea) and furfurylamine, featuring monomer short gelation time (145 s at 140 °C). The vitrimers exhibit self-healing, recycling, reshapability, and fast stress relaxation (116 s at 170 °C) enabled by a self-catalyzed dynamic transesterification with an activation energy of the order of 106–154 kJ mol^{−1}. Other

Table 3. Literature of benzoxazine vitrimers to date.

S/N	Dynamic bond exchange chemistry	Catalytic/autocatalytic	T_g [°C]	T_v [°C]	E_a [kJ mol ^{−1}]	$T_{d5\%}$ [°C]	T_{rep}^a [°C]	Stress relaxation	Refs.
1	Disulfide bond	Autocatalytic	40	−8.5	64.5	252	120	18 s [120 °C]	[159]
2	Transesterification	Autocatalytic	−34–125	88	106–154	—	170	116 s [170 °C]	[255]
3	Transcarbamoylation	Autocatalytic	55	—	92	—	130	600 s [130 °C]	[400]
4	Transesterification	Autocatalytic	143–193	—	126	244–304	175	300 s [180 °C]	[425]
5	Dioxaborolane metathesis	Autocatalytic	29	—	50–64	>260	35–100	—	[426]
6	Boronic ester	Catalytic	—	—	60.6	—	—	—	[427]
7	Boronic ester	Autocatalytic	224	—	—	325	—	—	[428]

^{a)} T_{rep} [reprocessing temperature].

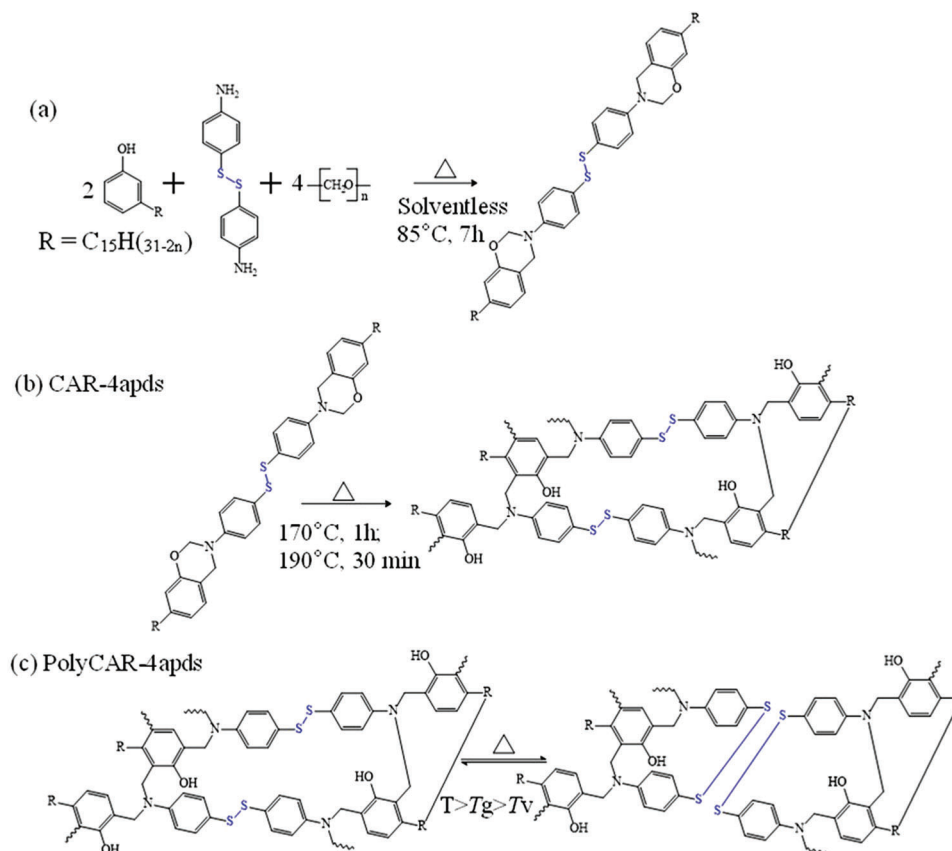


Figure 27. Benzoxazine vitrimer based on cardanol and 4-aminophenyl disulfide. a) Synthetic route. b) Polymerization conditions. c) Simplified cross-linked network and mechanism of chemical bond rearrangement upon heating.^[159]

reported properties of this vitrimeric benzoxazine include glass transition ranging between -34 and 125 °C and T_v of 88 °C for the vitrimer whose activation energy is 115 kJ mol $^{-1}$, only 9 °C higher than its T_g of 79 °C.

A polybenzoxazine-polyurethane vitrimer network endowed with carbamate bond can be derived from a solventless reaction between tyrosol, paraformaldehyde, and dodecylamine.^[400] The resin features monomer melt temperature of 125 °C, which would pose a processing challenge. The polymer features low cure glass transition (55 °C), low activation energy of transcarbamoylation (92 kJ mol $^{-1}$), accounting for full stress relaxation in 10 min at 130 °C with more than 90% recovery of tensile strength (11.7 – 10.2 MPa) and 80% strain recovery (from 51% to 41%). A vitrimeric character enabled by transcarbamoylation—a metathesis—would exhibit topological transition below its T_g . This is responsible for the low activation energy at temperatures above glass transition (110 °C and above), as the bond exchange for such vitrimer systems is known to be fast at temperatures immediately above the T_g .

A vitrimeric benzoxazine exhibiting high glass transition (143 – 193 °C) can be obtained by curing a di-telechelic benzoxazine-terminated isosorbide monomer formulated by a two-step procedure involving Fischer esterification and Mannich-like closure using isosorbide, 4-hydroxypropionic acid, paraformaldehyde, and various weight fractions of monoethanolamine and furfurylamine.^[425] This material is healable, chemically and me-

chanically recyclable, and degrades in acid and alkaline conditions while remaining stable in neutral pH conditions. It incorporates aliphatic hydroxyl and/or furan groups and exhibits furan ring-dependent glass transition, degradation temperature in the range of 244 – 304 °C, high char yield (31 – 47.3%), indicating fire retardant property and elastic modulus in the range of 3.5 – 4.1 GPa at 25 °C. The fully cured resin achieves topological transition via transesterification. The vitrimer containing 100% weight fraction of monoethanolamine with 0% furfurylamine features fast stress relaxation (300 s at 180 °C) with the activation energy of 126 kJ mol $^{-1}$ which slows down with furan content due to the addition of furfurylamine. These properties suggest that this benzoxazine vitrimer could be deployed for aerospace composites manufacturing.

A fully recyclable polybenzoxazine containing dioxaborolane bonds that enable moderate temperature fast healing (5 min at 100 °C) is synthesized by treating a thiol-endowed main-chain benzoxazine with 1,4-phenylenebisboronic acid and water in the presence of tetrahydrofuran.^[426] The material has T_g of 29 °C, low bond exchange activation energy in the range of 50 – 63 kJ mol $^{-1}$, and degradation temperature above 260 °C. This material exhibits an anti-bacterial behavior with an inhibition rate in the range of 95.6 – 99.98% and features good reprocessability and shape memory. By tailoring dioxaborolane content, the mechanical strength of this vitrimer can be controlled between stretchability and stiffness (elongation at break: over 58.7% ; tensile strength:

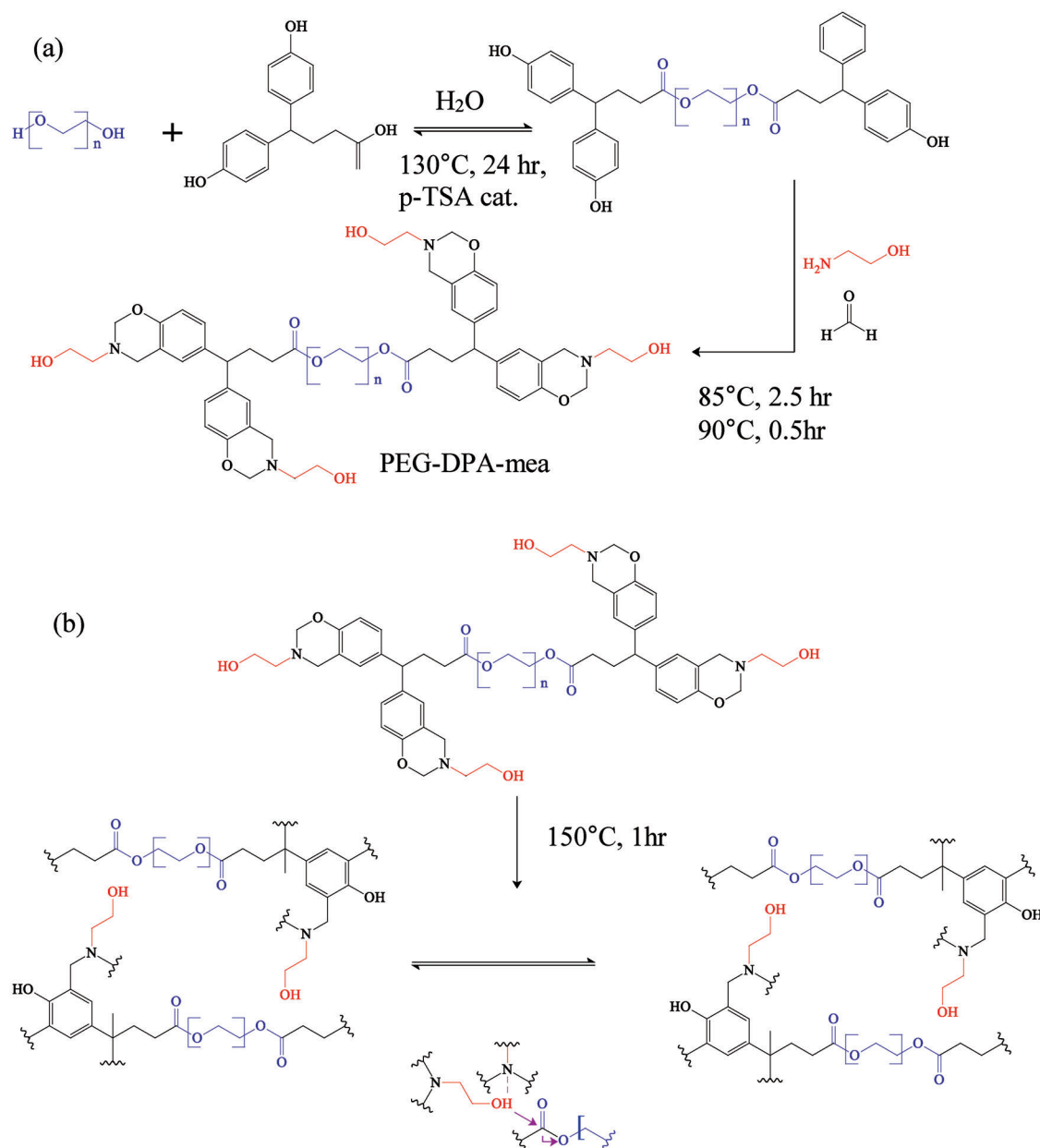


Figure 28. Benzoxazine vitrimer containing dynamic ester bonds.^[255] a) Synthesis route. b) Polymerization and reprocessing.

5.9 MPa). The material has uncompromised mechanical properties after multiple reprocessing times and fast healing with low activation energy, including topological transition enabled by dioxaborolane metathesis.

An organoboron-containing polybenzoxazine can be synthesized by treating a main chain benzoxazine monomer made from bisphenol A and poly(propylene/ethylene oxide) bisamine with phenyl boronic acid and casting in a mold.^[427] During cure, phenyl boronic acid reacts with phenolic -OH groups to form boronic ester, which then binds to the polybenzoxazine chain, added to Mannich bridge linkages and relatively weak boron-nitrogen bond present in the system (Figure 29). The presence of nitrogen-boron bond could speed up fast boronic ester exchange

reaction which could be either associative or dissociative depending on the favored reaction mechanism between:

- boronic ester hydrolysis to diol and boronic acid and re-esterification to reform boron-oxygen linkage—dissociative mechanism, leading to a dissociative CAN, and
- transesterification of the boronic ester with another neighboring hydroxyl—associative mechanism leading to a vitrimer.

Again, the bond exchange mechanism determines whether the material is a vitrimer. Two vitrimers based on two types of poly(propylene/ethylene oxide) bisamine exhibit self-healing at 110 °C for 5 h and at 160 °C for 5 h, respectively, with effective

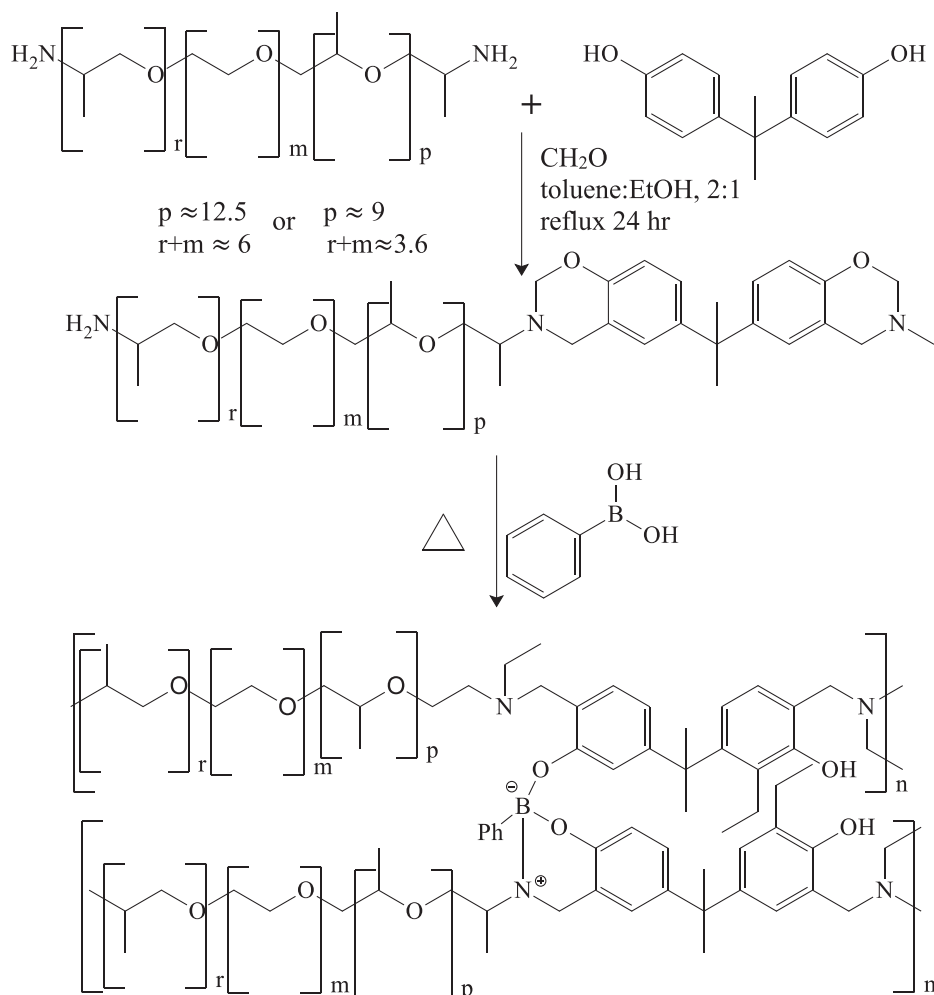


Figure 29. Synthesis of benzoxazine vitrimers based on two types of poly(propylene/ethylene oxide) bisamine and their simultaneous curing.^[427]

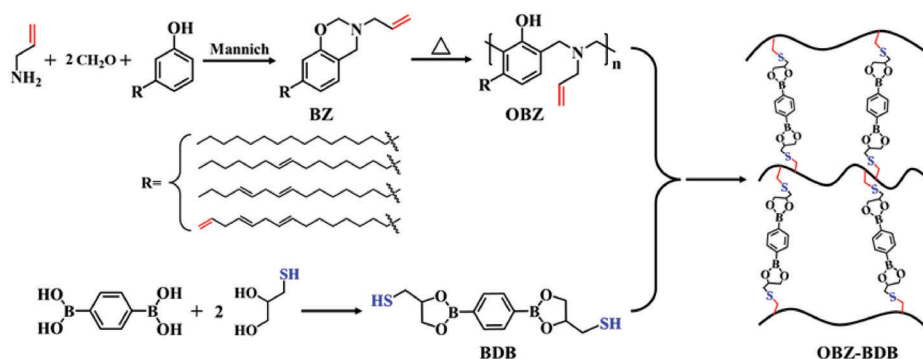


Figure 30. Synthesis and polymerization of OBZ-BDB. Reproduced with permission.^[428] Copyright 2022, Multidisciplinary Digital Publishing Institute.

recovery of mechanical properties (tensile strength: 60–98 MPa and Young's modulus: 4–6 GPa) after recycling.

The reaction of boronic ester crosslinker, 2,2'-(1,4-Phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane] (BDB) and a benzoxazine monomer made from cardanol and allylamine (OBZ) yields a boronic ester-enabled polybenzoxazine vitrimer (Figure 30).^[428] The vitrimer features a glass transition of 224 °C, degradation

temperature of 325 °C, and char yield of 30%, with over 80% and 75% retention of tensile strength and original elongation at break, respectively, after three reprocessing cycles. Also, the thermal properties are retained after three reprocessing cycles.

Polybenzoxazine vitrimer can be achieved by formulating a hybrid polymer which is essentially a blend of benzoxazine and other resin systems. For example, epoxies can copolymerize with

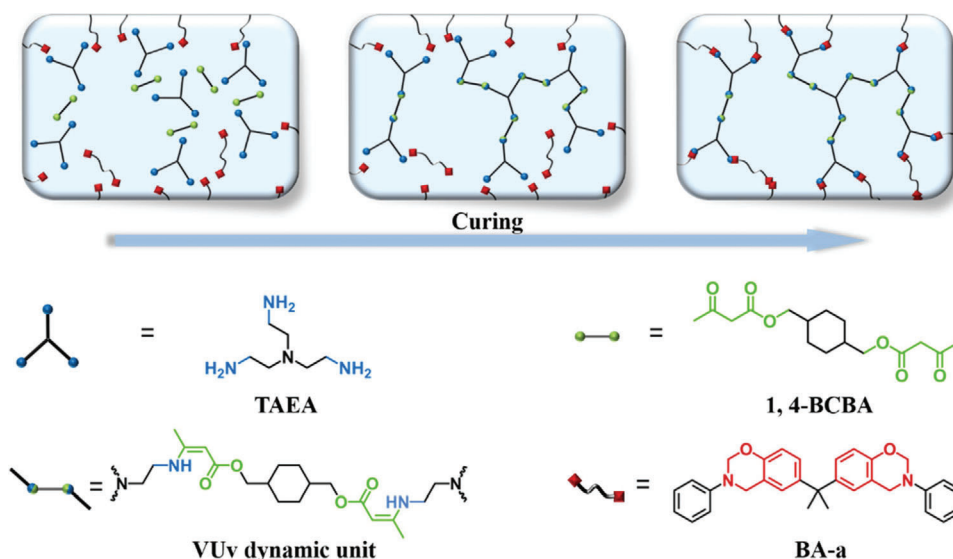


Figure 31. Curing process of benzoxazine modified with vinylogous urethane vitrimer. Reproduced with permission.^[430] Copyright 2022, American Chemical Society.

benzoxazines. Therefore, when an epoxy vitrimer copolymerizes with a benzoxazine, the resulting copolymer could feature some, if not all, of the vitrimeric properties of the original epoxy vitrimer. Some benzoxazines contain dynamic bonds, but they are not vitrimers due to the closeness of their T_g 's to their degradation temperatures, which does not provide a wide window for thermal healing, stress relaxation, or reprocessing without degrading the material. This is the case with benzoxazines containing disulfide bonds which are not vitrimers ($T_g = 250$ and 264 °C, while $T_{50\%} = 265$ and 270 °C, respectively).^[429] Copolymerizing these benzoxazines with a low T_g epoxy vitrimer could lower the overall T_g of the system by decreasing the crosslink density, while the degradation temperature remains high, thus providing enough window for a synergistic vitrimeric effect of the disulfide bond in the benzoxazine and the dynamic bond of the epoxy to be observed. A similar strategy was implemented from the design stage for vinylogous urethane vitrimers (VUVs) containing dynamic bonds and bisphenol A-aniline-based benzoxazine (BA-a), producing another vitrimer which is applicable to the fabrication of recyclable carbon fiber-reinforced composites (Figure 31).^[430] The T_g of the modified vitrimer (222 – 236 °C) is higher than that of the BA-a (204 °C) due to increased crosslink density but decreases with increasing VUV content due to local enrichment of the Vuv, which affects the crosslink density of the BA-a. The vinylogous urethane vitrimers are made from tris(2-aminoethyl) amine (TAEA) and 1,4-bis(hydroxymethyl) cyclohexane bis-acetoacetate (1,4-BCBA).

4.1. Catalytic and Catalyst-Free Benzoxazine Vitrimers

The majority of benzoxazine vitrimers feature autocatalytic dynamic bond exchange at elevated temperatures. Many associative dynamic bond transfer mechanisms governing vitrimer network topology rearrangement and material processability and reparability rely on the use of catalysts.^[104,116,431,432] This could be

a limiting factor of vitrimer application because if the catalyst concentration is not sufficient, the network topology reshuffling would not be effective.^[352] Moreover, incompatibility issues that may result from the use of a catalyst can lead to compromising the mechanical properties of the vitrimer, in addition to the risk of catalyst toxicity.^[433,434]

The development of catalyst-free vitrimers is key to avoiding the identified shortcomings that may be associated with catalyst-enabled vitrimers. Thus, robust catalyst-free vitrimers are currently receiving increased attention of researchers,^[44,352] and could play a role in the future of polybenzoxazine vitrimers.^[159] Based on this demand, imine bond, disulfide metathesis, transalkylation, transesterification, transcarbamoylation, transamination, and dioxaborolane bond transfer mechanisms are recommended. Among them, disulfide and dioxaborolane metatheses are the most efficient mechanisms for quick stress relaxation.

5. Concluding Remarks and Outlook

The high-level performance of benzoxazine systems, highlighted in this review, has raised the polymer chemistry and physics community's awareness of the prospects of polybenzoxazines replacing conventional resins in certain areas. In addition to this potential, extending the development toward vitrimerization of polybenzoxazines, to endow them with desirable functionalities, such as recyclability, weldability, self-healing, and shape memory, can lead to novel functional benzoxazine vitrimers capable of revolutionizing the polymer composite industry. Based on this motivation, this paper has reviewed the progress in benzoxazine research as well as in vitrimer chemistry, highlighting the vitrimerization of thermosetting resins, such as epoxies, polyurethanes, polyhydroxyurethanes, polyurethane urea, polycarbonates, and polyimides and identifying areas of potential crossover for the development of benzoxazine based vitrimers.

The various dynamic bond exchange mechanisms that lead to vitrimeric systems have been presented with specific examples of their applications. Advancing such chemistries toward the creation of high-performance polybenzoxazine vitrimers is a feasible path toward future developments. Furthermore, a suitable selection and incorporation of an appropriate bond exchange mechanism during benzoxazine monomer synthesis would endow vitrimeric polybenzoxazines with smart functionalities. The available literature shows that the disulfide and dioxaborolane metatheses are the most efficient bond exchange chemistries for catalyst-free stress relaxation at moderate temperatures and can endow polymers with effective self-healing and shape memory functionalities. Exploiting this property, together with the flexibility and compatibility of benzoxazine chemistry with biobased resources, would result in sustainable, versatile, high-performance benzoxazine vitrimers.

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F.I.A.: Funding acquisition, conceptualization, writing—original draft, writing—review and editing, visualization. V.K.T.: Conceptualization, supervision, writing—review and editing, visualization. A.A.S.: Conceptualization, supervision, writing—review and editing, visualization.

Conflict of Interest

The authors declare no conflict of interest.

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