

Elastomer-Based Vitrimers—A Review of the Preparation, Characterization, and Applications

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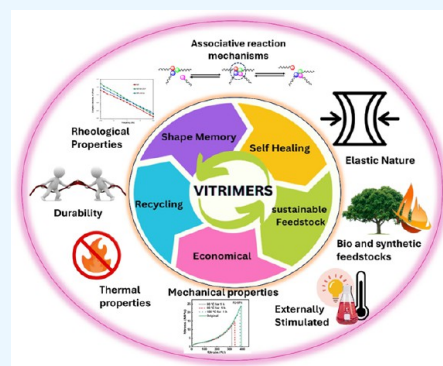
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ABSTRACT: Elastomer-based products are of prime importance in all aspects of modern society. Covalent cross-linked networks are highly desirable for achieving superior mechanical properties, heat resistance, and elasticity. However, these networks cannot break and reform, making traditional covalent systems challenging to reprocess and recycle. However, the permanent cross-links of those polymers enormously block their frontier developments and restrain them from being reused and reshaped. Consequently, the majority of waste materials end up in landfills and their incineration leads to serious environmental crises. An intense search to overcome the hurdles of the permanent cross-linking system has been underway for a long time, and a new group of polymers known as vitrimers has emerged, which work on the backbone of dynamic covalent networks. These exchangeable bonds give polymer reproducibility, self-healing, and recycling abilities along with enhanced mechanical properties. Vitrimers can be developed from bioresources or petrochemical origins, and various chemistries have been developed to formulate these polymers. Tremendous innovations have been employed in the area of elastomer-based vitrimers in recent years. The natural rubber-based vitrimers incredibly exceed the others in implementation and application segments, as they are developed from a bio origin. Here, our review enfoldes the various types of elastomer-based vitrimers and focuses on their synthesis routes, characterization, property evaluation, and potential applications, and we try to provide a comprehensive overview that combines the majority of elastomer-based vitrimers, their blends, composites, nanocomposites, and their potential future developments in a concise format.



1. INTRODUCTION

Cross-linked amorphous polymers with a glass transition temperature (T_g) lower than ambient temperature exhibit an “elastic state” under working conditions. These materials can be mechanically stretched or deformed to a certain extent reversibly and are referred to as elastomeric materials.¹ Elastomers hold prime importance in all aspects of modern society and have grabbed the attention of the scientific world because of their tremendous scope. At the same time, it is important to be aware of the environmental and economic barriers that have been created by them.² Vulcanization is an extensive process to cross-link rubber chains, thereby creating a three-dimensional network. Due to this network, the mechanical properties are enhanced. The sulfur vulcanization generally contains mono-, di-, and poly-sulfidic bonds with the vulcanizers. These networks have a great impact on the physical and mechanical properties of the system. According to the accelerator-sulfur ratio, the vulcanization processes are further classified into efficient, conventional, and semi-vulcanization. The initial history of vulcanization goes back to Charles Goodyear and Thomas Hancock, who added a small amount of sulfur to the Natural Rubber (NR). As the

research progressed, accelerators and activators were used to improve the processing of the rubber compounds and it helped to refine the vulcanization rate and cross-link density. It enhanced the mechanical strength of the rubber, and by this fascinating fact, researchers started to look for a faster cure rate. Among the activators, ZnO has a prominent place and is the most effective. Elemental sulfur is a common curing agent used for elastomers. Those sulfur donors, such as Tetramethylthiuram disulfide (TMTD), which can release sulfur upon heating, can be used as curing agents. Some peroxides are used as curing agents. They provide C–C links instead of strong sulfur bonds,^{3–6} but the permanent cross-links in elastomers enormously block their frontier developments and restrain them from being reprocessable and reshaped.¹ As a consequence, the majority of the waste cross-linked elasto-

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Associative reaction mechanism

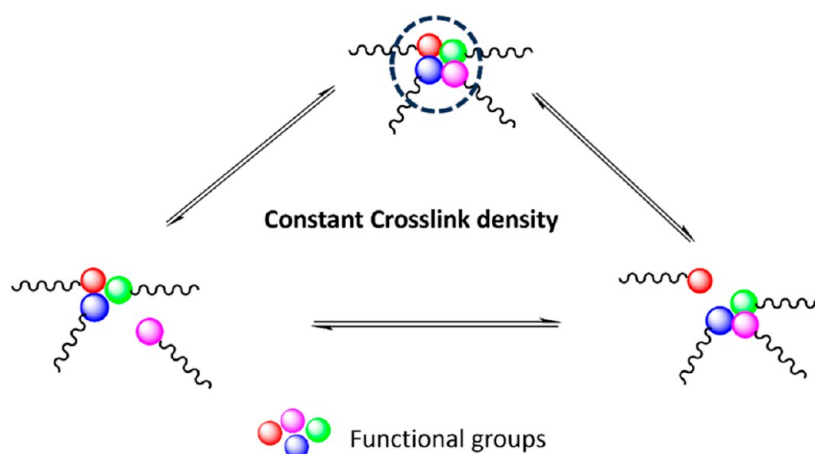


Figure 1. Scheme of the associative reaction mechanism.

meric materials are being used for incineration, and that leads to serious environmental crises. These days, a few of the waste rubber products, such as tires, are being used for regenerating carbon black (CB) and processing oils and other chemicals, but this technology is not fully developed. The suggested alternative for such issues is to use them as fillers in other thermosets. Unfortunately, this technology may not be able to produce high-performance products and causes uncertain impacts on future developments in the rubber industry. The concept of sustainability fueled the search for materials that can be reprocessed and reused.⁷

Apart from covalent cross-linked rubber, other kinds of elastomeric materials are also known, such as thermoplastic elastomers (TPEs) and their various types. TPE can be considered as a multiphase system or a physical mix of polymers. In this two-phase system, the soft phase contributes to the elastomeric character, and the hard phase represents the plastic phase. Among TPEs, the block copolymers are classified as Styrenic block copolymers, poly(ether ester thermoplastic elastomers), and thermoplastic polyurethane (TPU). The second class of TPUs includes blends of rubber and polyolefin, polyamide thermoplastics, and thermoplastic vulcanizates (TPV). The incompatibility of the monomers causes them to be in phase-separated microdomains.⁴ TPEs are intramolecular polymeric hybrid compounds that possess the property of reprocessability.⁵ Those TPEs exhibit rubber-like material with good extensibility and strength yet reprocessability like thermoplastic. The properties can be tailored by hard/soft segments. At the same time, reinforcing fillers and curatives are not required. However, elasticity, hysteresis, and creep resistance are not comparable to those of cross-linked rubbers. For TPE and TPV blends, the compatibility is also a main drawback of this material.^{8–11}

An intense search to handle the hurdles of the permanent cross-linking system began long before, with the history of the dynamic covalent networks (DCN) in the 1940s. The first work in the history of dynamic networks was done by Tobolsky's group,^{12,13} who noticed that ionic impurities caused disulfide bond exchange in cross-linked polysulfide rubbers. Later, Grubb's group^{13,14} noticed a similar mechanism of stress relaxation in cross-linked silicone rubber, which was started by siloxane equilibrium. It further advanced in the following years,

and Lehn^{7,15} modified and named it as “dynamers”. The DCN are preferably carried out by associative and dissociative mechanisms. Bowman^{13,16} designed a revised system of the three-dimensional dynamic covalent bonds termed as covalent adaptive network, which contains a sufficient number of covalent bonds. Vitrimers, the new line of polymers, were launched by Leibler's group^{13,17} in 2011 and are particularly grounded on the associative covalent adaptive networks, and their viscosity–temperature relationship bears a resemblance to that of vitreous silica, from which evolved the name “vitimer”. To elucidate the concept of dynamic bond exchanges, they chose the well-recognized “transesterification” reaction. The epoxy chemistry was carried out by reaction between the diglycidyl ether of bisphenol A and the mixture of di- and tricarboxylic acids.¹⁷ Due to the associative exchange mechanism, vitrimers are usually termed associative polymer networks. They maintain a fixed cross-link density during exchanges, which enables the system to follow the Arrhenius law while heating.¹⁸ This mechanism involves the formation of a new covalent bond in another position before a specified bond break.¹⁹ The mechanism is detailed below (Figure 1). They often show strong glass-forming behavior. When some force is applied to the system, they relax stress over time, like silica-based glasses.²⁰ The pioneer of vitrimers, Leibler, and his companions explained the type of dynamic bond as associative. It exhibits Arrhenius temperature dependence of viscosity while approaching T_g .²¹ This reversible or dynamic covalent bond works on the backbone of an external stimulus and offers durability, recyclability, and self-healing, along with enhanced thermal and mechanical properties beyond the permanent cross-links in the vulcanized elastomers. The incorporated reversible or dynamic covalent bond network to the elastomers serves as a safer approach to the unsolved issues of sustainability and has been the probing segment for the researchers until today.^{7,13,22}

In the past decades, vitrimers derived from the petrochemical resources and biosources progressed in parallel streams, but later a severe concern fell upon the bio feedstocks due to their renewability and abundance. To develop cross-linked rubbers through a greener strategy is to design a synthesis map, which includes ingredients and chemicals from the bio origin and completely avoids petrochemicals from the life cycle of the

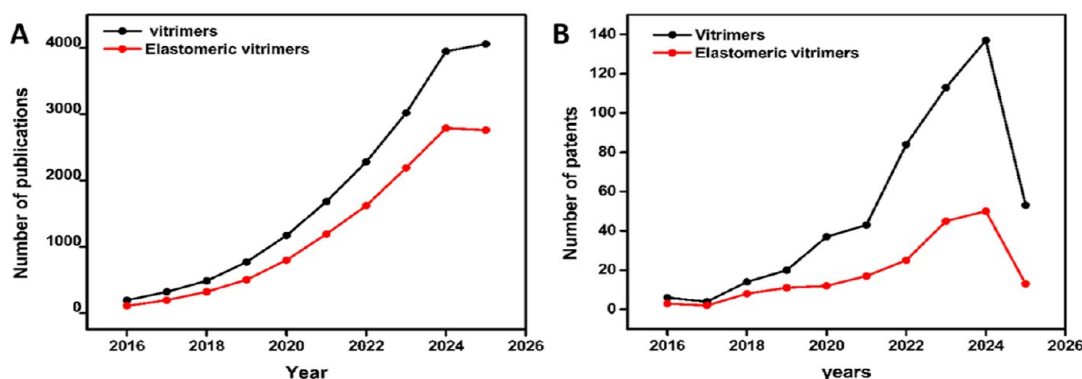


Figure 2. (A) Graph of the number of papers published in the area of vitrimers and elastomeric vitrimers according to the data by google scholar on 2 April 2025. (B) No. of patents published in the area of vitrimers and elastomeric vitrimers according to the data by Google patents on 2 April 2025.

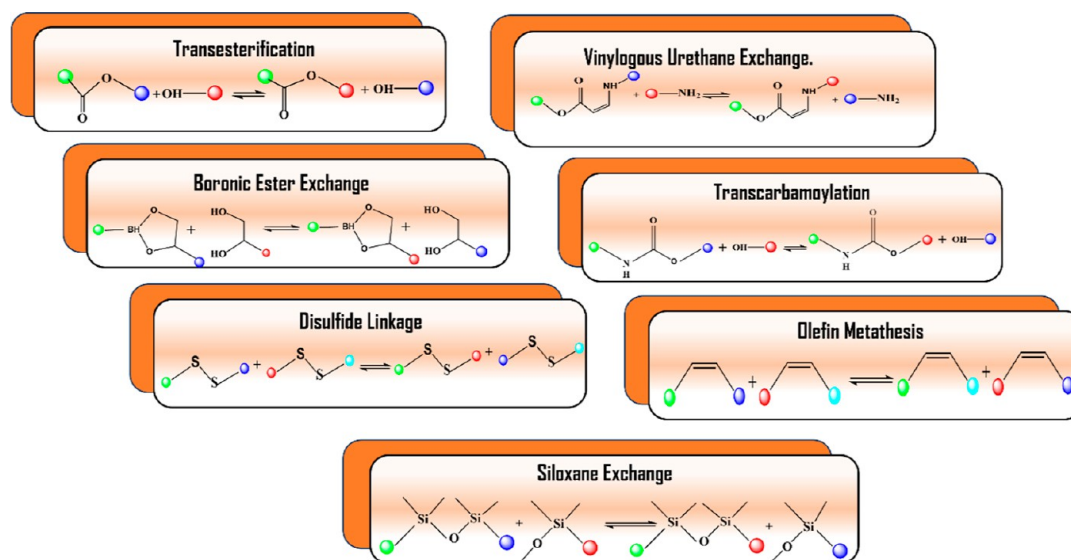


Figure 3. Schematic representation of different chemistries involved in vitrimer synthesis.

elastomers.²³ Nowadays, the nonpetrochemical sources have taken over a large area of the industry and research with their immense availability and vitality to provide an expanded raw material sector.²⁴ A great deal of research work has been conducted with biobased vitrimers, and among them, vegetable oil holds the prime position. Itaconic acid, lignin, NR, cellulose, turpentine, liquorice roots, grapefruit peel, and tannic apple are also claimed for their intrinsic roles.²⁵ Different chemistries of synthesis have been suggested by many researchers. Transesterification, sulfur chemistry, olefin metathesis, alkoxyamines, imine and vinylogous urethane exchange, urea/urethane exchange, siloxane exchange, and boronic ester exchange are the grounding bases where vitrimers have been propagated. Transesterification is the most tried-and-true method in vitrimer chemistries so far. Zn(II) containing catalysts have been used for the reaction. But several catalyst-free systems have also been noticed in vitrimer technology.²⁰ There are several fabrication methods frequently used; however, the method of melting polymerization, followed by hot-pressing, has been the most studied preparation method. The methods, such as mini emulsion-polymerization and a 3D printing technique, are well deployed now.²⁶

Vitrimers are well accepted for their enhanced thermal and mechanical properties, which potentially blend the properties, of the thermosets and thermoplastics and differ from those of TPE and other classifications in the bonding. The latter may be produced via the physical bonding, whereas the vitrimers are stabilized by the dynamic bonds. The recyclability, weldability, and shape memory that sprang from the dynamic covalent bonds increase the widespread application of vitrimers.²⁷ The shape memory attributed to the vitrimer system makes it ideal for unique applications in designing biomedical devices, robotics, and smart actuators. Self-healing property is not bound by an external macroscopic recovery; rather, it recommends the complete recovery of the internal mechanical properties.²² Tremendous innovations have been employed in the area of elastomer-based vitrimers in recent years. The NR-based vitrimers incredibly exceed the others in implementation and in application segments, as they are developed from a bio origin.²⁴ But the increasing needs of the industrial community cannot be fulfilled by NR alone. As a result, the demand for long-lasting and sustainable synthetic rubbers has propelled research into their synthetic routes. Everyday new methods and techniques for the preparation of vitrimers are being added to the list.²⁸ The majority of elastomers have been covered by researchers, but only a small number of review articles have

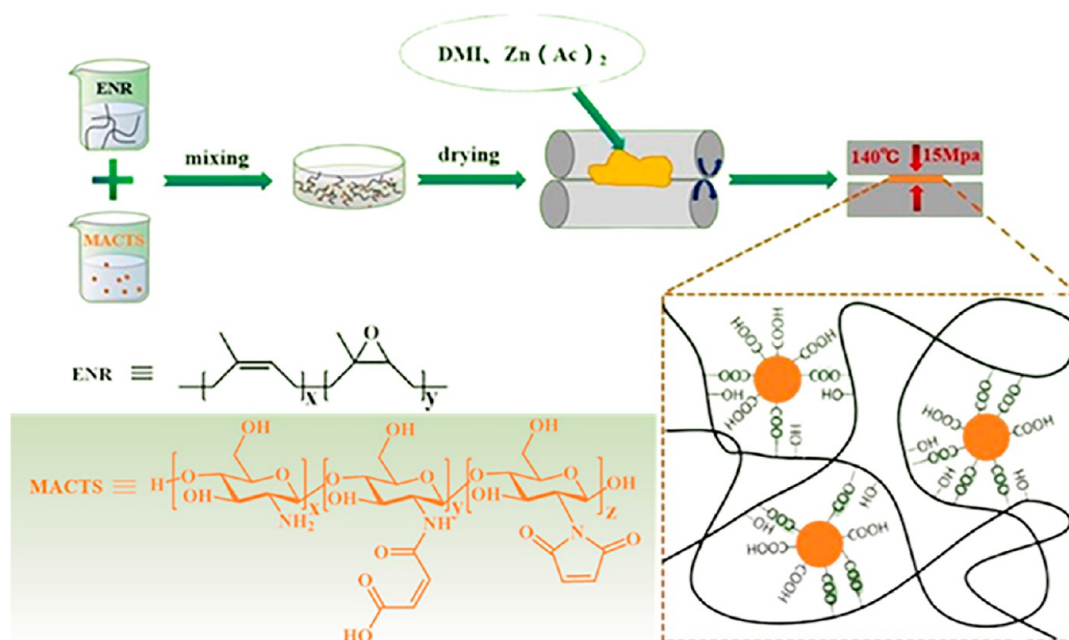


Figure 4. Schematic representation of the transesterification reaction between ENR and the maleated chitosan. Reproduced with permission from ref 34 Copyright@2023, Elsevier Ltd., Elsevier, Composites Communications.

been able to conceal the specifics. Thus, this review tries to investigate the recent studies on the elastomer-based vitrimers, and this attempt encapsulates all of the areas of vitrimers, their synthesis, characterization, and future outlooks.

The graphical study of publications and patents of vitrimers and elastomeric vitrimers (Figure 2) shows that vitrimers are a fast-growing field of research. Both data display remarkable growth tendencies over the last ten years. In the initial state, they appeared in a few academic publications for vitrimers and elastomeric vitrimers; but the number has rapidly increased, surpassing over 3950 papers by 2024 for vitrimers and 2750 papers for elastomeric vitrimers. Comparable tendencies can be seen in patent filings, which increased gradually between 2015 and 2017 before experiencing a loud exponential increase after 2020. Almost 50% is the patents filed for elastomeric vitrimers are from the year 2016 onward. The development of vitrimer research launches a discrete intellectual pattern: as the discipline advanced, the early literature shifted progressively toward application-oriented research, with a prime focus on its theoretical fundamentals. Current patterns point to an imminent shift in research and innovation development to an industrial focus. This methodical bibliometric analysis determines vitrimers' development in scientific circles and their rising technological significance in polymer and materials research. Thus, as years advance, the number of publications increases for vitrimers. A similar trend has been observed in the elastomer-based vitrimers data set. Till 2019, patents were minimal for vitrimers and elastomeric vitrimers, but a steep rise was observed afterward, which clearly shows the paradigm shift from theory to practical applications. This graph concisely says that elastomer-based vitrimers primarily contribute to the area of research on vitrimers.

2. CHEMISTRIES OF VITRIMERS

A great deal of research has been carried out in the field of vitrimers, and they have been classified mostly by their mechanisms.²⁹ In this section, we try to analyze the different

chemistries behind the preparation of vitrimers and their characteristics. A schematic representation of the discussed mechanisms is summarized below (Figure 3).

2.1. Transesterification. Transesterification is noted as the most studied mechanism, and due to the wholesome nature and the commonly used feedstocks for preparation, transesterification in vitrimers has grabbed attention since their introduction. Mainly, it has been carried out in epoxy systems due to the availability of a large number of epoxide groups, anhydrides, and acid groups. All of these factors make the reaction easier, feasible, and applicable. In several works, the reaction has been accelerated via the introduction of catalysts. Zinc-containing catalysts such as zinc acetyl acetate and zinc acetate dihydrate²⁶ have been employed for this purpose. Furthermore, organo catalysts such as 1,5,7-triazabicyclo[4.4.0]Dec-5-ene (TBD), dimethyl-imidazole (DMI), (1,2-dimethyl) triphenylphosphine (PPh), 1-methyl-imidazole, 2-methylimidazole, and 4-dimethylamino-pyridine (DMAP) are also found in use.^{20,26,30,31} A study on the transesterification reaction between dodecanedioic acids and Epoxidized Natural Rubber (ENR) was proposed by Feng et al. It is discovered that the resulting vitrimer can undergo topology shifting at high temperatures via the transesterification reaction. According to an additional interpretation, the cross-link density does not vary as a result of the bond exchange since the transesterification process causes the bonds to interchange under the same conditions and rate. For the recycled samples, the mechanical qualities may be preserved (about 88% after the third recycling). In the three recycling cycles, there was no evidence of thermal damage in either.³² Zhao et al. suggested the development of a highly functional vitrimer derived from ENR and CMCS, marking the first fully biobased vitrimer able to both reinforce and be recyclable. Since the CMCS reacts with the oxirane groups in the ENR network, the material undergoes a transesterification reaction and can readily form β -hydroxyl ester bonds and effective interface contacts, which makes the material significant. It may also form efficient disulfide connections, as it has been cured

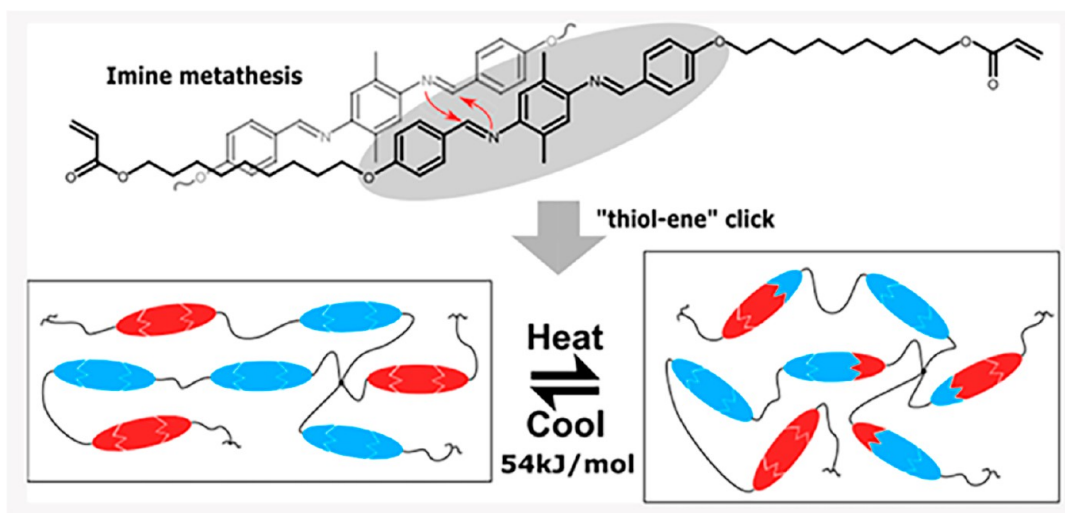


Figure 5. Imine metatheses in the liquid crystal vitrimer.

by 4,4'-dithiodibutyric acid, which contains binary carboxyl and disulfide groups. The comparative analysis between the vitrimer that was produced and the close ENR shows that the dynamically crossed material has better thermal stability and mechanical strength of over 83%, as well as increases of 55% and 16%, respectively, in the ENR-7.5 composite's tensile strength and elongation at break.³³ An upfront and promising approach to vitrimer technology was presented by another study that was proposed in the ENR and the maleated chitosan, which works by the transesterification process. The esterification reaction provides the vitrimer with mechanical, self-healing, and recyclable properties because of the abundant carboxyl sites generated on the chitosan surface. Additionally, it has noted reasonable potentialities and a desired strain response in flexible electronic devices that effectively control damage.³⁴ A schematic representation (Figure 4) of the formation of vitrimers is shown below.

2.2. Sulfur Chemistry. It is considered to be a weak dynamic covalent bond and can undergo exchange reactions without catalytic action, even at room temperature. The higher reactivity was observed in aromatic disulfide linkages. The preparation strategies involve disulfide-containing aromatic diamines, thiols, anhydrides, and acids. We find them in dual cross-linking systems. Mostly, the dissociative pathway has been noticed in sulfur chemistries. The bioderived sources are rarely observed as raw materials, and the elemental sulfur is widely used for this reaction mechanism. Disulfide exchange can happen in an associative or dissociative manner, or both, depending on the circumstances and the disulfide substitution patterns, under the influence of heat, UV light, basic catalysts, or mechanical force. Numerous research teams have created a number of catalysts that enable the disulfide bonds in the networks to run smoothly. According to the researchers, some examples of compounds that have demonstrated effective reactivity in elastomeric vitrimers are the tri-*n*-butyl phosphine and copper(II)-based complex.^{20,25,26,35} In the case in point, a work suggested by Wu et al., an asymmetric alicyclic structure next to aromatic disulfide was discretely added to the polyurethane (PU) elastomer's core. In particular, a one-pot process of polycondensing poly(tetramethylene ether glycol) (PTMEG), isophorone diisocyanate (IPDI), and *p*-hydroxydiphenyl disulfide (HPS) was used to create this type of elastomer, known as PU-HPS. It is possible to modify the

molecular mobility and phase morphology of PU-HPS by varying the HPS concentration. As a result, it is possible to customize the dynamic interchange of disulfide and hydrogen bonds in the hard segment domains. The optimized sample exhibits exceptional toughness (109.1 MJ/m³), total scratch recovery (100%), excellent self-healing efficiency after fracture (90.3%), and exceptional tensile strength (46.4 MPa).³⁶ Another strategy of introducing disulfide bonds to the ENR network was suggested by Liu et al. He envisioned a simple one-step method through the reaction of 2,2'-dithiobenzoic acid (DTSA). The processing temperature was 165 °C, and a proton (H⁺) from the acid group initiated the nucleophilic attack on the epoxy groups, resulting in a ring-opening reaction. A significant enhancement is noted in the mechanical properties, where the tensile strength has been increased to 7 MPa and elongation at break noted in the range of 1100%.³⁷

2.3. Olefin Metathesis. Earlier studies showed that olefin metathesis works under catalysts, and the main reported catalyst is a Grubbs second-generation Ru catalyst. The olefin metathesis is assumed to be a powerful methodology to bring out highly efficient vitrimers. It is believed that olefin metathesis is a potent technique for producing vitrimers that are incredibly effective. Lu et al. presented Ru Grubbs' catalyst as a means of accelerating the reaction in their early investigation on olefin metathesis. A polybutadiene (PBD) network with dynamic cross-linking has been created. It demonstrated a flexible mannerism without restricting its mechanical attributes. The findings demonstrate that the Ru-catalyzed olefin metathesis processes directly led to improved malleability of the material. It could demonstrate the non-cross-linked polymers' processability and the cross-linked polymers' mechanical strength, producing bendable and insoluble networks. Because of its effectiveness and the availability of numerous polymers containing olefins, this approach has been discovered to have a wide variety of applications in the development of responsive materials.^{20,38}

2.4. Alkoxyamines. This mechanism is known for its capacity to endure reversible homolytic bond cleavage at optimum temperatures. Nitroxide-mediated radical polymerizations, which control the formation of radical propagating polymers through an equilibrium activation–deactivation mechanism, have been developed using reversible bonding.

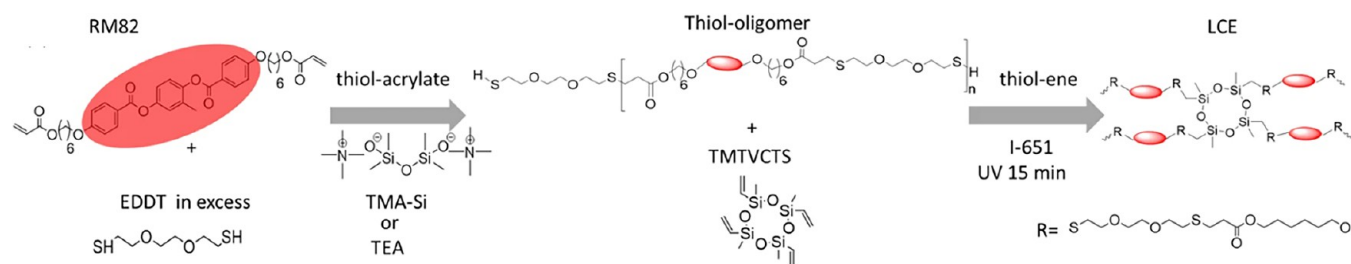


Figure 6. Graphical representation of the double click chemistry in the formation of LCE.

These stable nitrosyl radicals are used in several cross-linked systems to provide processability.²⁰

2.5. Imine and Vinylogous Urethane Exchange. Imine bonds usually exchange via imine–imine metathesis or an imine-amine exchange occurs between them. Schiff bases, also known as imine bonds, are mostly created when an amine and an aldehyde react. It is clear that under moderate circumstances, they can proceed through imine–amine exchange or imine–imine metathesis without the use of a catalyst. Because multifunctional aromatic aldehydes are more readily available and exhibit greater stability than aliphatic aldehydes, they are used as cross-linkers in the majority of situations where they react with amino-modified polymers. A lot of research has been done on elastomers like PB and Styrene Butadiene Rubber (SBR).³⁵ In a study published earlier in 2022, Lin et al. described a novel class of reactive mesogens that are entirely based on the aromatic imine structure and that permit stable and rapid bond exchanges in imine-based liquid crystal elastomers. Here, they discovered that because of their structural resemblance to the resveratrol molecule, they had a well-known scavenging capacity. Compared to other vitrimer systems, this bond exchanges considerably more quickly because of its short relaxation time, as reported by the literature, and the pictorial representation is given (Figure 5).³⁹

The vinylogous urethane reactions can be considered as a feasible method to produce the reprocessable elastomers.²³ Imine bonds frequently occur in the dual cross-linking strategy of vitrimers. A recent research has occurred in which imine bonds, together with boronic ester linkages, formed the dual cross-linking vitrimers.⁴⁰ The synthesis of an elastomeric vitrimer based on the vinylogous urethane mechanism is presented in a study proposed by Stukenbroeker et al. Using a bis-vinylogous urethane cross-linker, the polydimethylsiloxane with pendant amino works as mentioned. By adjusting the cross-link density, the elastic characteristics of this material may be controlled over a broad range of moduli. At 100 °C, reshaping and recyclability were seen. Double relaxations were found upon closer examination of the dynamic nature; they might be suppressed by hiding free amino groups. Ultimately, a single-pot, solution-castable formulation of a nondynamic permanent elastomer was created as a result of these investigations. These findings pave the way for the creation of quenchable vitrimers or cross-linked materials that display typical elastomer qualities during shaping or recycling.⁴¹

2.6. Urea/Urethane Exchange. The urea exchange occurs frequently in poly(urea-urethane)s under dissociative mechanisms, but in some situations it will be carried out via an associative mechanism of aromatic urea and pendant aromatic amine groups.⁴² Transesterification is mostly exploited by researchers, but transcarbamylation has been underexploited by the science community. It is also called transurethanization,

or urethane exchange. This can be related to the production of toxic isocyanates and tin-based catalysts involved in the processing of carbamates or polyurethanes.⁴³ A reversible and automatically repairable polymer synthesized via hindered dynamic urea bonds. They try to attach amine-containing, bulkier substituents to urea nitrogen. Its dynamic behavior can be altered by varying the bulky substituents attached to the urea nitrogen.⁴⁴

2.7. Siloxane Exchange. Siloxane exchange was introduced in 2012 by McCarthy. Siloxane vitrimers are known for their good rearrangement capability, which, in turn, improves the reprocessability of the entire system. This mechanism is actualized by common reagents.²⁶ Because these mechanisms have outstanding thermomechanical features, such as high failure strain and high actuation stroke, they are well-known for producing high-performance materials.³⁵ According to Saed and Terentjev, the siloxane mechanism produces programmable elastomeric liquid crystals. To produce networks that are consistently cross-linked, they suggest a strong reaction known as the “double-click” chemistry of thiol-acrylate and thiol-ene. Liquid-crystalline elastomers (LCEs) with adjustable characteristics, a low glass transition (−30 °C), a controlled nematic to isotropic transition (32 to 75 °C), and a very high vitrification temperature (250 °C) are produced when the siloxane cross-linker and click chemistry are combined. Thus, across several thermal actuation cycles without any creep, this class of dynamically cross-linked LCEs exhibits thermal stability throughout the operating temperature range (−50 to 140 °C). Finally, materials that experience several phase changes in separate regions of the sample sequentially and reversibly may be created by welding multiple LCEs with the same siloxane exchangeable bond into a single structure.⁴⁵ The schematic illustration of the double click chemistry for the formation of the siloxane dynamic bonds is represented below (Figure 6).

2.8. Boronic Ester Exchange. Boronic ester linkages are another class of dynamic bonds often used for the preparation of vitrimer systems. Imine bonds, which are prone to hydrolyze under simple circumstances, have a striking resemblance to boronic ester bonds. It is discovered that the highly dynamic, low activation energy elastomeric vitrimers based on imine exchange and boronic ester connections exhibit poor creep resistance. This creep can be suppressed by including a small fraction of permanent cross-links, strong noncovalent bonds such as metal–ligand bonds.³⁵ Huang et al. suggest a boronic exchange mechanism with the 4-carboxyphenylboronic acid pinacol ester, and in this formulation, silica was used as a filler in the ENR matrix. This boronic exchange endows the system with self-healing and reprocessability. This type of interfacial cross-link is believed to be observed in hydroxyl-rich nanomaterials and the commonly used epoxy polymers. The

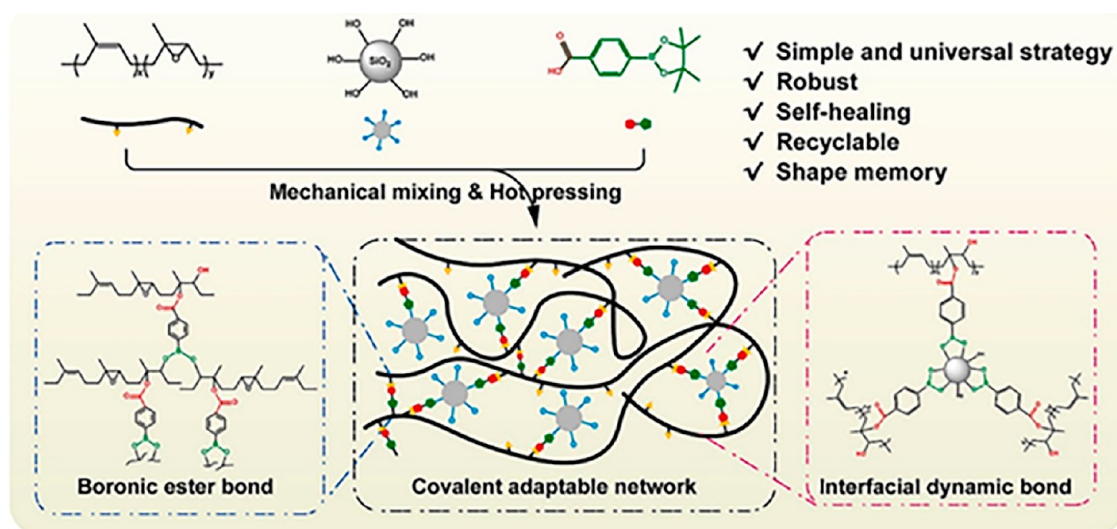


Figure 7. Boronic ester linkages. Reproduced with permission from ref 46, Copyright@2022, Elsevier Ltd., Composites Science and Technology.

construction scheme of the network is given below (Figure 7).⁴⁶ Boronic ester bonds can also function effectively in dual cross-linking systems. This approach gives the vitrimeric systems more property improvement. In an intriguing study published recently, Wang et al. attempted to combine dynamic boronic ester bonds with supramolecular hydrogen bonds. For this aim, modified rubber was cross-linked with dimercaptoborate (BDB), which serves as a source of boronic ester linkages using SBR rubber. There was a noticeable improvement in the mechanical characteristics.⁴⁷ In a recently discussed work, they show how to construct dynamic dual cross-links of boronic esters and coordination bonds into a commercial rubber to prepare mechanically tough, yet healable, and recyclable elastomeric vitrimers straightforwardly. In particular, a boronic ester cross-linker containing dithiol is covalently cross-linked with ENR by a chemical interaction between epoxy and thiol groups. Through boronic ester transesterifications, the covalently cross-linked networks can change their topologies, giving them the capacity to heal and reprocess. Specifically, the incorporation of sacrificial metal–ligand coordination connections into the networks can significantly improve their mechanical characteristics without sacrificing their capacity to heal or reprocess.³⁰

3. VITRIMERS—A SUSTAINABLE APPROACH

Polymers have offered precise answers to all of the demands of contemporary living and have been warmly accepted in all spheres of human life. But, in the current scenario, “eco consciousness” more or less catalyzes the innovation and industry. Preserving the world for the coming generation has become the aim of science today. This concept intuitively triggers the research community to design and redesign materials that establish a circular economy, apart from the existing linear economic models. Endurable polymeric materials with enhanced properties possibly appear as an urgent need of the day. Thermosets excel in thermomechanical stability and chemical resistance and go further with the lightweight applications, whereas the thermoplastics out-compete in their reprocessability. The thermoset polymers with a 3D network of interconnected chains are unusable for reprocessing or remolding, whereas the thermoplastics gradually undergo harder and traditional mechanical recycling

processes. Thus, they significantly diminished their mechanical properties. Since polymer recycling requires an advanced level of sophisticated methods and technical challenges, a counter-plan to industrialize the hybrid form of thermosets and thermoplastics through vitrimers can be considered the unique solution to the prevailing issues. Vitrimers, termed as the new generation polymers, concurrently exhibit the mechanical and thermal properties of thermosets and the malleability and reprocessability of thermoplastics.^{27,29,48,49}

4. ELASTOMER-BASED VITRIMERS—AN OUTLOOK

By considering the fast growth of research in vitrimers, a great deal of work has been carried out in the area of elastomer-based vitrimers. Despite their soft nature and ability to distort, elastomers are frequently utilized in a variety of applications. The material can be made recyclable and developed for more complex uses with the aid of reversible covalent networks. Additionally, it can lessen the negative effects that the irreversible covalent networks produce.⁵⁰ Vitrimers are a new development in the field of polymers that have the potential to produce a great deal of effort and outcomes for science. Epoxidized elastomeric vitrimers consistently rank the highest due to their superior mechanical, electrical, and flexible qualities. ENR is noted as a unique elastomer. The excellent weather/oil resistance and low air permeability can be attributed to the presence of polar oxirane groups in its backbone. A synthesis of ENR-based vitrimers suggested by Feng et al. follows a photoinduced self-healing behavior and responsiveness to pH, attributed to the addition of aniline trimer amino-terminated aniline trimer (ACAT), which accelerates the transesterification reaction in turn.³¹

A different study shows how biobased polylactide (PLA) and layered double hydroxide can be produced on the ENR. The presence of extra β -hydroxyl esters between PLA and ENR can give the system a number of benefits, including the ability to heal. The rearrangement of cross-linking rubber networks can be accomplished through dynamic mixing between PLA and ENR chains due to the transesterification reactions of β -hydroxyl ester bonds between PLA and ENR. Concurrently, the E-LDH takes part in the formation of the network of hybrid rubber. These elements lead to the conclusion that it is a promising area for industrial

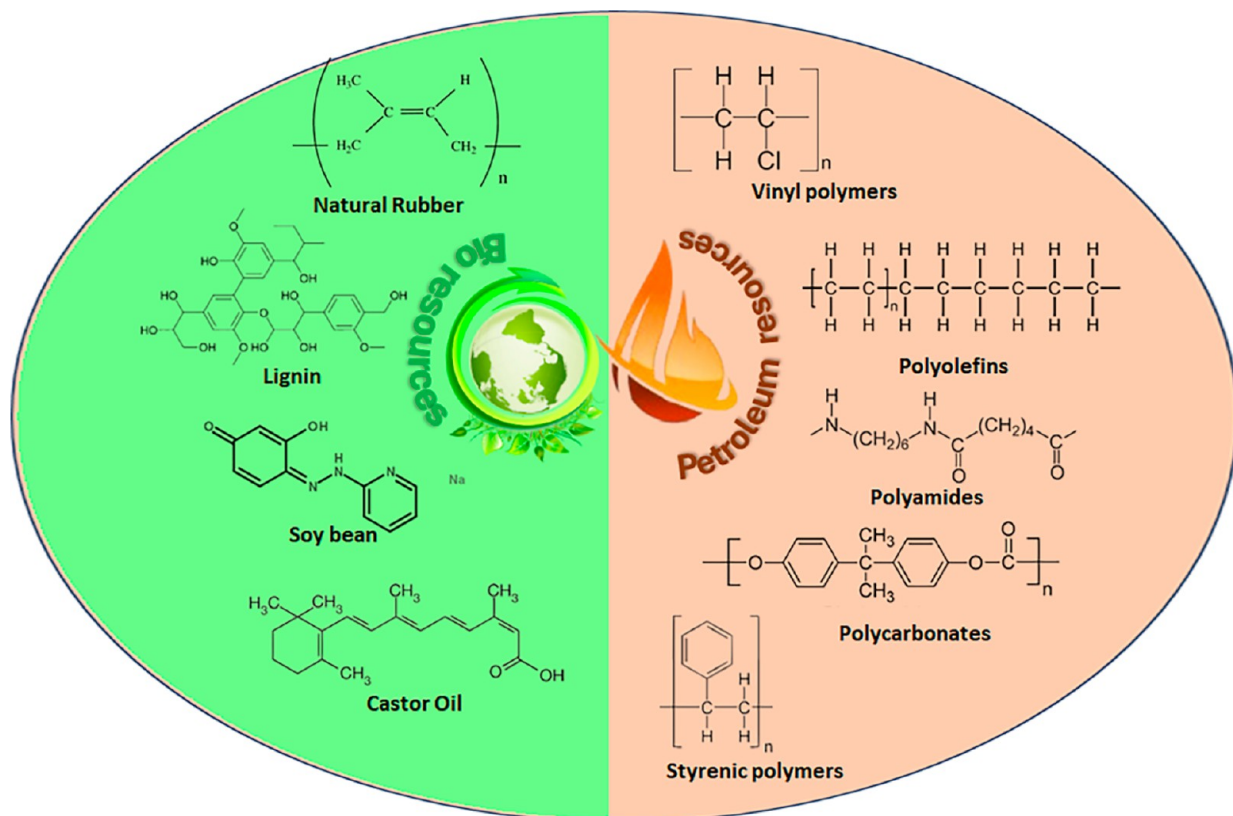


Figure 8. Graphical representation of bio and petroleum resources of vitrimer synthesis.

applications.⁵¹ The development of a biobased ENR vitrimer using oxidized starches (OST) as a cross-linker was proposed as a green approach. The varying content of the OST and the dynamic bonds developed from the β -hydroxyl ester bonds resulted in improved tensile strength, elongation at break, and elastic resilience of ENR, as well as excellent shape memory performance and reprocessing capability for ENR/OST. The ENR/30OST-57 vitrimer reaches 9.0 MPa tensile strength, 1108% elongation at break, and 88% elastic recovery when the content of OST-57 is 30% phr.⁵² Yang et al. suggested a novel approach in which they used adipic acid as a cross-linker for ENR and simultaneously incorporated CNC to produce β -hydroxyl ester bonds. It would provide a large number of H–H-bonds and help to enhance the properties of the system.⁵³

4.1. Elastomer-Based Vitrimers—Evolution and Importance. Elastomers play the chief role in the life cycle of modern society. Its multidisciplinary potential uses make it an unavoidable part of modern society, yet the nonbiodegradability has been a long-term challenge for the elastomer industry. Mitigating some of the sustainable trials into elastomers gives way to better prospects. Many devulcanization procedures are found in use, and ultrasound, microbial degradation, and pyrolysis are some of the noted concerns. Dynamic covalent bonding and its integration into elastomeric networks have been the subject of promising studies.²³ A graphical illustration of the various bio and petroleum sources of vitrimers^{19,29,54–56} are shown below (Figure 8).

5. TYPES OF ELASTOMERS BASED ON VITRIMERS

A large number of vitrimers have been developed using the elastomers as a matrix. They include NR and other synthetic rubbers. The table (Table 1) below represents some reported

works of elastomeric vitrimers, their components, cross-linkers, and processing temperatures.

5.1. Natural Rubber Vitrimers. The dynamic bond concept has been integrated into elastomeric networks to enable recycling of covalently cross-linked elastomers.⁵⁸ Numerous studies in this field, in NR latex and other rubber varieties, have been published. It is fascinating to observe that the materials introduced to the matrix affect the features and characteristics of the ENR vitrimer. With the alcoholysis of Maleic Anhydride (MAH), a bio- and catalyst-free vitrimer has been created using ENR and several carboxylic acids (Maleic anhydride). The cross-linked and ENR have strong reprocessability because of their ability to achieve topological rearrangements by transesterification, which was made possible by the inclusion of β -hydroxy ester connections in the covalently cross-linked networks.⁵⁷ Trinh et al. have brought forth innovative work on the vitrimer from Maleic anhydride-grafted ENR vitrimers. After multiple recycling cycles, the mechanical qualities were thoroughly examined by using tensile strength analysis. Even after numerous recycling runs, the NR vitrimer continued to show only slight indications of heat damage. The stress–strain curve, tensile strength, elongation at break, and elastic modulus of the NR vitrimer showed minimal reduction in properties, even after four cycles of recycling. The tensile test revealed that the vitrimer after the second, third, and fourth cycles of reprocessing retained the same mechanical properties as the initial vitrimer, showing that dynamic networks remain dominant. Furthermore, the created NR vitrimer demonstrated exceptional self-healing characteristics with up to 96.5% efficiency. The NR samples may be welded together while maintaining their original mechanical properties by using heat to promote the quick dynamic exchange vitrimer

Table 1. Different Types of Elastomer-Based Vitrimers Reported in the Literature

elastomer matrix	materials	chemistry involved	cross-linker	processing temperature (°C)	ref
epoxidized Natural Rubber (ENR)	ENR/poly(lactide (PLA)/layered double hydroxide (LDH)	transesterification	DCP	170	51
	ENR latex/OST (oxidized starch)	transesterification	oxidized starch with 57% carboxyl content (OST-57)	140	52
	ENR/maleic anhydride/carboxylic acids	transesterification	maleic anhydride	180	57
	XNBR/ENR	transesterification		160	58
	ENR/silica	boronic ester linkages	silica	180	46
	ENR/sodium alginate (SA)	ester linkages		180	50
	(ENR)/citric acid-modified bentonite (CABt)	ester linkages	citric acid	160	59
	ENR/Diacid/Tri acids	β -hydroxy ester bonds	diacids	150	18
	ENR/TEMPO oxidized cellulose nanocrystals (TOCNs)	β -hydroxy ester bonds	TEMPO oxidized cellulose nanocrystals (TOCNs)	180	60
	ENR/Thiol/BDB	boronic ester bonds	dithiol-bearing boronic ester	160	30
styrene butadiene rubber (SBR)	ENR/dimer fatty acids (DFA)	β -hydroxy ester bonds	dimer fatty acids (DFA)	170	61
	ENR/dodecanedioic acids (DAs)/(ACAT, a oligoaniline)	esterification	dodecanedioic acids	180	31
	ENR/functional carboxymethyl chitosan (CMCS)	β -hydroxy ester bonds		170	33
	SBR/aniline trimer (ACAT)	boronic esters linkages and imine linkages	(ACAT and 4-formylbenzene boronic acid (FBA))	80	40
	SBR/2-ureido-4-[1H]-pyrimidinone (UPy)/dimercapto-borate	multiple hydrogen bonds (H-bonds) and boronic ester bonds	dimercapto-borate	80	62
silicone rubber	SBR/ β -mercaptoethanol	transesterification	dimercapto-borate	80	63
	methyl vinyl silicone rubber (MVQ)	boronic ester linkages	2,2'-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane] (BDB)	150	64
	silicon vitrimer/functionalized boron nitride nanosheets (fBNNS)	disulfide linkages	octaglycidyl polyhedral oligomeric silsesquioxane (POSS)	150	65
polyimine elastomer	polyimine vitrimers derived from renewable vanillin	condensation polymerization	diethylenetriamine (DA)	120	66
	polyimine Vitrimers	dynamic imine linkages	benzene-1,3,5-tricarbaldehyde (TFB)	60	67
EPDM	(EPDM)/carbon black (CB)	β -hydroxy ester bonds	decanedioic acid (DA)	180	68
poly butadiene elastomer	PBD with 1% benzoyl peroxide (BPO) vitrimers	olefin metathesis	benzoyl peroxide (BPO)	100	38
polyurethane-urea elastomer	3,5-dimethylthio-2,4-toluenediamine (DMTDA)	urea-urethane exchanges	N,N'-diaryl urea	100	69
XNBR	carboxyl nitrile butadiene rubber (XNBR)/TEMPO-oxidized cellulose nanocrystals (TO-CNC)	β -hydroxyl ester bonds	epoxidized soybean oil (ESO)		70
elastomer blends	vanillin derivatives (PV)/1,2-polybutadiene rubber	imine cross-links	4-hydroxybenzaldehyde	150	70
	polydimethylsiloxane	vinylous urethane exchanges	aminopro-pylmethylsiloxane	150	71
	polydimethylsiloxane	siloxane exchanges	2,4,6,8-tetramethyl-2,4,6,8-tetravinyl cyclotetra-siloxane (TMTVCTS)	250	45
	(BNR-1% E-PABI, epoxy natural rubber vulcanized with bis (6-membered cyclic carbonate)	hydrogen bonds	bis(6-membered cyclic carbonate)	80	72
	carbon black (CB)/polysiloxane	imine bonds	poly-dimethylsiloxane (PDMS)	100	73
	terpene-based β -myrcene/2-(acetoacetoxy)ethyl methacrylate (AAEMA)	vinylous urethane exchanges	priamine 1075 and tris(2-aminoethyl)amine (TREN)	110	74
	commercial poly(ethylene- α -octene) (POE) vitrimer	dynamic dioxaborolane cross-links	dioxaborolane	170	75
	polydimethylsiloxane (PDMS)/polyborosiloxane (PBS)	boron/oxygen dative bonds	polydimethylsiloxane (PDMS)	160	76
	poly butadiene rubber	disulfide linkage	disulfide-containing dicarboxylic acid	160	77

network, demonstrating the rubber vitrimer's considerable potential for use in advanced material applications.⁷⁸ The schematic representation of the NR vitrimer formation is given below (Figure 9).

Amines are considered to be more efficient curing agents than carboxylic acids. An amine-based epoxy vitrimer reported by Sun et al. shows high quality, and it possesses dynamic dual cross-links due to the presence of hydroxyl ester groups and the integrated disulfide linkages.⁷⁹ The use of silica for cross-linking was another inventive idea by Huang et al. ENR is cross-linked through silica by adding 4-carboxyphenylboronic

acid pinacol ester (carboxyphenylboronic acid pinacol ester (CAPE)). Reversible networks are formed through interactions between the carboxyl groups of CAPE and the epoxy functional groups of ENR, with silica serving as the cross-linking agent. This vitrimer met the primary goals of self-healing and recyclability of vitrimer systems. The cross-linker silica and CAPE with ENR produce the boronic ester interface by ring opening transesterification. Such ester bonds can form through the interaction of the hydroxyl groups in silica.⁴⁶ Functional carboxymethyl chitosan (CMCS) was used to construct a biobased vitrimer from ENR. This filler

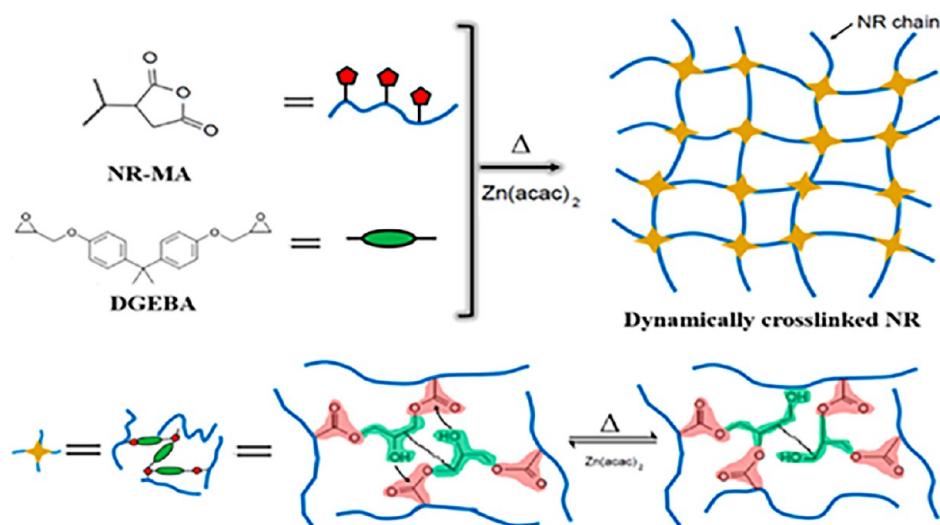


Figure 9. Schematic representation of the vitrimer formation in the anhydride epoxy NR system. Reproduced with permission from ref 78, Copyright@2023, American Chemical Society, ACS, Applied Polymer Materials.

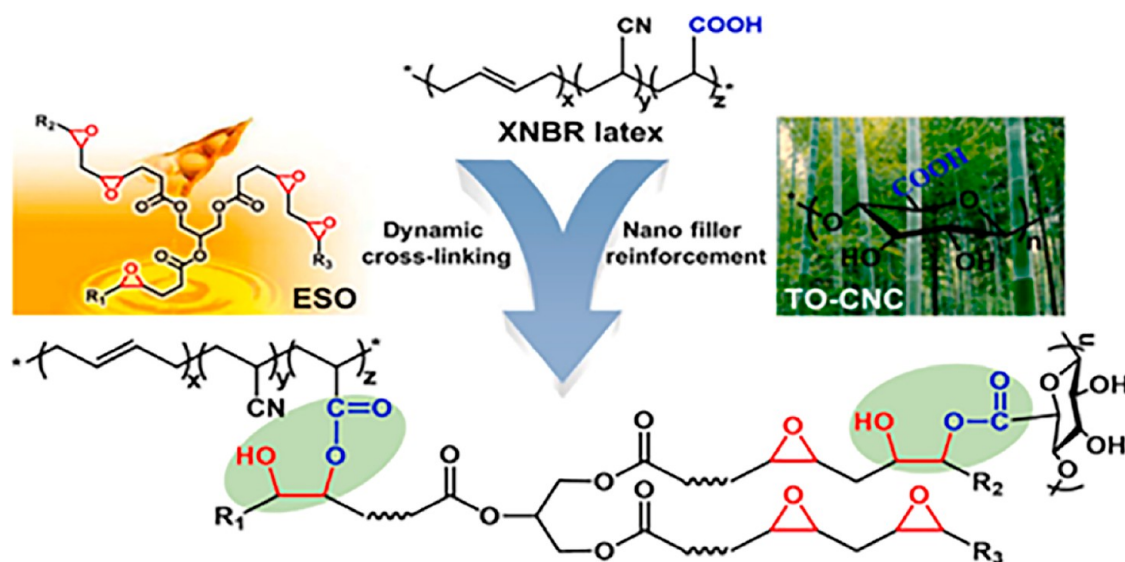


Figure 10. Schematic representation of the cross-links in the TO-CNC system. Reproduced with permission from ref 70, Copyright@2023, Elsevier Ltd., Composites Communications.

demonstrated outstanding efficacy since its uniform dispersion makes it a fitting option for vitrimers and its topological rearrangements.³³

5.2. Styrene Butadiene Rubber Vitrimers. A very interesting study reported by Wang et al. focused on the styrene–butadiene rubber (SBR) and introduced the amide functionalities by synthesizing it with 5-benzyl-3,6-dioxo-2-piperazineacetic acid (DKP) and further cross-linked by dimercapto-borate via thiol-ene “click” chemistry. The hydroxyl-functionalized SBR was obtained by the grafting of commercialized SBR with the β -mercaptoethanol followed by the grafting of DKP. The product was equipped with amended creep resistance and extended malleability by the incorporation of the quadrupole hydrogen bonding, which keeps it as a substantial vitrimer.⁶³

Recent observations of elastomeric vitrimers brought out a new type of cross-linking called dual cross-linking, which is most commonly observed in SBR-based vitrimer systems. Wang et al. designed and synthesized a series of vitrimer

networks by incorporating multiple hydrogen bonds (H-bonds) and boronic ester bonds into SBR.⁶² Specifically, SBR was first modified with 2-ureido-4-[1H]-pyrimidinone (UPy) and subsequently cross-linked using dimercapto-borate. The π - π stacking of the UPy rings, combined with lateral multiple H-bonds between ureido groups, promotes the aggregation of grafted UPy moieties, resulting in a microphase-separated structure.

Analysis of the mechanical properties of the boronic ester cross-linked SBR vitrimer revealed that the UPy modification significantly enhances mechanical performance. For instance, the Young’s modulus, ultimate stress, and fracture energy of the optimized sample were measured at 2.14 MPa, 3.01 MPa, and 3.15 MJ/m³, respectively—representing 2.5, 3.3, and 2.1 times the values of unmodified SBR systems. The boronic ester bonds provide flexibility to the network, while the H-bonds connecting the UPy dimers improve the overall mechanical strength. Additionally, UPy aggregations act as sacrificial units, dissipating energy through reversible rupture and reformation,

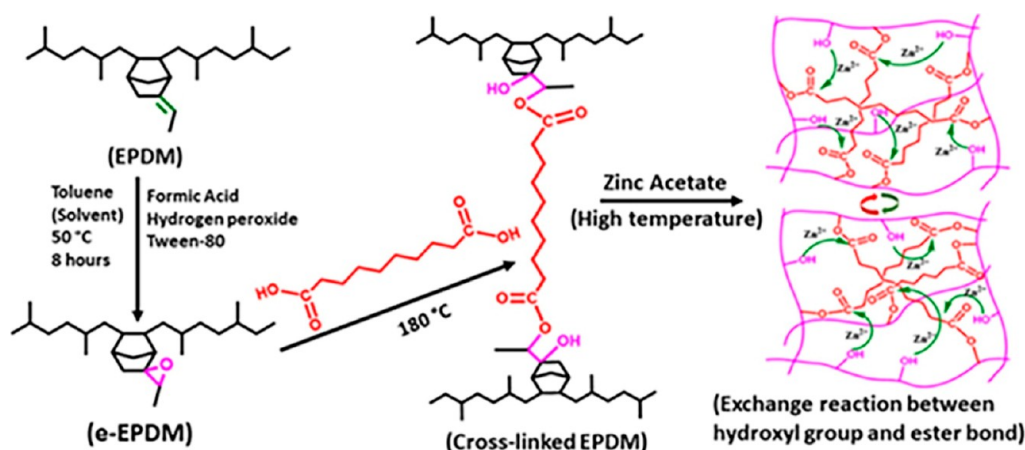


Figure 11. Schematic representation of the transformation of EPDM into e-EPDM, followed by the phenomena of cross-linking and vitrimeric bond exchange. Reproduced with permission from ref 82, Copyright@2024, American Chemical Society, ACS Sustainable Chemistry & Engineering.

thereby further enhancing the mechanical properties of the rubber vitrimer.⁶² Some of the works were reported for carboxylated SBR (XSBR). The influence of ester bonds and the properties of XSBR was evaluated by Yang et al. A synthetic diglycidyl ether (DGESA) and 1,4-butanediol diglycidyl ether (DGEBO) were used to fabricate two such vitrimers. The observed cross-link density was two times greater for DGESA cross-linked ester bonds. It possesses a shorter relaxation time and exhibits higher healing efficiency than those cross-linked by DGEBO. All these properties are attributed to the large number of ester bonds formed in (DGESA) cross-linked vitrimers than (DGEBO) cross-linked vitrimers.⁸⁰

5.3. Acrylonitrile Butadiene Rubber (NBR) Vitrimers.

5.3.1. Carboxylated Nitrile Butadiene Rubber (XNBR). Most of the time, NBR mixes have been used in place of NBR vitrimers. Typically, carboxylated nitrile butadiene rubber (XNBR) has been used extensively. Wang et al. reported a recyclable elastomeric vitrimer prepared by blending XNBR and ENR, which demonstrated superior mechanical strength compared to other studies documented so far.⁵⁸ Creating a vitrimer using TEMPO-oxidized cellulose nanocrystal (TO-CNC) and XNBR composites was another effective technique. Remarkable mechanical reinforcement and increased tensile strength are attractive factors of the system.⁷⁰ The graphical representation of the cross-linking through acid epoxy groups is given below (Figure 10).

5.4. Ethylene Propylene Diene Rubber Vitrimers.

Ethylene propylene diene monomer (EPDM) rubber has been widely used as a synthetic rubber that exhibits higher elasticity, stability, impressive electrical insulation, and remarkable aging resistance. Its wide application band includes cables, sealing elements, and gaskets used in automotive and construction fields.⁸¹ Zhang and co-workers presented an innovative green curing approach for creating elastomeric vitrimer composites using commercial EPDM. The assembled epoxy rings strengthen the cross-linking sites and give the system dynamic connections. Exchangeable β -hydroxyl ester linkages were then created by cross-linking the epoxy-functionalized EPDM (e-EPDM) with dicarboxylic acids. Preferably, CB loadings result in a particular improvement in the system's modulus, which is explained by the greater restriction on chain mobility brought on by the interphase that forms between CB and EPDM.

Additionally, the recycled e-EPDM/CB composites had tensile strengths and elongations at break of more than 15 MPa and 200%, respectively.⁶⁸ The freshly developed biobased EPDM rubber promotes the circular economy and sustainability. Aziz et al. proposed a similar strategy and developed an EPDM vitrimer. The study's objectives were to analyze the epoxidized and diacid (decanedioic acid)-cured EPDM rubber samples' mechanical qualities, stress relaxation, cure characteristics, and recyclability. All four of the developed samples showed great promise for real-world uses based on the results of the mechanical, stress relaxation, and physical tests. When compared to those documented in the literature, the recycled sample exhibits better mechanical qualities, indicating that it would be suitable for application in the rubber industry. Below is the schematic illustration (Figure 11) of how EPDM is converted to e-EPDM and then to vitrimers. Consequently, the created epoxy rings actively increase the cross-links of the system.⁸²

5.5. Silicone Rubber Vitrimers. Methyl vinyl silicone rubber (MVQ) is an extensively used rubber material and is transformed to a vitrimer by the introduction of boronic ester linkages. More or less, it possesses a thermoplastic character, shows rate-dependent mechanical properties, and is applied in the areas of impact resistance.⁶⁴ Catalytic activation is primarily responsible for the formation of cross-links in the vitrimer matrix. However, Ishibashi and Kalow suggested that the silicone elastomer undergoes an uncatalyzed reversible conjugate addition. In essence, it was a thiol-ene reaction, which typically happens in systems of typical polymers. After ten reprocessing cycles, tensile testing of the recycled rubbers reveals very little change in Young's modulus. The rubbery plateau has a storage modulus E' of about 380 kPa, according to the DMTA data. The glass transition temperature (T_g , peak of $\tan(\delta)$) is 106 °C, and it is accompanied by a significant increase in the storage modulus. Ten cycles of reprocessing left these features essentially unaltered.⁸³ A novel methodology for constructing a dual-bonding recyclable and reprocessable system has been suggested by Bai et al. Introducing Zn (II) amino coordination linkages into the cross-linked system of imine-CB/PDMS (propyl methyldiethoxysilane) on the silicone elastomer evidently shows the enhancement in the mechanical parameters. An activated electroconductivity is also observed in this system.⁷³ The graphical illustration (Figure

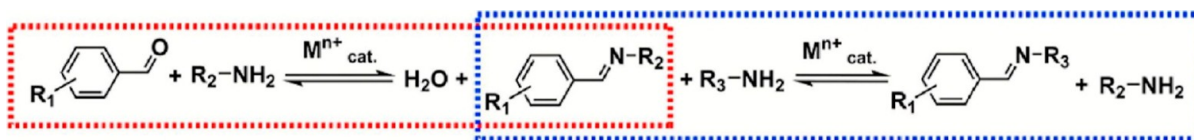


Figure 12. Reaction mechanism of the Schiff-base reaction and transimination reaction. Reproduced with permission from ref 73, Copyright@ 2021, Elsevier Ltd., Composites Part B: Engineering.

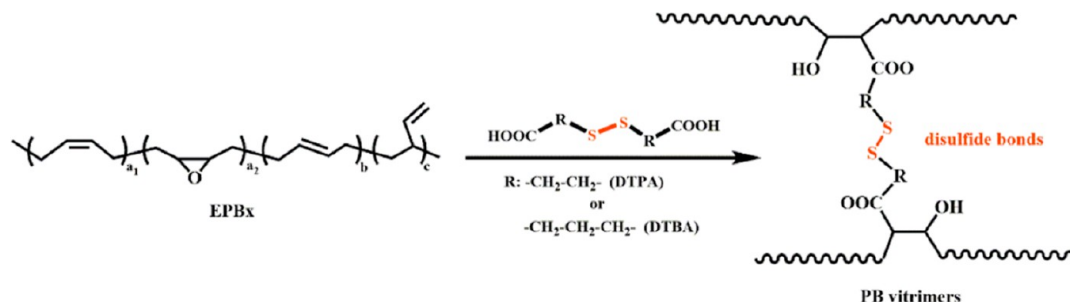


Figure 13. Disulfide bond formation of the carboxylic acid groups and epoxy groups of the PB vitrimer.

12) of the Schiff-base reaction and transimination reaction is given below.

5.6. Polyurethane Vitrimer. The conventional polyurethane thermosets are usually upcycled to vitrimers by introducing covalent adaptable networks into them. There are very limited works occurring in the research field based on the vitrimer synthesis from polyurethane elastomers. Sarkari-Oskuei et al. introduced a pseudopolyurethane vitrimer with unique mechanical properties in addition to the polyurethane vitrimer. A comparison between a pseudovitrimer and normal polyurethane reveals that the latter has inferior recycling efficiency and lacks the former's superior thermomechanical qualities. A cysteine dichloride chain extender is used along with triethylamine and dithiothreitol catalysts to make a polyurethane vitrimer. The extended use of cysteaminium dichloride has been ascribed to the repeatable behavior.⁸⁴ Another vitrimer was formed from the commercial compounds such as 4,4'-diphenylmethane diisocyanate (MDI), Poly-(oxytetramethylene)glycol (PTMG) and 3,5-dimethylthio-2,4-toluenediamine (DMTDA) are used to create cross-linked polyurethane-urea elastomers, which exhibit exceptional mechanical performance with tensile strength and elongation at break exceeding 20.0 MPa and 529%, respectively. At 120 °C, these elastomers' *N,N'*-diaryl urea can exchange by an associative process. Reshaped and reprocessed samples of these elastomers exhibit improved mechanical qualities.⁶⁹

5.7. Polybutadiene Vitrimer. Yang et al. propose recycling end-of-life rubber as a more environmentally friendly way to lower the large annual consumption of the polybutadiene elastomer. Using a catalyst-free, one-pot technique at room temperature, they envisioned incorporating the imine-coordinated boroxine into the polymer network to create flexible, high-strength polybutadiene-based (PB) transparent materials with shape-memory behavior and recyclability. By first grafting the PB rubber with amino groups and then inducing the N-coordinated boroxine, it operates using a dual dynamic bond mechanism. By combining the benefits of imine (toughness) with N-coordinated boroxine (strength), the exceptional mechanical qualities (tensile strength up to 12.35 MPa) can be adjusted by varying the cross-linking density. Excellent malleability, reprocessability, and thermally induced shape-memory behavior are all displayed by the material.⁸⁵ An

epoxidized PB was synthesized via a reaction-controlled phase transfer catalyst. The increased number of epoxy groups enhances the exchange of disulfide bonds effectively. Its cross-link density plays a significant role in the mechanical properties. The topological rearrangement was observed at elevated temperatures. It was evident that their mechanical properties could be preserved after recycling.⁷⁷ A graphical representation of the PB vitrimer formation through disulfide bonds is given below (Figure 13). High-performing recyclable and renewable vitrimers have been formulated from a biooriginated vanillin derivative and 1,2-polybutadiene rubber. PB is a renewable monomer resource abundant with aldehyde groups that may supply a stiff backbone structure, a multitude of reactive sites, and good mechanical qualities to materials. The imine junction is also dynamic. The material gains self-welding, solid-state malleability, and thermally induced reprocessing features through metathesis, while solvent recycling at room temperature is made possible through transamination. Additionally, the material has strong antimicrobial qualities and good shape memory behavior.²

5.8. Elastomer Blends. Recently, growing attention has been given to elastomeric blends due to their multiple properties in comparison to their individual properties. The blend of XNBR and ENR exhibited a self-cross-linking nature as a result of the epoxy acid reaction that took place in XNBR and ENR. Under suitable conditions, the blend can form β -hydroxyl ester linkages, which further undergo topological rearrangement through transesterification. A significant enhancement was observed in the mechanical properties, even after several cycles of recycling. This can be attributed to the strain-induced crystallization character of ENR.⁵⁸

6. PROPERTIES OF VITRIMERS

6.1. Recycling Ability. Because of their recycling qualities, vitrimers are superior to conventional polymers and have been recommended as a way to cross the barriers to a sustainable environment. This property falls into both chemical and physical recycling categories. Physical recycling involves physically reprocessing the material by a few different methods. Chemical recycling is further divided into two categories: bond exchange reprocessing and recycling to monomers or oligomers.⁸⁶ Below T_v (transition temperature), the vitrimers

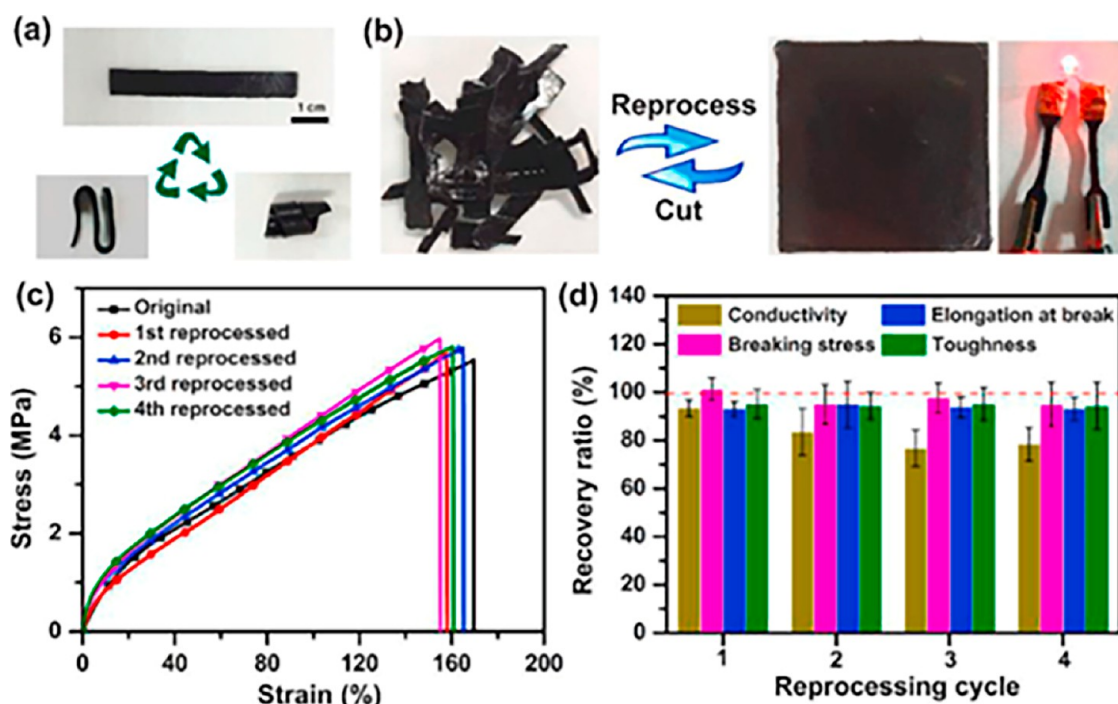


Figure 14. ((a) Reshaping and (b) reprocessing of the samples, (c) stress–strain curves of samples after multiple cycles of reprocessing (100 °C, 10 MPa, 30 min) at a constant strain rate of 20 mm/min. (d) Recovery ratio of electrical and mechanical properties of samples after multiple cycles of reprocessing. Reproduced with permission from ref 73, Copyright©2021, Elsevier Ltd., Composites Part B: Engineering).

can act as thermosets or ordinary elastomers; the malleable property is directly correlated with temperature enhancement. Since its viscosity drops with temperature, vitrimers can also be thermally recycled.⁷

In order to analyze the recycling properties of the vitrimer, the sample is made to evaluate its mechanical strength and the chemical structure by FTIR spectra after each cycle of reprocessing. A 3D printable elastomeric vitrimer was proposed by Niu et al., stressing the recycling property of the compound. The 3D printable ink that they have created can be reused up to five cycles without placing any further effort.⁸⁷ The recyclability of the (XNBR)/TEMPO-(TO-CNC) vitrimeric system is attributed to the dynamic β -hydroxy ester linkages, which cause topological rearrangement. Its mechanical qualities are compatible with the original for up to two cycles.⁷⁰

It has been demonstrated that vitrimers are recyclable and that a number of parameters influence how differently they may be recycled. A recent study demonstrates how the recycling property is impacted by the cross-linkers' length. Through the sequential coordination polymerization of myrcene and isoprene as well as epoxidation, an uneven distribution of functional groups was achieved. The samples underwent mechanical investigation to determine their strength and elongation at the break. They were crushed, repressed, and dried. The cross-linker's length has decreased, and the recovery percentage was around 59.24%, indicating an increase in recovery ability.⁸⁸ Considering the study presented by Yang et al., it is discovered that the material is highly reprocessable under thermal settings and solvent recyclable at room temperature. After multiple iterations of recycling, the material did not undergo degradation or modification. This remarkable characteristic is ascribed to the dynamic imine moiety, and it has been determined that its metathesis plays a

pivotal role in this vitrimeric structure. Although there is a slight loss of these qualities, it might be because some of the dynamic connections have broken. The mechanical properties are nevertheless comparable to the original.⁸⁹ The pictorial representation (Figure 14) shows that the current study of CB/silicone rubber demonstrated remarkable results in terms of shape and recycling characteristics. It is seen that even in the fourth cycle, the mechanical qualities were restored.⁷³

6.2. Self-Healing. Self-healing is a smart property that has been grabbing the attention of the entire science community today. Self-healing polymers involve molecular-level physical or chemical processes, sometimes overlapping. Interchain diffusion, phase-separated morphologies, shape-memory effects, and superparamagnetic nanoparticles are examples of physical self-healing mechanisms. Covalent, free-radical, or supra-molecular dynamic linkages are involved in chemical reactions. Physical and chemical activities are combined in many self-healing processes, like augmented van der Waals forces.⁹⁰ The reversible dynamic networks, which respond to the external stimulations, enable the vitrimeric sample to consequently endow it with healing and reprocessing ability.³⁰ The healing property has been analyzed mainly from the microscopic images of the cracked as well as the healed sample. The work suggested by Yuan et al. draws attention to the self-healing property of the vitrimeric sample inherited by the dynamic cross-links. A room temperature is found to be sufficient for repair, and within an hour, complete healing of the crack had occurred. The XPS spectra of the vitrimeric elastomers with varying cross-link densities have been checked. It found that with lower cross-linking content and possessing higher disulfide content on the cracked periphery, they thus performed well in healing.⁹¹ Lai et al. prepared a blend of NR and polycaprolactone (PCL) by melt blending. They have grafted different amounts of acrylic acid to the PCL backbone,

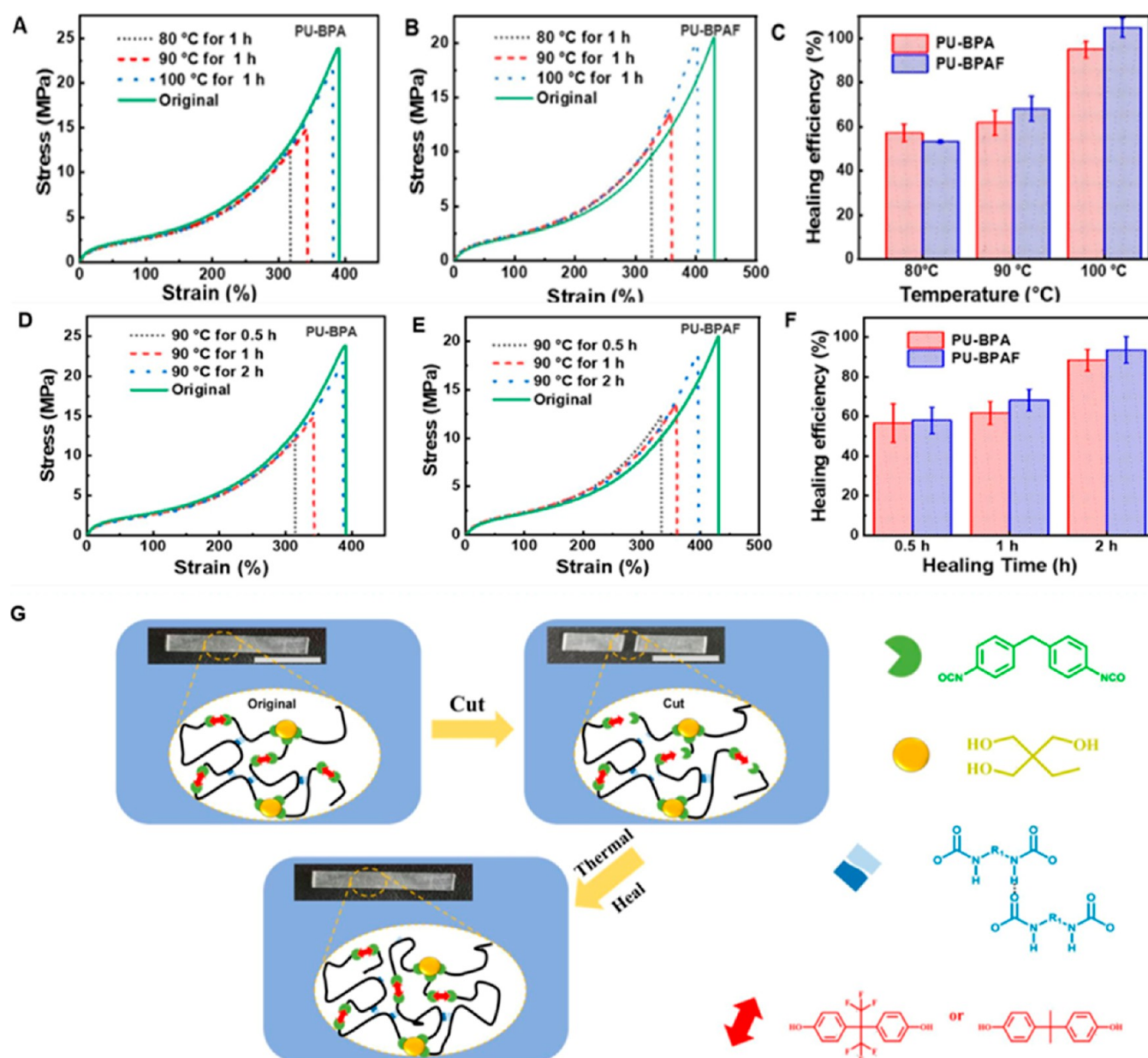


Figure 15. Self-healing properties of two elastomers. Typical tensile stress–strain curves of original and healed (A) PU-BPA and (B) PU-BPAF (healing for 1 h at different temperatures). (C) Healing efficiency at different temperatures for 1 h. Typical tensile stress–strain curves of original and healed (D) PU-BPA and (E) PU-BPAF (healing for different times at 90 °C). (F) Healing efficiency for different times at 90 °C. (G) Schematics of molecular evolution of the self-healing process of the PU-BPAF strip. Reproduced with permission from ref 94, Copyright@2022, Elsevier Ltd., Chemical Engineering Journal).

and the efficiency of healing improved due to the supra-molecular hydrogen bond interaction force.⁹² The self-healing ability assisted by the photo thermal induction was presented by Feng et al., and they reported that the two-halves of the sample had been cured completely after heating at 200 °C. The stress strain graph showed similar properties for the original as well as for the healed sample. The self-healing did not belong to the periphery alone but had occurred at the sectional periphery of the dumbbell sample.³¹ According to the study of Yang and team, the sample which possesses more ester groups enhances the transesterification reaction and in turn increases the healing, which is in conformity with the previous study.⁵⁵ The epoxy vitrimer by Chen et al. showing rapid self-healing (10 min for a 36 μm scratch) in an oven at a temperature of

130 °C for 5 min has been taken to consideration. The optical microscopic images show excellent results.⁹³ Jia et al. have published a unique study that offers an effective method for creating Turbo Electric Nano Generators out of Poly Urethane elastomers. Two vitrimers were synthesized from Bisphenol A (BPA) and Hexafluoro bisphenol A (BPAF). Approximately 100% of the healing efficiency has been seen in a brief treatment period at a moderate temperature. A stretchable and self-healing conductor PU-vitrimer was created because of its great self-healing efficiency and elongation at break.⁹⁴ The graphical representation (Figure 15) of the results of the recent work is given below.

6.3. Shape Memory. The shape memory is an interesting smart property that makes the vitrimer system dominant to

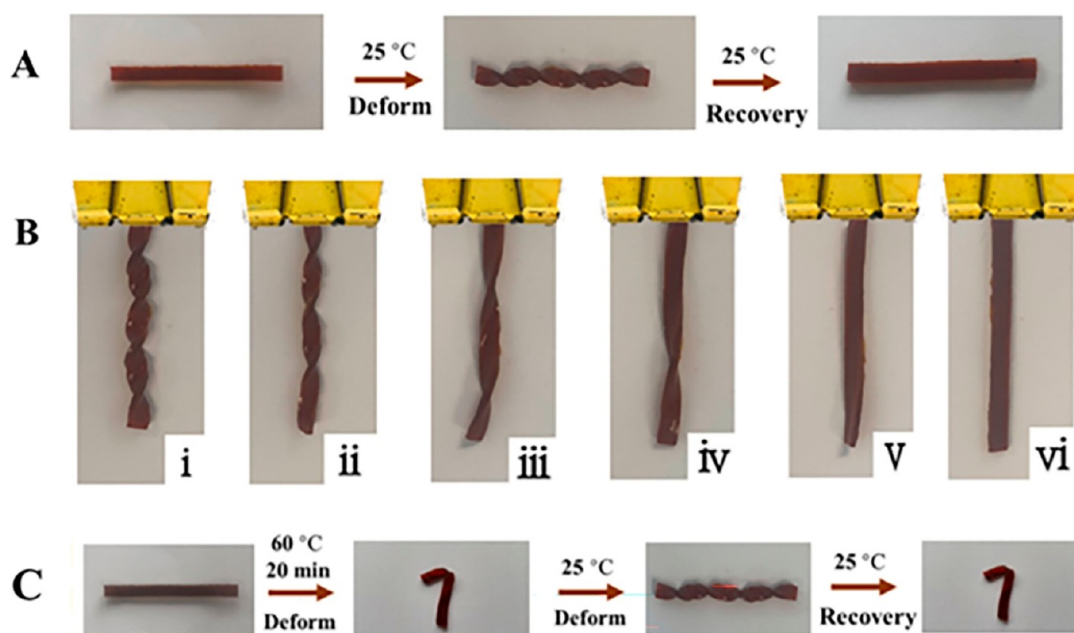


Figure 16. Shape Memory tests conducted on an ETOD-SA vitrimer. (A,C) Shape recovery process on the ETOD-SA vitrimer (B). Reproduced with permission from ref 94, Copyright@2022, Elsevier Ltd., Composites Part B: Engineering.

other polymeric materials.⁷ The construction and biological aerospace sectors have recognized shape memory composites and polymers as innovative and cutting-edge materials. If it only adapts one shape, it may have dual shape memory; if it adapts two shapes, it provides a triple shape memory. The multishape memory is now being used. It has been discovered that extrinsic stimuli such as pH, water, redox conditions, and certain solvents will cause the shape memory behavior. Systems can also be triggered by mechanical loads and ratios with varying wavelengths.⁹⁵ The role played by dynamic covalent bonds in shape memory is crucial especially in 3D shape control that may include programming, reconfiguration, and surface patterning along with reversible actuation. The shape memory property works on the mechanism of stress relaxation, entropy elasticity preservation, and structure fixation. With the introduction of dynamic bonds to the 3D networks microscopic bond exchange takes place, which may further move to macroscopic stress relaxation and results in the induced stimuli response plasticity to the materials.¹³ A pH-induced shape memory has been demonstrated in an SBR elastomeric vitrimer, according to research by Liu et al. Three forms of shape memory are displayed by the vitrimer when the submerged solutions are changed from acidic to basic.⁴⁰ By creating a segregated structure of sodium alginate (SA) in the continuous matrix of ENR and further cross-linking the composite by exchangeable hydroxyl ester bonds at the ENR-SA interfaces, shape memory has been observed in the fabricated catalyst-free and mechanically robust elastomeric vitrimer, which is discussed. It demonstrates that the rectangular sample of the resulting vitrimer exhibited shape memory behavior, deforming at 90 °C and fixing at 0 °C under a transient strain of around 75%. After that, the sample was heated gradually, with a step interval of 15 °C, from 0 to 90 °C, allowing each step to recover for 15 min. The sample appears to exhibit multishape memory activity. Because of this, the sample may be folded into various temporary forms at various temperatures in a sequential manner. Once heated to the appropriate fixing temperature, the sample can gradually regain

its original shape.⁵⁰ Siloxanes and a dynamic transesterification process were used in a study by Chen et al. to create a new closed-loop recyclable epoxy vitrimer that resembles an elastomer (ETOD-SA). Upon examining its shape memory, it was discovered that after 20 min at 60 °C, a permanent-memory 7-shaped ETOD-SA would be produced by using external force to bend the rectangular-shaped ETOD-SA into a 7-shape. Next, at room temperature, an external force was used to bend the 7-shaped ETOD-SA into a coiled shape. This curled shape persisted even after the sample was cooled to −6 °C and the external force was removed. Furthermore, when heated to 25 °C, the coiled form may revert to the original 7-shaped sample. Such a promising phenomenon suggested that ETOD-SA may show both transient memory properties and permanent shape memory properties.⁹³ The pictorial representation of the vitrimer (Figure 16) is given below.

6.4. Viscoelastic Properties. Vitrimers are known for their viscoelastic behavior. Mainly, they are characterized by two types of temperatures. The glass transition temperature is marked as T_g , and the topology freezing temperature as T_v . The former one explains the transition between the rubbery and glassy states, but the latter signifies the transition from viscoelastic solid to viscoelastic liquid state, respectively. This transfer from a viscoelastic solid state to the liquid state differentiates vitrimers from other materials. It can preserve the constant number of covalent bonds during this transition process, and it endows the vitrimer with enhanced thermo mechanical and flow properties. A change in topology is related to the second category of temperature. Above T_v , exchanges take place at faster rates, but the rate could be slow when the temperature falls below T_v . The position marked for T_v is always prone to follow the Arrhenius Temperature equation ($\tau^* = \tau_0 \exp(E_a/RT)$). It will result in minimizing the activation energy or the minimum required energy to begin an exchange reaction. Vitrimers flow like fluid when they were heated above the topology freezing transition temperature, and they closely resemble the behavior of vitreous silica, hence the name “Vitrimer”. During the cross-links reactions, the time gap

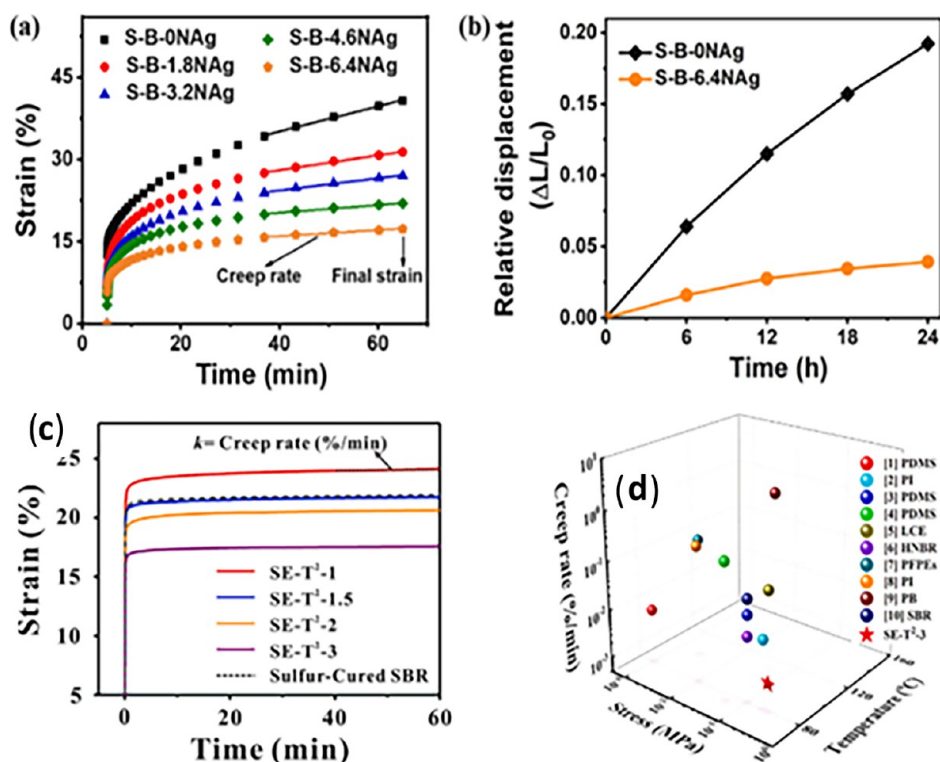


Figure 17. One: (a) Creep profiles of the SBR elastomer at 80 °C with an applied force of 0.10 MPa; (b) dependence of relative displacement (ΔL and L_0 are representative of the change in sample length and original sample length, respectively) on creep time at 80 °C. Two: (c) Creep recovery experiments of samples with a nominal stress of 0.25 MPa at 80 °C. (d) Comparison of creep rate, temperature and stress values of optimized sample with those of previously reported elastomeric vitrimers. Reproduced with permission from ref 100, Copyright@2022, Elsevier Ltd., Polymer.

assigned for the bond exchanges becomes lesser in comparison with the material deformation, which may further lead to the topological rearrangement.^{26,29,96,97} Usually, glass transition temperature T_g is obtained from Differential Scanning Calorimetry (DSC) and the DMA $\tan \delta$ curves and the studies showed that it has a close relation with cross-link density.⁹⁸

6.5. Cure Characteristics. Cross-linking density is a reference factor of vitrimeric network, which defines the mechanical, thermal stability, and chemical resistance of the polymers.²⁰ The cross-link density strongly influences the viscoelastic nature of the vitrimer. The changes occur in the cross-link density, explicitly, the relative distances among the network motifs may affect the flow. The cross-link density drives the diffusion, availability of the network reacting groups, and the mobility of the system. These will be limited while the cross-link density increases on its part.⁴⁸ A number of approaches have been proposed to calculate the cross-link density. Although swelling procedures are commonly used tools, they can also be carried out theoretically using calculations based on thermomechanical data.

6.6. Creep and Stress Relaxation. The viscoelastic qualities discussed above cause the vitrimer to progressively relax and produce creep at a steady pace. It is discovered that there is a relationship between the vitrimer's viscosity and its distinct relaxation time, τ^* .³⁵ After a thorough investigation, Liu and colleagues discovered that adding Zn^{2+} imidazole complexes to the matrix increased the vitrimer's creep resistance while maintaining its malleability. Here, the chemical functionalities serve as a cross-link to support the external

force, limit segment motion, and enhance creep resistance. Interestingly, the same creep displacement for these samples shows that the network organization ability remains unaffected at higher temperatures, namely, at 150 °C. When it comes to enhancing creep resistance by adding static cross-links to dynamically cross-linked networks, this technique offers notable improvements over earlier research since the static cross-links invariably decrease the dynamic features, such as reprocessability.⁹⁹ In engineering applications, the creep of vitrimeric systems, especially elastomeric ones, is a serious problem. An interesting work of recent years communicates that the major mechanical properties have been exhibited by the directly engineered dynamic silyl ether-based networks in a diene-rubber matrix without any modification of the molecular architecture. At the service temperatures, the silyl ether metathesis process may enhance creep resistance. The Silyl ether containing ethanethiol grafted to SBR skeleton (SE-T2-y) samples at 80 °C exhibits a time-independent strain platform according to creep experiments. The creep rate is unprecedented in comparison to earlier research, sluggish, and equivalent to traditional sulfur-cured SBR. Improved creep resistance in elastomeric vitrimers might result from the use of silyl ether-based networks.¹⁰⁰ A pictorial representation (Figure 17) of the data presented above is shown below. A rational design approach for elastomeric vitrimers has shown promising results in suppressing low-temperature creep. This was achieved by introducing dual cross-linking through hydrogen bonds and boronic ester linkages into the SBR network, which underwent extended creep testing. The intermolecular forces from hydrogen bonds effectively enhance

the viscoelastic properties of the elastomer vitrimer by constraining segmental mobility and impeding the exchange dynamics of boronic ester cross-linkers. Consequently, the creep resistance of the material is significantly improved.⁴⁷

In a recent study by Jiang et al., they analyzed the creep resistance and stress relation of a poly(styrene-*b*-isoprene-*b*-styrene) (SIS) and modified it by Boronic Ester linkages (Figure 18). Considering its creep resistance with the pure SIS

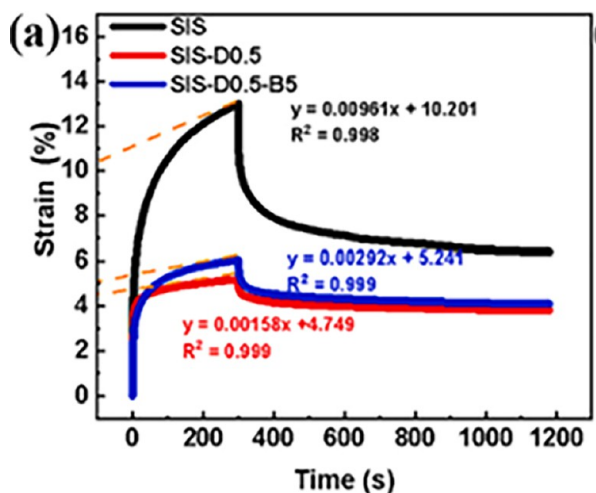


Figure 18. Scheme of SIS, SIS-D0.5, and SIS-D0.5-B5 creep-recovery behavior at 70 °C and 0.001 MPa fixed stress. Reproduced with permission from ref 101, Copyright@2022, Elsevier Ltd., Reactive and Functional Polymers.

sample, the modified vitrimeric sample shows a decreased strain under a constant stress of 0.001 MPa. The elastic recovery calculated for the system analyzed 11.3% for the modified and optimized sample, which was almost lower than that of the pure sample, while the viscous loss of the sample is 51.7%, showing closeness in the value with the pure sample. Hence, it can be concluded that the SIS vitrimer shows favorable creep resistance with dimensional stability at higher temperatures. The dual cross-linking in the vitrimeric sample can enhance the flow behavior of the vitrimer.¹⁰¹

6.7. Mechanical Properties of Vitrimers. Research and challenges in the field of vitrimers have been motivated by improvements in their mechanical properties. The mechanical properties of the material are significantly influenced by both the cross-links and the cross-link length.⁸⁸ The chemical structure and molecular architecture play crucial roles in the vitrimeric network and can be customized to change the network's ultimate characteristics. The molecular weight of the chains, cross-link functionalities, and cross-link stiffness all have a significant impact on how the network behaves mechanically.¹⁰² The alteration implemented by UPy moieties enhances the mechanical qualities of the boronic ester cross-linked SBR vitrimer, as demonstrated by the analysis of its mechanical properties suggested by Wang et al. Particularly, SBR is first modified by UPy and subsequently cross-linked by dimercapto-borate. With a combination of π - π stacking of the UPy rings and the lateral multiple H-bonds between two ureidos in structure, the grafted UPy moieties tend to aggregate to form a microphase-separated structure. The modified samples propose more properties than the Neat samples. For example, the S-B-2.8UPy has Young's modulus, ultimate stress, and fracture energies that are 2.5, 3.3, and 2.1

times higher than those at 2.14 MPa, 3.01 MPa, and 3.15 MJ/m³, respectively. Here, the H-connections connecting the UPy dimers improve the overall mechanical properties while the boronic ester bonds provide the network's flexibility. UPy aggregations serve as sacrificial units that waste energy through reversible rupture and reformation events, improving the rubber vitrimers' overall mechanical properties.⁶² A recent study by He et al. in Elastomeric polyolefin vitrimers presents considerably high mechanical properties for the sample. More specifically, an associative reversible cross-linking network based on dynamic imine bonds was created in ethylene/propylene copolymer rubber (EPR) chains by including aldehyde pendants and using tris(2-aminoethyl) amine (TREA) as a cross-linking agent. The findings demonstrated that cross-linked EPR strength may be considerably enhanced by raising TREA concentration. The tension at break increased from 0.83 to 1.81 MPa, the modulus improved from 0.99 to 5.41 MPa, and the elongation at break dropped from 135% to 42% when the NH₂/-CHO ratio climbed from 0.3 (AEP1-0.3) to 1.0 (AEP1-1.0). Consequently, network structure management might be used to modify the mechanical properties of cross-linked EPRs.¹⁰³ According to Zhao et al., MVQ vitrimers' mechanical behavior has been analyzed, and they can obtain a simultaneous high mechanical strength and tensile toughness. It can be attributed to the rearrangement of dynamic cross-links at a low stretching rate and, in turn, causes a decreased stress. At high stretching rate, effective chain stretching occurs, which contributes to mechanical strength, while the existence of bond exchange can be favorable for high ductility.⁶⁴ The mechanical characteristics of an ENR that was cross-linked using Dimeric Fatty Acids (Dimer fatty acids (DFA)) may be examined (Figure 19). The cross-link-free sample has a high extensibility (>1000%) and a low stress break (~0.85 MPa). However, the cross-linked vitrimeric samples exhibit an enhanced tensile strength, rising from 0.85 to 6 MPa, which may be attributed to the vitrimeric sample's creation of a 3D network. Varying the DFA cross-linker dosage may control the tensile strength and elongation at break.⁶¹

6.8. Thermal Properties. Techniques such as Thermogravimetric Analysis (TGA) and DSC have been used to analyze the glass transition temperature and the associated thermal stability. A recent research on the creation of a dynamic elastomer based on the bio feedstock 4(4-Hydroxyphenyl)-2-butanone, often referred to as raspberry ketone or frambinone, has been introduced. The carbonyl group of raspberry ketones was reacted with hydroxylamine to create a vitrimeric sample, which showed excellent thermal characteristics and a T_g increase from -55 to -40.2 °C. The integration of the bulkier groups limited chain mobility, which is why the T_g increased. With a weight loss of 6–10% at 270 °C, the TGA findings demonstrated strong thermal stability, which may be attributed to the system's greater cross-link density when compared to the other combination.¹⁰⁴

The previously mentioned epoxidized SBR vitrimer functions on a reversible hydrogen bond with strong emphasis on its thermal characteristics. At higher temperatures, the efficient assimilation of hydrogen bonds contributes to its structural stability. The optimized samples were subjected to both TGA and DMA analyses, which revealed that G' rose from 0.36 to 1.28 MPa at 180 °C and is influenced by the cross-link density increment. Thermogravimetric analysis (TGA) revealed that elastomers' thermal stability was unaffected by the insertion of imine cross-linking because

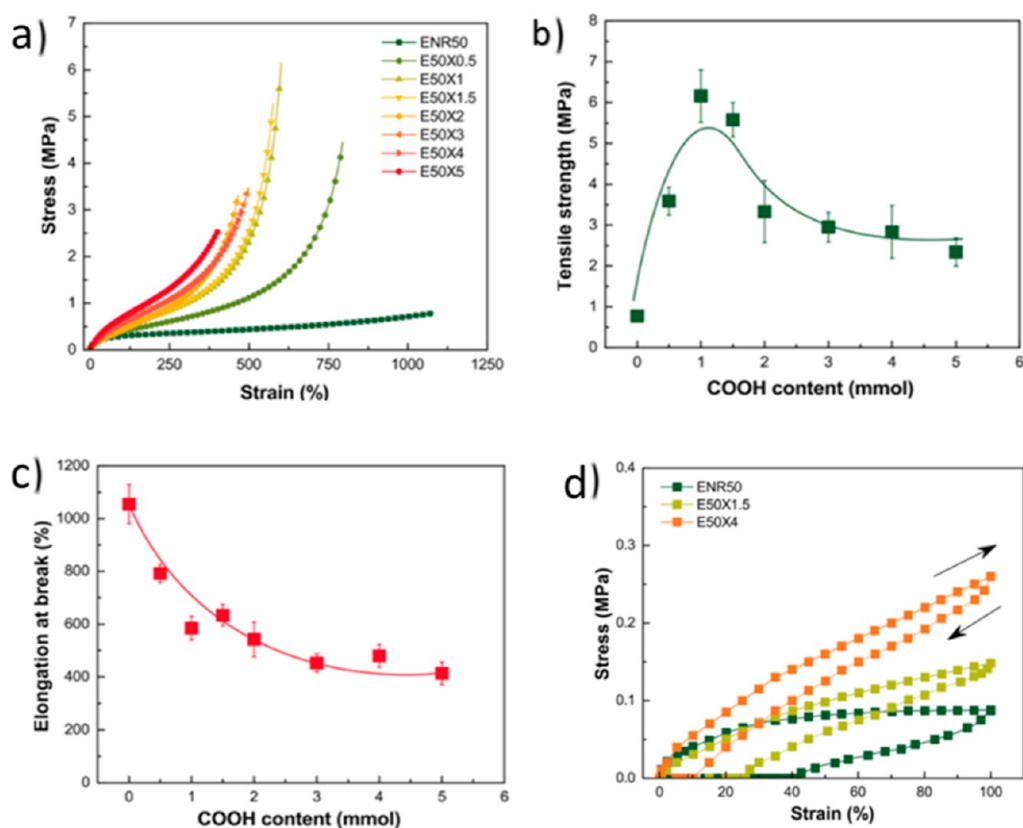


Figure 19. (a) Stress–strain curves of ENR50 cross-linked with different DFA doses, (b) tensile strength as a function of DFA dose, (c) elongation at break as a function of DFA dose, and (d) cyclic stress–strain curves of vitrimer-like ENR50 cured DFA. Reproduced with permission from ref 61, Copyright@2021, Elsevier Ltd., European Polymer Journal.

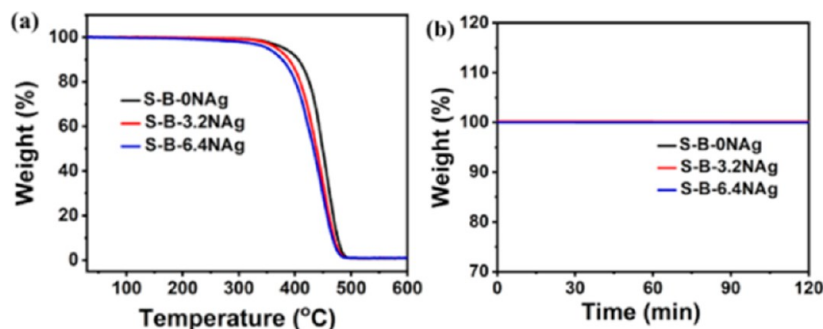


Figure 20. (a) TGA curves for S–B-0NAG, S–B-3.2NAG, and S–B-6.4NAG; (vitrimeric samples with different percentages of *N*-acetylglucine (NAG)). (b) Isothermal TGA curves of S–B-0NAG, S–B-3.2NAG, and S–B-6.4NAG at 180 °C for 2 h. Reproduced with permission from ref 100, Copyright@2022, Elsevier Ltd., Polymer.

SBR vitrimers had a higher starting decomposition temperature than e-SBR. The DMA result demonstrates that the physical cross-linking network made possible by hydrogen bonding raised the vitrimers' storage modulus.¹⁰⁵

Polybutadiene vitrimers were recently developed using a bis-thiol dioxaborolane cross-linker, enabling the synthesis of vitrimers with varying cross-linking densities in a single step. The impact of cross-linking density on the thermomechanical properties of these materials was investigated. As the cross-linking density increased, both the storage modulus in the rubbery plateau region and the glass transition temperature (T_g) showed significant increases, which is typical for highly cross-linked elastomers. The thermal stability of the vitrimer and corresponding static networks was evaluated through TGA using heating ramps from 25 to 500 °C. Both the vitrimer and

static networks exhibited similar thermal stability trends, further confirming the robustness of dioxaborolane cross-linkers at elevated temperatures.¹⁰⁶ The initial degradation temperatures (T_d) of the SBR vitrimeric system modified by *N*-acetylglucine (NAG) have been analyzed in the work proposed by Wang et al., and they have been found to exceed 300 °C. It is commonly observed that the T_d values of S–B-yNAG (vitrimeric sample) decrease slightly as the NAG content increases. Furthermore, after 2 h at 180 °C, practically little mass loss is seen for S–B-yNAG, indicating that the networks remain thermally robust throughout high-temperature measurements.⁴⁷ The results are illustrated (Figure 20).

6.9. Rheology. The linear viscoelasticity under tiny deformations was the primary focus of the rheology experiments on vitrimer systems. Utilizing Arrhenius plots and

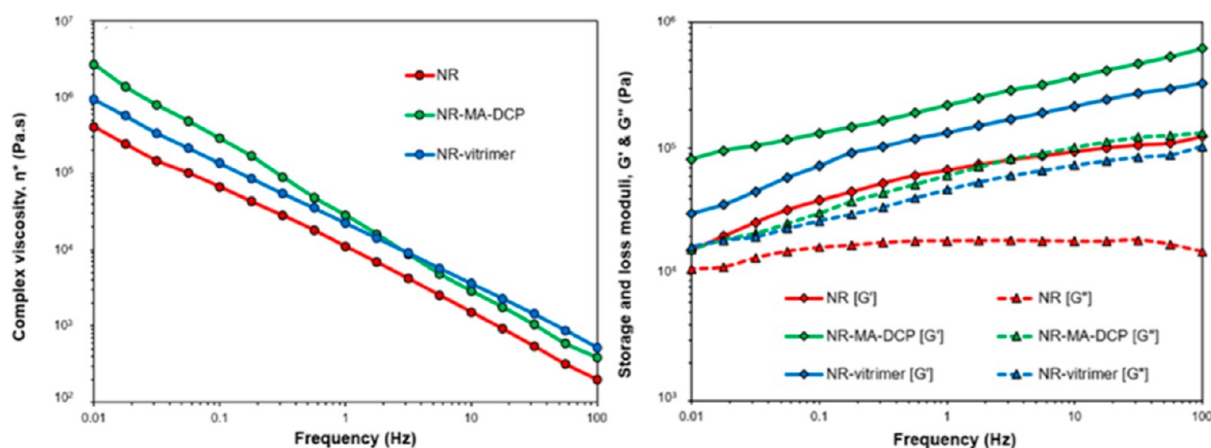


Figure 21. Graphical data of the complex viscosity and storage and loss modulus of the vitrimer systems. Reproduced with permission from ref 78, Copyright@2023, ACS, Applied Polymer Materials.

fitting, the majority of research in the literature calculates the activation energy of the thermally activated process and the characteristic relaxation time, $\tau(T)$, using the stress relaxation approach. Gaining a thorough rheological grasp of the vitrimer response is crucial, since it encompasses both the large-deformation (plastic flow) regime and the small-deformation elastic (or viscoelastic limit) domain.¹⁰⁷ Rheology and solid-state NMR spectroscopy used in tandem can provide incisive details about the cross-linking structures. Wang et al. created a solid liquid elastomeric vitrimer after researching the system's rheology. The master curves derived from frequency-dependent rheological studies at varied temperatures also show that chain relaxation becomes more heterogeneous as the filler content increases.⁷⁶ Recent research was conducted to investigate the introduction of boronic exchangeable linkages into a triblock thermoplastic elastomer. The sample's linear viscoelasticity was measured at a 0.5% strain in the temperature range of $T = 140$ to 180 °C, and the results showed a very elastic, solid-like viscoelastic response. The microphase-separated network structure that localizes the cross-links at high concentrations in the filler phase and places further restrictions on network strand diffusion is responsible for the increase of rheological characteristics. In contrast to the Neat NR and traditional DCP-cured systems, Trinh et al. analyzed the rheological properties of vitrimer systems. As the viscosity dropped with an increasing shear rate, they all exhibited the usual shear-thinning tendency. In comparison to the Neat sample, the vitrimer system had a higher complex viscosity in addition to that of the conventionally cured polymer. Even though the two materials had similar cross-linking densities, the complex viscosity curves also revealed that NR-MA-DCP had a steeper slope at low frequencies than NR vitrimers. This suggests that the dynamic cross-linking network of NR vitrimers is more robust because the mobility of elastomer chains is less constrained than that of DCP-cross-linked chains.⁷⁸ The schematic representation (Figure 21) is given below.

7. APPLICATIONS

The advanced application of vitrimers is in the field of actuators (Figure 22). A work on the dielectric ENR vitrimer preparation is suggested by Bui et al., in which the ENR/acidic cross-linkers cured vitrimeric sample showed better actuation abilities at a lower electric field, which is found to be higher



Figure 22. Various applications of vitrimers.

than that of the DCP cured traditional one.¹⁸ LCEs are unique, large, reversible, high-speed actuators that arise from the isotropy to anisotropy transition among several reported polymer soft actuators. A new strategy has been envisioned by Chen et al. in developing a vitrimer-based liquid crystal elastomer by varying the catalytic amount. Using 82% strain, the aligned sample can be used for mechanical tasks, such as lifting a weight approximately 676 times its own weight. The monodomain alignment can be completely erased and realigned, attaining almost the same actuation strain as the first alignment because of the high temperature trans-esterification process. Furthermore, reversible actuators with intricate 3D structures can be produced by immediately

reconfiguring the resultant monodomain sample into 3D structures at high temperatures while retaining part of the orientations.¹⁰⁸ There has been a novel 3D programmable soft actuator that is easy to use and is quite environmentally friendly. It was created using an ENR network and the inflexible inverse opal mimetic skeleton of SA (NaAlg). The vitrimer has exceptional recycling capacity and 3D geometric programming and reprogramming capabilities due to the β -hydroxyl ester interactions at the interfaces.¹⁰⁹

Flame retardants are advancing smart materials that have grabbed the attention of researchers and industrialists over the years. One of the applications of vitrimers is as flame retardants. The introduction of boron, nitrogen, and halogen into the matrix can enhance the flame-retardant ability of flame retardancy. Li et al. suggested an epoxy vitrimer containing sulfur and nitrogen as flame retardant elements, with excellent flame retardancy and self-healing activity.¹¹⁰ It is interesting to note that a recent study by Liu et al. reveals phosphate-based dynamic covalent bonds with flame resistance. The strong flame retardancy was ascribed to the phytic acid's phosphorus concentration, which had been combined with the vitrimer matrix.⁵⁶

Epoxy adhesives and coatings play vital roles in industry. The difficulty in repairing the damaged coating can be overcome by the introduction of dynamic bonds. Studies show that vitrimers can be used for coatings as well as adhesion. It is noted that autocatalytic reported systems exhibit more repairing property.¹¹¹ Nanofiltration membranes are another modern application of vitrimers. It more or less works on the ability of the dynamic bonds to be broken and be formed again, hence the pore size can be altered accordingly.²⁶ A study led by Gilmer and Bowden says that a dynamic disulfide bond-based vitrimer can act as a nanofiltration unit. The bonds can be broken by inducing a chemical reaction, and the selectivities and the flux can be rearranged via a chemical stimulus. When such bonds break, the pore size can be increased, and it can be minimized further by forming the bonds through a chemical stimulus.¹¹² Dicarboxylic acid esters have excellent low-temperature lubricating qualities, low atmospheric emissions, biodegradability, and low toxicity, making them effective bio lubricants. They serve to raise the energy efficiency. Generally, catalytic transesterification is used to prepare dicarboxylic acid ester bio lubricants by reacting fatty acids with methyl esters or triglycerides.²⁶ Vitrimers are notified for their action to act as bio lubricants. Bio lubricants provide efficient lubricity over the petroleum-based ones.¹¹³ An effective, durable vitrimer based on a PU elastomer has been developed for wearable electronics, although the mechanical qualities and the self-healing capability were discovered to be mutually exclusive. The criteria are fulfilled by a phenolic urethane bond. The development of a self-healing triboelectric generator has been prepared, and it is effective in transforming mechanical motion into electrical energy that can be employed to utilize that energy for the next generation of wearable devices.⁹⁴

8. FUTURE DIRECTIONS AND NEW CHALLENGES

The inherent shortcomings of traditional thermosets and thermoplastics have been addressed by vitrimers. Innovative opportunities in several domains, including tissue engineering, drug administration, and biodegradable implants, are made possible by vitrimers' variable mechanical properties, biocompatibility, shape memory, and self-healing capabilities.¹¹⁴

Yet vitrimers suffer with low mechanical and thermal properties in comparison with the conventional systems. A common technique to enhance vitrimers' mechanical strengths, electrical conductivity, thermal conductivity, external stimulus response, and other properties is to dope them with nanoparticle fillers. Because of their superior mechanical qualities, photothermal effect, and high electrical and thermal conductivity, carbon nanotubes and graphene are perfect fillers for polymers. To improve their qualities, vitrimers were doped with graphene. However, because of their high π - π interactions and huge aspect ratio, graphene particles are challenging to disperse uniformly. Reduced graphene oxide, which has good dispersion in the vitrimer matrix and is more compatible with polymers, was employed to improve the dispersion. Because of their great electrical, thermal, and chemical stability, as well as their huge surface area and high aspect ratio, carbon nanotubes (CNTs) are also commonly used as fillers for vitrimers.²⁶

Self-catalyzing vitrimers are the subject of numerous investigations, which avoid serious drawbacks such as toxicity, environmental hazards, volatility, and migratory problems. Nevertheless, the encouraging advantages of catalyst-free vitrimers, many drawbacks, and other difficulties need to be resolved before they can be used in practice. Scalability is still a major issue, especially for synthesis-based methods that could run into logistical and technological issues when they move to large-scale manufacturing.¹¹⁵

Bioderived vitrimers are a solid concern for the future since they will address the issues of sustainability and the unavailability of petroleum resources. Unique molecules and monomers that are difficult to obtain from petroleum-based substances could be created using biobased vitrimers. Significant challenges must be addressed among the bio derived vitrimers, though, to meet market expectations. These include increasing sustainable manufacturing, addressing the affordability and accessibility of biobased building blocks, and altering vitrimers' properties to comply with conventional polymer processing techniques. For biobased materials to succeed in the future, problems such as performance, raw ingredient management, and production costs must be resolved. There are not many high T_g transesterification vitrimers, and thermal stability is another issue in the field of bio derived vitrimers.^{7,24,29} The intricate and varied architectures of biobased monomers frequently require many petrochemical reagent modifications, producing substantial waste byproducts.¹¹⁶

Dual cross-linking is a promising strategy to improve the properties of the vitrimers. It has recently been shown that adding noncovalent sacrificial bonds—such as hydrogen bonds, coordination, and ionic bonds—is a viable way to improve the mechanical characteristics of polymer materials. In vitrimer systems, they offer an effective energy-dissipating mechanism for reinforcement at the molecular level by gradually rupturing before covalent polymer networks. But bringing them back to the mild processing conditions is still a challenge to solve.⁷³ Carboxy exchange via the conjugate substitution reaction of acyloxy methyl groups has been shown in some elastomer vitrimer-like material, which can be considered an area that may be exploited in the near future.¹¹⁷ Future studies might discover appropriate methods for processing genuine and compatible vitrimers, which might entirely substitute for thermosets and thermoplastics.

9. CONCLUSION

The conventional polymers are equipped with stability and rigidity, but their resistance to degradation and reprocessing limits their application. The dynamic covalent linkages incorporated into the matrices offer the material recyclability and self-healing abilities. These characteristics, along with the other improved parameters of the vitrimer system, make them exemplary providers in the area of polymer chemistry. The elastomer-based vitrimers play a vital role in preserving the circular economy and give way to the sustainable materials over the thermosetting polymers. The dissociative and associative mechanisms in the dynamic bond formation may work through diverse chemistries, and they can be altered according to the materials and the application. The physical characteristics of the reported elastic vitrimers—such as their mechanical parameters, dynamic behavior, high-temperature performance, solvent resistance, recyclability, and self-healing ability—were the main emphasis of this review in comparison to the traditional elastomers.¹ Dual cross-linking and the addition of the nanofillers definitely enhance the strength and properties, yet optimized conditions and the materials need to be explored.

Despite their numerous advantageous properties, vitrimers have predominantly remained within academic research and have not yet been widely adopted by industry. This gap between academia and industry persists due to various challenges in developing vitrimers with the desired properties for practical applications. Although a variety of chemical approaches have been explored to create vitrimers, each presents its own obstacles to achieving the required performance characteristics. Consequently, extensive research efforts are ongoing to address these significant challenges and facilitate the transition of vitrimers from laboratory to industrial use. The limited commercial availability of dynamic chemical precursors on a large scale is another issue in the industrialization of vitrimers.¹¹⁸

Another emerging challenge of vitrimers is to get along with the mechanical strength of the thermosets. The dense cross-linking system in the conventional polymers supports the enhancement in the mechanical stability, while that factor is heavily lacking for the vitrimeric materials since it cannot hold stable covalent cross-links.²³ Yet by their unique applications, vitrimers have created a space for themselves in the polymeric world. It is a promising material that can replace polymers in the near future.

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Notes

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