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Vitrimers: Permanently crosslinked polymers with dynamic network topology

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ABSTRACT: The study of synthetic organic polymers rapidly expanded since Staudinger's recognition of the covalent structure of macromolecules. Today, these materials are far from just an academic concept—they are produced industrially and have become ubiquitous in everyday life because of their low cost and desirable physical properties. Nevertheless, a difficult choice between durability and reprocessability continues to hamper efforts to design synthetic organic polymers to be more recyclable. A new class of materials, vitrimers, has emerged as an intriguing approach to circumvent this tradeoff. Vitrimers are permanent networks of polymer chains connected via dynamic covalent bonds, which allow the network to change its topology while maintaining a constant number of chemical bonds at all temperatures. Characterized by both high mechanical performance and facile processing, vitrimers are well positioned to transition from academic labs to industrial production. The aim of this Trend article is to review the concept of vitrimers, describe their most unique properties, and present our outlook on outstanding challenges that must be met to realize vitrimers as a next generation solution for recyclable high performance materials.

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Abbreviations

T_g , glass transition temperature; T_m , melting transition temperature; K , thermodynamic equilibrium constant; k , rate constant; WLF model, Williams, Landel, and Ferry model; T_v , topology freezing temperature; TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene; HDPE, high density polyethylene; PMMA, poly(methyl methacrylate); CNT, carbon nanotubes; THF, tetrahydrofuran; DMA, dynamic mechanical analysis

1. Introduction

Since the seminal work of Hermann Staudinger, who first postulated the covalent structure of polymers,[1, 2] advances in polymer chemistry and physics have led to new fields and concepts with applications covering essentially all industrial sectors. The omnipresence of synthetic organic polymers in everyday life stems from their low cost and light weight, as well as their wide range of properties. Over the last century, chemists have developed numerous tools that allow for precise control over the size and dispersity of synthetic polymers, as well as their composition, functionality and topology, which in turn dictate their chemical, physicochemical and mechanical properties.[3-10]

A common classification of polymers is based on how they respond to heat, which is directly linked to the topology of the polymer chains. The first family is thermoplastics, which macroscopically flow like viscoelastic liquids when heated above the glass transition temperature, T_g (or the melting temperature, T_m , in the case of semi-crystalline polymers).[11-13] They are constituted of polymer chains that are not chemically connected to each other but have a sufficient molecular weight to be entangled. Their molecular mobility in the molten state permits them to be repeatedly melted and molded.[14] However, thermoplastics are not suited for applications requiring rubbery solids, dimensional stability at high temperature, or superior environmental stress cracking resistance.

To address these limitations, polymer chains can be covalently crosslinked to form thermosets, the second category of polymeric materials. The formation of the three-dimensional network suppresses polymer chain diffusion under the action of heat or a solvent, making thermosets inherently insoluble. Above the T_g , thermosets present a theoretically infinite rubbery plateau because they cannot flow and exhibit an elastic modulus that is a function of the crosslinking density. These characteristics enable thermosets to be useful for applications requiring creep resistance, solvent resistance, or high mechanical

strength, such as structural applications, coatings, adhesives, electronics and composites.[15] However, the topology of the network and the macroscopic shape of thermosets are "set" once they are cured, preventing them from being processed multiple times.[15, 16]

Difficult tradeoffs with respect to processability, durability, and recyclability thus beset the choice between using a thermoplastic or a thermoset for a given application. Motivated by both the intellectual challenge and societal demand for recyclable high performance materials, scientists have sought to marry the malleability of thermoplastics with the performance advantages of thermosets. The prevailing strategy is to create a network of polymer chains in which the crosslinks can be broken and reformed within a desired temperature window and using a triggered stimulus. The earliest examples are nanostructured thermoplastic elastomers that rely on phase separation to physically crosslink polymer chains,[17, 18] as well as polymers that feature polar or hydrogen-bonding groups in the main chain (*e.g.*, nylon).

This approach has been broadly expanded to supramolecular networks[19-21] containing non-covalent transient crosslinks that operate through hydrogen bonds,[22] π - π interactions[23] and metal complexation.[24] These interactions are described by a thermodynamic equilibrium constant K , which dictates the equilibrium between the associated and the dissociated forms and therefore the connectivity of the system. Such systems are also characterized by rate constants for the bond formation and rupture of the transient links, which relates to the dynamicity of the system. The thermodynamic and kinetic constants are temperature dependent and both greatly impact the viscoelastic properties of reversible networks. Supramolecularly crosslinked materials tend to have K values that strongly decrease with temperature as well as high rates of exchange, which are not ideal for applications that demand creep resistance.

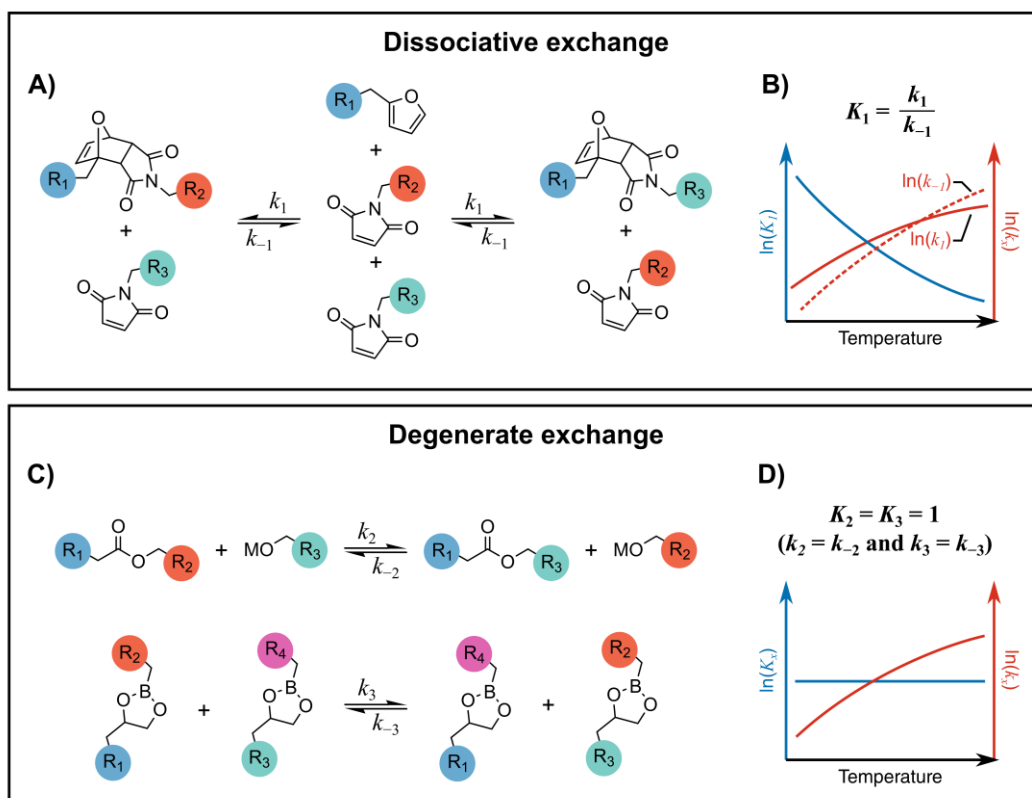


Figure 1. A) Dissociative exchange exemplified with consecutive Diels-Alder adduct dissociation and cycloaddition in the presence of a free maleimide. B) Qualitative plot of $\ln(K_1)$ (solid blue line), $\ln(k_1)$ (solid red line), and $\ln(k_{-1})$ (dashed red line) versus temperature for the dissociative exchange between Diels-Alder adducts. C) Degenerate exchange exemplified with the transesterification of an ester with an activated alcohol (top, M = metal catalyst) and the metathesis of boronic esters (bottom). D) Qualitative plot of $\ln(K_x)$ (solid blue line) and $\ln(k_x)$ (solid red line) versus temperature that applies to both the degenerate exchange of ester transesterification and boronic ester metathesis.

Polymer networks that are crosslinked via reversible covalent bonds are conceptually similar to non-covalently crosslinked networks, but they are distinguished by the strength and life-time of the covalent interaction. Depending on the nature of the reversible covalent bond, various stimuli can be used to push the equilibrium between the associated and dissociated states. For example, reversible covalent networks have been prepared using thermally

activated groups (*e.g.*, Diels-Alder adducts,[25, 26] alkoxyamines,[27] urethanes and urea,[28, 29] triazolinediones,[30] 1,2,3-triazoliums,[31] and aniliniums,[32]); photo-activated groups (*e.g.*, coumarin dimers,[33-35] trithiocarbonates,[36] disulfides,[37] and diarylbibenzofuranone derivatives[38]) and chemically activated groups (*e.g.*, boronic esters,[39, 40] disulfides,[41, 42] acylhydrazones,[43, 44] imines,[41, 45] and acetals[46]). The observed modulation of macroscopic properties is primarily driven by a change in the degree of crosslinking, which is dictated by the equilibrium constant of the reversible covalent crosslinking group (Fig. 1A). At high temperatures, the rate of the dissociation reaction becomes faster than the rate of the association reaction (Fig. 1B). These materials thus experience a loss of network integrity in the dissociated state, which is disadvantageous in applications that demand facile shaping and welding.

Recently, a conceptually unique approach to polymer networks was introduced that combine the temperature-independent and permanent structure of thermosets with the malleability and reprocessability of thermoplastics. These new polymer materials are called vitrimers and were introduced by Leibler and co-workers in 2011.[47-49] Vitrimers feature dynamic covalent crosslinks that do not dissociate in the course of the exchange reaction. However, despite a constant degree of crosslinking, these materials can flow under the action of heat depending on the kinetics of the exchange reaction. Vitrimers are able to achieve a compelling balance of robust mechanical properties and processability. We believe that this approach will be key to realizing recyclable high performance materials in the future. The aim of this Trend article is to describe the most important fundamental aspects of vitrimers, present the synthetic routes to access these materials, and finally discuss the challenges that we believe must be addressed to transition vitrimers from an academic concept to commercial products.

2. Vitrimers: Definitions and key properties

2.1 Definition of dynamic covalent bonds in the context of vitrimers

Vitrimers are permanent chemical networks with dynamic covalent bonds that allow the network to change its topology while maintaining a constant number of chemical bonds in the system at all temperatures below degradation. The term “dynamic” is defined with deference to Lehn’s pioneering work on dynamers.[50] Dynamic covalent bonds are reversible and can rapidly reach thermodynamic equilibrium in response to a stimulus. In the context of vitrimers, the topological rearrangement of the network operates through thermally activated degenerate reactions between dynamic covalent units, allowing these systems to fully relax external stresses.

In a degenerate process, the chemical entities are identical on both sides of the equilibrium (Fig. 1B) and the thermodynamic equilibrium constant is by definition 1 at any temperature; that is, the forward and reverse exchange reaction rates are equal to each other at all temperatures (Fig. 1C). This characteristic provides vitrimers with a constant number of chemical bonds regardless of the temperature. On the other hand, the lifetime of the dynamic bonds, and therefore the flow properties of vitrimers, are temperature-dependent. Vitrimers can thus undergo a thermally triggered and reversible transition from a (visco)elastic solid to a viscoelastic liquid while preserving a constant number of crosslinks. This characteristic distinguishes vitrimers from dynamic networks that experience a decrease of their connectivity with increased temperature (Fig. 1B) and provides vitrimers with different thermomechanical and flow properties.[51-53]

2.2 Thermally triggered solid-to-viscoelastic-liquid transition: T_v and viscoelastic properties

Thermosets behave as glassy solids at temperatures below their T_g and as elastomers above their T_g or T_m for amorphous or semi-crystalline polymers, respectively. Thermoplastics, on the other hand, flow when heated above their T_g or T_m for amorphous or semi-crystalline polymers, respectively. The viscosity of amorphous thermoplastics sharply drops above the T_g , following the Williams, Landel, and Ferry (WLF) model[54] between the T_g and approximately 100 °C above the T_g ; it then follows Arrhenius-type temperature dependence at higher temperatures.[55-58] In the case of semi-crystalline thermoplastics, the viscosity abruptly drops at the T_m and then follows an Arrhenian temperature dependence as long as the T_m is approximately 100 °C higher than the T_g . [56, 58, 59]

Vitrimers behave in a strikingly different way. For vitrimers to flow, the molecular network must be able to reorganize its topology, which requires enough energy to both break the physical interactions preventing long range motion of polymer chains and to allow degenerate reactions between the dynamic links to proceed. The liquid-to-solid transition in vitrimers thus reflects either the freezing of the motion of polymer chains [47, 60-62] or the quenching of the exchange reaction.[47, 48] In the latter case, vitrimers present a new characteristic transition temperature, the T_v , which is defined as the temperature at which the melt viscosity is equal to 10^{12} Pa·s.[47, 63] The T_v corresponds to the freezing of network topology due to the absence of exchange reaction on the timescale of the observation.

The position of the T_v compared to that of the T_g (and the T_m in the case of a semi-crystalline vitrimer) dictates the thermo-mechanical profile of the material. For example, consider an amorphous vitrimer that has a T_v that is greater in value than its T_g . When this material is heated above its T_g (Fig. 2A), it undergoes a transition from a glassy to a rubbery state. Upon further heating, the kinetics of the degenerate exchange increase, and thus the

lifetime of the dynamic bonds proportionally decreases. Yet, within the temperature range between the T_g and T_v , the material behaves as an elastomer because the exchange reactions are slow enough such that the topology remains frozen. When the temperature reaches the T_v , the exchange reactions become sufficiently fast to allow macroscopic flow. The material starts to behave as a viscoelastic liquid, with a melt viscosity that gradually decreases following an Arrhenian dependence with temperature. Similarly, in the case of a semi-crystalline vitrimer with a T_m lower than the T_v (Fig. 2B), the material behaves like an elastomer between the T_m and T_v , and then, above the T_v like a viscoelastic liquid with a melt viscosity that gradually decreases with temperature according to Arrhenius law.

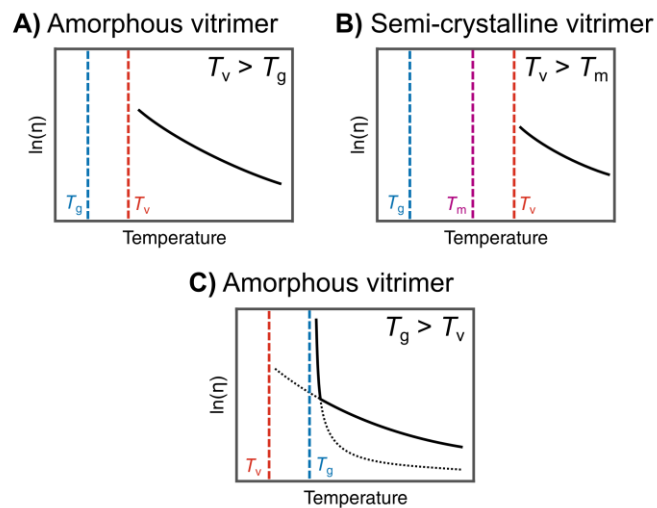


Figure 2. A) Plot of $\ln(\eta)$ versus temperature of an amorphous vitrimer in which the topology freezing transition temperature, T_v , is greater than the glass transition temperature, T_g . B) Plot of $\ln(\eta)$ versus temperature of a semi-crystalline vitrimer in which T_v is greater than the melting temperature, T_m . C) Plot of $\ln(\eta)$ versus temperature for a vitrimer that features a T_g that is greater than its T_v .

Alternatively, the hypothetical T_v of the vitrimer can be lower than the T_g , causing the material to behave like a viscoelastic liquid at high temperature with a melt viscosity

following the Arrhenius law. In such a case with an amorphous vitrimer, as the temperature is lowered and approaches the T_g , the degenerate reactions are still fast while long range segmental motions of polymers become the limiting factor for the topological rearrangement of the network. The melt viscosity then deviates from an Arrhenian dependence towards WLF behavior as a function of temperature (Fig. 2C).[51, 64] When the temperature reaches the T_g , the suppression of long range molecular motion induces the transition from a viscoelastic liquid to an elastic solid, as the dynamic exchangeable links are trapped in a glassy matrix. Similar considerations can be applied to semi-crystalline vitrimers as well.

Characteristic Arrhenian temperature dependence on melt viscosity has been demonstrated with various vitrimer systems relying on different types of exchangeable bonds, establishing that the melt viscosity can be controlled by manipulating the lifetime of the dynamic covalent bonds.[47, 48, 60, 61, 65-68] As an example, Leibler and co-workers[48] illustrated this principle by catalyzing the degenerate transesterification between esters and alcohols in an epoxy matrix derived from bisphenol A diglycidyl ether and a mixture of tricarboxylic and dicarboxylic fatty acids. To induce vitrimer behavior, these epoxies were loaded with varying kinds and amounts of transesterification catalysts. Their zero-shear melt viscosity, obtained from stress relaxation experiments, were compared as a function of temperature.

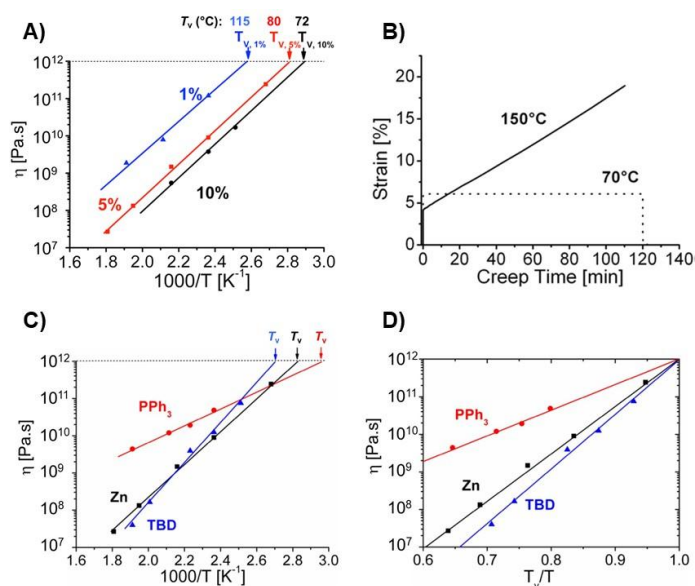


Figure 3. Viscoelastic properties of β -hydroxyl-ester vitrimers obtained from bisphenol A diglycidyl ether and a mixture of tricarboxylic and dicarboxylic fatty acids A) Arrhenius plot of the viscosity for vitrimers containing 1 (blue), 5 (red), and 10 (black) mol % of $\text{Zn}(\text{OAc})_2$. B) Elongational creep experiments at 70 and 150 °C for a vitrimer catalyzed with 10 mol % of $\text{Zn}(\text{OAc})_2$. C) Arrhenius plot of the viscosity for vitrimers containing 5 mol % of $\text{Zn}(\text{OAc})_2$ (black), PPh_3 (red), and TBD (blue). D) Angell fragility plot, normalized at T_v , for vitrimers containing 5 mol % of $\text{Zn}(\text{OAc})_2$ (black), PPh_3 (red), and TBD (blue). [48]. Copyright 2012. Adopted with permission from the American Chemical Society.

As the loading of zinc acetate is increased (*i.e.*, 1, 5 and 10 mol%), the zero-shear melt viscosity shifts to lower values for a given temperature, while the activation energy of the viscous flow remains unchanged (*ca.* 90 kJ mol^{-1}) (Fig. 3A).[48] This behavior reflects the increase of the rate of exchange of the dynamic links with the catalyst concentration while the activation energy of the degenerate reaction remains the same. Increasing the catalyst loading in vitrimers thus does not modify the temperature dependence of the melt viscosity, but it allows lowering the viscosity at a given temperature, and therefore T_v . In the present system, the T_v decreases from 115, to 80 and finally 72 °C, as increasing zinc acetate concentration

from 1, to 5 and finally 10 mol%.[69] In other words, increasing the catalyst loading in vitrimers affects both their processability and their temperature window of usage.

This material is expected to behave like an elastomer between its T_g (15 °C) and T_v , and like a viscoelastic liquid above its T_v , which is clearly evident by elongation creep experiments performed at 70 °C and 150 °C with the vitrimer containing 10 mol% of zinc acetate (T_v of 72 °C) (Fig. 3B).[48] At 70 °C, the vitrimer exhibits the typical behavior of an elastic solid obeying Hooke's law. Under the application of an elongational stress, the material deforms instantaneously, with a strain equal to the ratio of the tensile stress to the elastic modulus. When the stress is removed, the material recovers its original dimension and show no sign of creep. When subjected to the same elongational stress at 150°C, the materials show an instantaneous elastic response and then exhibits linear deformation over time, which is consistent with the vitrimer flowing like a viscoelastic liquid obeying Maxwell's law as a result of dynamic exchange reactions.

Changing the catalyst nature affects both the rate of exchange and the activation energy of degenerate reactions. In vitrimers, this translates into materials with different viscous flow activation energy (Fig. 3C). By keeping the catalyst concentration constant but changing its structure (*i.e.* 5 mol % of either zinc acetate, triphenylphosphine, or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)), vitrimers with significantly different viscous flow activation energies (86, 43 and 106 kJ mol⁻¹, with zinc acetate, triphenylphosphine and TBD, respectively) are accessed.[48, 69] Thus, by adjusting the nature of the catalyst and its concentration, it should be possible to design vitrimers with the same T_v , *i.e.* the same temperature window of usage, but adjustable processability, *i.e.* with different melt viscosity temperature dependence (Fig. 3D).

The possibility to control the flow properties of vitrimers via the catalysis or quenching of the degenerate reactions was also demonstrated on other vitrimers relying on

transesterification,[60, 66, 70-72] as well as by Du Prez, Winne and *al.*[65] and Nicolay, Leibler and *al.* [73] on vitrimers incorporating vinyllogous urethane dynamic crosslinks, confirming that manipulating the rate of exchange of the dynamic links is an efficient and powerful tool to tune the viscoelastic properties of vitrimers.[64, 67, 68, 74]

2.3 Adhesion

Another important property of vitrimers relates to their ability to weld objects together. Indeed, the malleability of vitrimers is conducive to obtaining a good interfacial contact, while the formation of interfacial crosslinks reinforces the polymer-polymer interface and permits the formation of strong adhesion between vitrimeric objects. In addition, the Arrhenian temperature dependence of the melt viscosity of vitrimers permits welding to be performed with or without molds, while preserving the shape of the objects to be assembled. Numerous examples of welding of vitrimers of similar chemical natures have been described in the literature.[49, 60, 75, 76] Typically, welding of vitrimers that contain a higher concentration of exchangeable links yield greater weld strength. Increasing the temperature, as well as the catalyst loading, where appropriate, accelerates welding.[49] It is important to note that functional groups at the interface of two welded vitrimers are exchanged and not consumed in the course of welding. Thus, in the case that a joint debonds, it is possible to reform the joint without modifying the surface of the vitrimer—one must simply apply the appropriate stimulus while the two surfaces are in contact to repair the weld.[49]

It was recently demonstrated that vitrimers of different natures can be assembled together.[62] High density polyethylene (HDPE) and poly(methyl methacrylate) (PMMA) vitrimers containing dioxaborolane dynamic crosslinks were welded together, even though HDPE and PMMA are incompatible and yield very weak interfaces (Fig. 4). After pressing together the two materials at 190 °C and 11 kPa of pressure for 20 minutes, the adhesion

between the two materials was so strong that mechanical failure occurred in the PMMA bulk material and not at the welded joint.

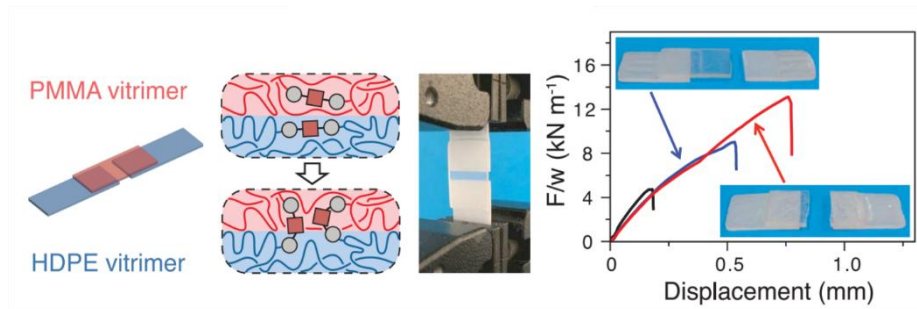


Figure 4. Adhesion between poly(methyl methacrylate) and high density polyethylene vitrimers. Displayed are a schematic representation (left), photo (center), and plot of lapshear testing results (right). In the lapshear testing plot, the PMMA/HDPE dioxaborolane thermoplastic precursors are in black (contact time 10 min, adhesive failure), and the PMMA/HDPE vitrimers for two contact times, 10 min in blue (adhesive failure) and 20 min in red (bulk failure in the PMMA component). [62]. Copyright 2017. Adopted with permission from the American Association for the Advancement of Science.

Vitrimer composites can also be welded and assembled into new shapes, using heat as a stimulus,[77, 78] microwave radiations[79] or light, thanks to the photothermal effect of carbon nanotubes (CNT),[80] gold[81] and polydopamine[82] nanoparticles. Composites with hard and soft polyester, polyurethane, polyimine, or polydiene matrixes, incorporating glass[77] and carbon[78] fibers, as well as CNTs,[79, 80, 83] silica,[84, 85] gold,[81] or organic[82] nanoparticles can be efficiently welded, opening new opportunities to engineer advanced materials for aerospace, automotive, shipbuilding, energy, and electronics industries.

2.4 Recyclability

The ability to flow allows vitrimers to be reprocessed and recycled. In a typical exemplification, a vitrimer specimen is cut or ground into small pieces and then reformed into a new specimen that is evaluated by physicochemical and mechanical characterization. Multiple cycles of reprocessing and characterization are usually performed, and the recyclability is assessed by comparing the properties of the recycled vitrimers to those of the initial material. The properties that are typically evaluated include the T_g , the value of the elastic modulus of the rubbery plateau, the thermal stability, the tensile properties, and the gel content.

However, the routine battery of benchmarks provides limited information on side reactions that can transform dynamic crosslinks into static crosslinks, as the formation of static crosslinks may not prevent processing by compression molding[86, 87] and can occur without changing the overall crosslinking density. This uncertainty is further accentuated by the dependency of mechanical recovery on the processing conditions. The selective cleavage of the dynamic links in vitrimers allows differentiating dynamic crosslinks from static crosslinks. Such tests give access to a precise and quantitative characterization of the molar mass, molar mass distribution, and functionality of the polymer chains constituting the vitrimer,[62, 87] thereby providing valuable information at the molecular level for precisely evaluating the long-term recyclability of vitrimers.

The selective cleavage of the dynamic links can also serve as a practical route to the closed-loop recycling of vitrimer composites. This approach was successfully used to quantitatively recover and separate the carbon fibers and the polymer matrix in polyimine[78] and polyester[88] vitrimer composites (Fig. 5). The reclaimed fibers and resin could be reused to produce new composites that exhibited the same mechanical properties as the original material. The selective cleavage of the dynamic links has also been successfully used to recover glass fibers in vinylogous urea based composite vitrimers.[89]

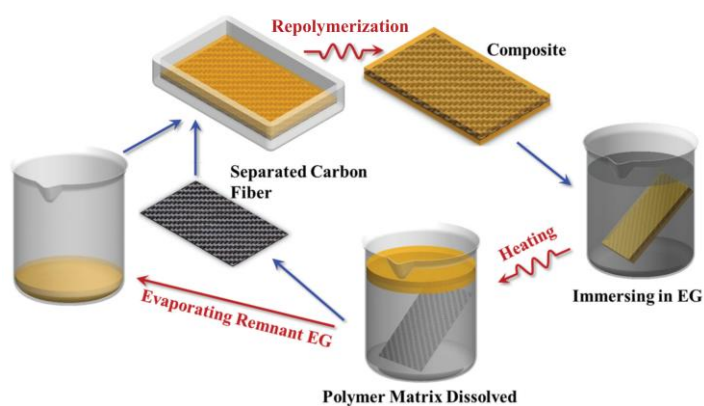


Figure 5. Recycling of a carbon fiber-reinforced vitrimer through depolymerization of the vitrimer matrix. [88]. Copyright 2017. Adopted with permission from Elsevier Science Ltd.

3. Vitrimers: Chemistry

3.1 Synthetic strategies to prepare vitrimers

There are two main strategies for preparing vitrimers—the polymerization of multifunctional monomers and the crosslinking of thermoplastics. The first strategy consists of curing a mixture of multifunctional monomers to generate a network containing dynamic covalent bonds. In the case of a step-growth process, the dynamic covalent links can be generated during network formation[31, 45, 47, 67, 90] (Fig. 6A) and/or can already be present in at least one of the monomers (Fig. 6B).[37, 91, 92] In some cases, commercial resins can be converted into vitrimers by merely adding an appropriate catalyst that facilitates exchange reactions or by adjusting the composition of the resins.[47, 65] In the case of chain-growth polymerizations, the most direct route is to perform a copolymerization in the presence of a bifunctional crosslinker that contains a dynamic covalent bond, as exemplified by Nicolaÿ, Matyjaszewski and co-workers for vinyl monomers (Fig. 6C).[93] This strategy was also recently employed by Bates *et al.* to prepare polyester vitrimers through the ring opening copolymerization of 4-methylcaprolactone with a bis-lactone crosslinker.[66]

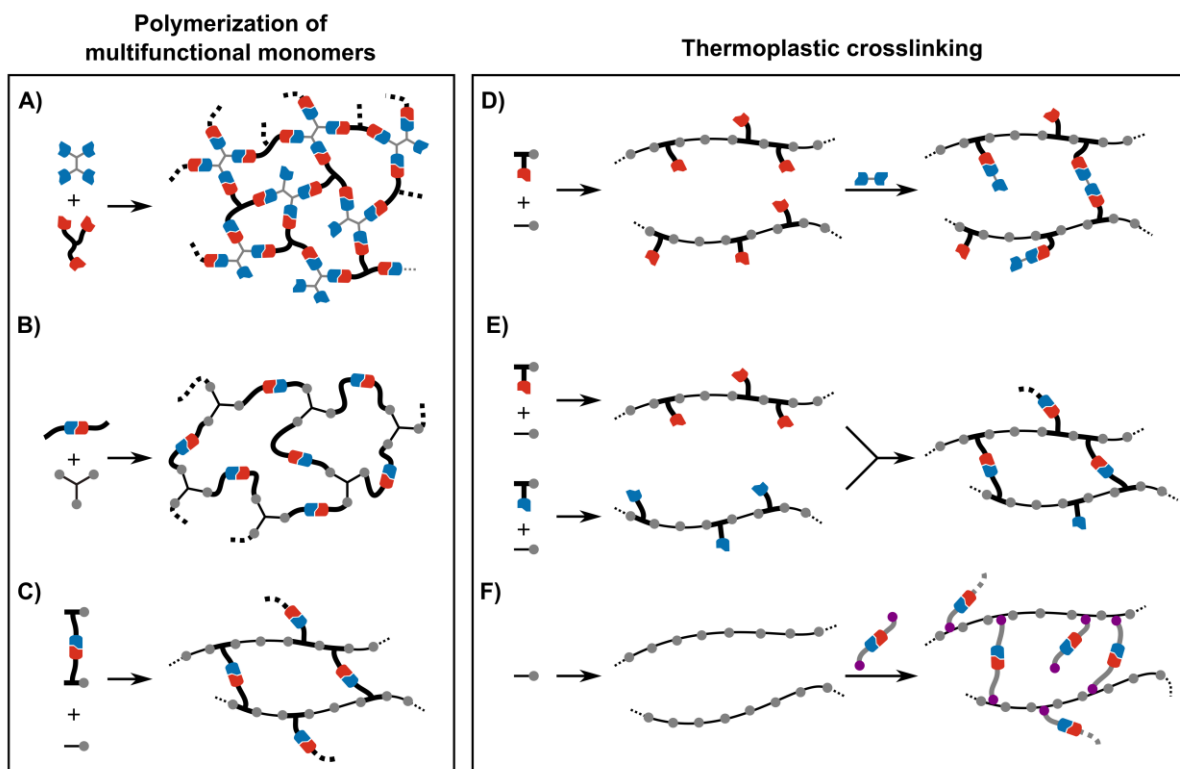


Figure 6. Synthetic strategies for creating vitrimers.

The synthesis of vitrimers from multifunctional monomers requires the dynamic covalent chemistry to be compatible with the active species involved in the polymerization, as well as with the different monomers under the conditions of the polymerization. This approach offers the advantage of yielding vitrimers in a single-step. One of the potential difficulties is the necessity to remove the unreacted monomers or residual solvent from the vitrimer. In terms of process, this approach implies going from a solution or melt to a gel or bulk network, which may be dynamic or not under the polymerization conditions.

The second approach is to transform thermoplastic polymers into vitrimers. Two main scenarios exist. In the first, the function(s) involved in the degenerate reaction are present in the backbone of the polymers or as pendant functions. The dynamic functions can be intrinsically present in the polymer, like the ester or terminal alcohol functions of polyesters, for vitrimer relying on transesterification as exchange reactions,[60, 94, 95] or the alkene

bond of polydienes for vitrimers relying on alkene metathesis, for example.[96] Otherwise dynamic functions can be introduced on purpose during the synthesis of the polymers, by copolymerizing a comonomer containing the exchangeable group.[62, 64, 73, 74, 97, 98] Then, the functional thermoplastic polymers are crosslinked into vitrimers, either in solution or in the melt, with a multifunctional molecule or a polymer (Figs. 6D and 6E). This approach offers the most flexibility in terms of polymer matrices, dynamic bonds, and synthesis conditions.

Existing thermoplastics can also be turned into vitrimers even if they do not carry any functions involved in the degenerate reaction. In that case, the dynamic linkages are introduced via post-polymerization functionalization (Fig. 6F).[62, 87, 99] The chemistry required to attach the crosslinkers depends on the reactivity of the parent polymers and should also be compatible with the exchangeable links. This process is particularly appealing because it directly converts conventional polymers into vitrimers without modifying the already existing and optimized syntheses. However, this approach can be very challenging due to the low reactivity of the polymers to be transformed (*e.g.*, polyolefins and fluoropolymers) or because of their low solubility and/or high melting temperature (*e.g.*, polyethylene terephthalate and polyamides), which significantly limit the processing parameter window. In such cases, reactive extrusion is a relevant technique to accomplish this functionalization, which typically operates via radical-initiated reactions. Nicolaÿ, Leibler, and co-workers used this strategy to introduce dioxaborolane units to prepare HDPE vitrimers.[62]

3.2 Exchangeable chemical bonds

The dynamic covalent bonds are directly responsible for vitrimers' characteristic properties. Numerous degenerate reactions are known, and many have been successfully used

to prepare vitrimers. Several recent reviews provide excellent discussions of these chemistries in general, as well as in the context of vitrimers more specifically.[51-53, 100-106] In Fig. 7, a sampling of dynamic reactions are presented along with representative references for their respective synthetic implementation into vitrimers. Below we describe important practical considerations for implementing such reactions into vitrimers.

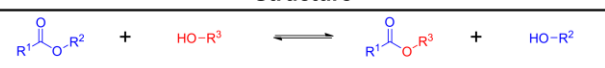








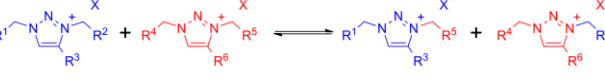

Group name	Structure	Multicomponent polymerization	Thermoplastic crosslinking
Esters		[47]	[94, 95, 107]
Carbonates		[72]	
Urethanes		[67, 108, 109]	
Ureas (hindered)		[29, 110, 111]	
Vinylagous urethane and diketoenamines		[61, 112]	[73, 98]
Imines		[45, 113, 114]	
Disulfides and related groups		[91, 93, 115]	
Olefins			[76, 96]
Boronic esters and boroxines		[116, 117]	[62, 74, 87, 99]
1,2,3-Imidazoliums		[31, 68]	
Siloxanes and silyl ethers		[118, 119]	[64]

Figure 7. Selection of dynamic covalent reactions employed to make vitrimers. References are provided for representative examples of the different routes to incorporate these bond exchange reactions into vitrimers.

Some dynamic covalent reactions are more practical to use in one route over the other. For instance, many kinds of dynamic covalent bonds are already generated in thermosets that are synthesized via step growth polymerization (*e.g.*, esters, carbonates, and urethanes).

Given the similarity between conventional thermoset synthesis and multicomponent polymerization vitrimer synthesis (Figs. 6A, 6B, and 6C), a simple way to access vitrimers is to modify the conventional synthesis to incorporate the components or additives necessary to make the system dynamic under the desired conditions (*e.g.*, adjusting the ratio of monomers or the addition of a catalyst). It is of course also possible to use these kinds of bonds in a thermoplastic crosslinking approach (Figs. 6D, 6E, and 6F), but it may require precautions (*e.g.*, protection and deprotection of functional groups) to ensure that the dynamic covalent bonds are chemically orthogonal to the functionality used to create the network. In designing a vitrimer, it is essential to avoid side reactions that would consume the dynamic links during the synthesis, usage and (re)processing of the material.

The use of catalysts is an important consideration that entails tradeoffs in vitrimer design. Both the structure and concentration of the catalyst impact the lifetime of dynamic covalent bonds,[48, 60, 65, 66, 70-72] making it a useful parameter for tuning the physical properties of vitrimers. However, catalysts can be susceptible to degradation and leaching over time, and toxicity concerns can preclude their use in commercial products. Some dynamic covalent reactions offer flexibility in being able to operate under catalyzed and non-catalyzed conditions. For instance, in the original report of vitrimers,[47] dynamic transesterification between ester bonds and stoichiometric number of hydroxyl groups was activated through the addition of a zinc-based catalyst. Later, Guo, Zhang, and co-workers[120] found ester-based vitrimers could be self-catalyzed by incorporating an excess of hydroxyl groups into the polymer matrix; the authors posit that the hydroxyl groups activate the ester groups via hydrogen bonding.

In some cases, it can be advantageous to deliberately introduce non-dynamic crosslinks to boost the mechanical properties. Elastomeric vitrimers, for example, would benefit at service temperature from some proportion of static crosslinks to suppress creep. The dynamic

linkages would allow these materials to still be (re)processable and unlock self-healing capabilities. The Torkelson,[86] Sumerlin,[116] and Nicolaÿ[87] groups have demonstrated this practical approach to tuning the mechanical properties of a dynamic material.

All of these synthetic issues must be considered in tandem with the thermo-mechanical demands of the application at hand, with a focus on the processing and usage temperature windows. There is not a universally ideal behavior in terms of life-time of the dynamic bonds as a function of temperature, as all applications have their own unique demands. Thus the dynamicity of the bonds must be balanced with the physical properties of the matrix and the targeted properties.

4. Vitrimers: present and future

4.1 New chemistries and synthetic routes

Transitioning vitrimers from academic materials to industrial products is contingent upon using inexpensive feedstocks in synthetic processes that are both fast and scalable. Drop-in solutions are ideal because they require minimal modification to existing polymer syntheses and processing infrastructures. The synthesis of vitrimers by reactive processing of commercial thermoplastics with functionalized additives is thus particularly appealing. Vitrimers can be obtained without modifying existing syntheses and without adding any additional synthetic steps because the transformation is done during processing. Only a few examples of vitrimer synthesis by reactive processing of thermoplastics have been reported to date.[62, 99, 121, 122] For the future, we believe it will be advantageous to develop new grafting chemistries and dynamic covalent bonds that are compatible with this processing technique.

4.2 Solubility

The original description of vitrimers states that the number of chemical bonds in the network is constant at all temperatures. This principle is the basis for a prerequisite that has been commonly invoked in previous reports to decide whether a material should be designated as a vitrimer: vitrimers should be insoluble at all temperatures.[47-49, 51] However, bond reshuffling in vitrimers can lead to the formation of loops, which can be accompanied by the release of soluble linear, cyclic and/or (hyper)branched polymers, all while maintaining a constant number of chemical bonds. Vitrimers could thus partially or completely dissolve depending on the network topology, chemical functionality, lifetime of the dynamic bond under the swelling conditions, experiment duration, solvent properties, and solvent volume fraction.

We recently confirmed this possibility with a polybutadiene vitrimers derived from polybutadiene oligomers that were functionalized with dynamic dioxaborolane crosslinks.[87] Samples with a low degree of crosslinking were highly insoluble in THF after 24 hours of immersion at room temperature (insoluble fraction of ca. 90 %), but were entirely dissolved after 120h. Solubility tests can thus be misleading for assessing the crosslinking density of vitrimers. Theoretical and experimental model studies should be conducted to predict and quantify the kinetics of dissolution of vitrimers as a function of the topology and functionality of the network, lifetime of the dynamic links, and solvent fraction and quality.

4.3 Flow properties

The development of models to reliably predict temperature-dependent melt flow properties will be invaluable because these properties are essential for designing vitrimers that can be processed with industrial equipment. A good starting point is the “sticky reptation” theory used to model the dynamics of networks and entangled solutions of polymers bearing functional groups that form transient crosslinks.[123-125] This model

predicts that the motion of polymer chains (and thus the terminal relaxation time the reversible network) depends on the chain length, the concentration of the polymer chains, and the lifetime of the transient crosslinks.[123] At high association degree of the stickers, the activation energy for viscous flow is substantially larger than the activation energy of the isolated transient crosslink.[124, 125] This is a consequence of the low concentration of available crosslinking partners under these conditions.

Vitrimers present new wrinkles that are not yet accounted for in this model. Many vitrimers contain exchangeable links in the main chain, and thus the backbone dimension of polymer chains can change on a timescale comparable to the lifetime of the dynamic links. This phenomenon will significantly impact the motion of polymer molecules. Furthermore, degenerate reactions may involve reactive partners with non-equivalent functionality, such as alcohols (monovalent) and esters (divalent) in the case of transesterification (Fig. 1B). These different groups may be present in stoichiometric or non-stoichiometric ratios. For example, when pendant and terminal hydroxyl groups are in large excess as compared to ester groups present in the backbone or as a crosslink, many exchange reactions may be necessary before a dynamic ester bond linking two polymer chains is exchanged. This situation should lead to vitrimers with a viscous flow activation energy significantly larger than that of the analogous small molecule degenerate exchange. On the contrary, when both types of bonds are present in an equimolar ratio and at a high concentration, the viscous flow activation energy of the vitrimers is comparable to that of the exchange reaction on small model molecules. This hypothesis is consistent with the reported relaxation of β -hydroxy ester based vitrimers (with equimolar hydroxyl and ester groups)[47] and polylactide vitrimers (with an excess of ester groups compared to hydroxyl groups)[60]. The development of a theory that could account for such behavior would be a useful tool in designing the dynamics of vitrimers for specific applications.

A related challenge is to develop new protocols for quantitatively describing the intrinsic properties of vitrimers. Given that the T_v is defined as the temperature at which the melt viscosity is 10^{12} Pa·s, the methods most commonly used to determine this value are dilatometry, stress-relaxation, and creep experiments. All of these experiments require the sample to be subjected to an external force. Although relevant for material processing applications, such measurements are not appropriate for understanding the material under static conditions, which can be critical for self-healing. Wei, Ji and co-workers[126] reported a new protocol that makes use of aggregation-induced-emission (AIE) as an alternative means to probe the topology freezing temperature of vitrimers. The fluorescence intensity of a AIE probe dispersed in a vitrimer matrix is correlated with a T_v under static conditions. We expect future research to further explore new protocols for quantifying the relationships between temperature, exchange kinetics, and mechanical properties, permitting deeper insight into the underlying chemical and physical properties of vitrimers.

4.4 Advanced vitrimers

The concept of vitrimers has addressed limitations of many old concepts and opened doors to new possibilities. For example, shape memory materials based on conventional thermosets were initially limited by the inability to program more than one permanent shape. The introduction of vitrimer chemistry to this application overcomes this limitation, as vitrimers can shuffle their topology to accommodate the programming of a new “permanent” shape when heated above the T_v . [75] For similar reasons, vitrimers have unlocked new possibilities in the field of liquid crystalline actuators, which are valuable for applications of mechanical actuation such as synthetic muscles or valves in microfluidic systems. [127, 128]

A better understanding of the correlation linking the structure and the functionality of vitrimers with their dynamics will greatly facilitate the rational design of advanced vitrimers.

Already exciting contributions toward this goal have been made. As mentioned above, the groups of Torkelson,[86] Sumerlin,[116] and Nicolaÿ[87] have recently reported how introducing a proportion of non-dynamic crosslinks gives rise to improved creep resistance. Alternatively, the incorporation of two (or more) kinds of dynamic links with different lifetimes (*e.g.*, one very short at service temperature and one dynamic only at processing temperature) is an elegant path to tuning a vitrimer's viscoelasticity profile.[129, 130] Ricarte, Leibler and co-workers[131] recently described the consequences of phase separation between polyethylene domains and grafted boronic ester domains in polyethylene vitrimers. Sumerlin and colleagues[132] recently showed how the microphase separation of well-defined vitrimer block copolymers gives rise to enhanced creep resistance, representing another vital tool for controlling vitrimer viscoelastic properties.

The implementation of all these principles into new dynamic and responsive devices is a promising approach to valorizing vitrimer technology. Examples include biomedical devices,[133] 3D printing,[134, 135] and photolithography applications.[136] We anticipate that new relationships between vitrimer chemistry and old concepts of polymer chemistry will continue to drive innovation. We hope that this technology will ultimately spur completely new ideas that contribute to the next great expansion to the frontier of polymer chemistry.

5. Conclusion

Vitrimers are materials of contrast. They are permanent networks of polymer chains, yet the topology of this network can change in response to external stimuli. The crux of this behavior is the dynamic covalent bonds that hold the polymer network together; the unique macroscopic properties of vitrimers are based on the lifetime of these bonds as a function of temperature. The primary advantage of this approach is that vitrimers exhibit properties that

were previously thought to be mutually excluding—vitrimers are processable like thermoplastics, but at the same time feature the robust mechanical properties of thermosets. Since the groundbreaking contribution of Leibler and co-workers[47] in 2011, much progress has been made on developing the underlying chemistry of vitrimers and prototyping them in commercially relevant applications. However, there are clear obstacles that must be overcome to produce these materials in industry, which encompass design principles, synthesis, processing, and recycling. We are optimistic that the polymer chemistry and physics communities will continue to push the concept of vitrimers forward and harness it to make sustainable high performance materials.

6. References

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