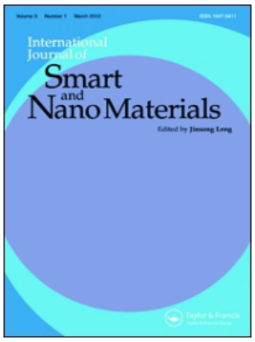

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Recycling strategies for vitrimers

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ABSTRACT

Vitrimer is a new type of material that combine the advantages of thermoplastic and thermoset materials. The rapid dynamic exchange reactions at high temperature allow the topology of cross-linked networks to change and rearrange while keeping material structures and properties intact. The concept of vitrimer has emerged to provide a viable strategy for the recycling of high-performance polymer materials, and lots of research works have been carried out for the development of various types of vitrimers. In addition, the recycling strategies for vitrimers are particularly important to determine the performance and potential applications of the recovered materials. Therefore, it is an innovative and valuable perspective to discuss vitrimer materials according to their different recycling strategies. In this review, we start with a brief overview of vitrimers, and then, focus on recycling strategies for vitrimers. Specifically, we highlight the advantages and disadvantages of the two different recycling strategies: physical and chemical recycling methods, and then explore the feasibility of upcycling vitrimers using 3D printing technology. Finally, the impact of recycling strategies on vitrimer materials and the prospects for maximizing the use of vitrimer materials are discussed.

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1. Introduction

Plastics are important organic synthetic polymer materials, which have been widely used in every aspect of the human life. However, with the rapid increase in plastic consumption over a short time, there are no widely applicable methods to the disposal of waste plastics worldwide [1,2] Therefore, the 'white pollution' phenomenon caused by waste plastics becomes more and more serious. To achieve a sustainable society, how to efficiently recycle plastics has been becoming a hot topic.

In general, plastics can be divided into thermoplastics and thermosets according to their differences in chemical structures [3,4]. Thermoplastics are a class of plastics that are malleable at a certain temperature, and solidify upon cooling, which can repeat this process. The molecular structure is characterized by linear polymer compounds, which generally do not have reactive groups and do not undergo intermolecular cross-linking when subjected to heat [5] (Figure 1). Due to their good fluidity at high temperatures, thermoplastics can be manufactured by a variety of methods, including extrusion, injection molding, thermoforming, and vacuum forming [6]. However, thermoplastics are usually less resistant to organic solvents and less stable than thermosets, limiting their further applications requiring high mechanical performance. Thermosets [7] are a type of polymers where the macromolecular chains covalently bond with each other, forming the chemically cross-linked three-dimensional (3D) networks (Figure 1). Due to the chemically cross-linked property, thermoset materials [8] exhibit excellent mechanical properties, heat resistance, chemical resistance and dimensional stability, which have been used in a wide range of applications, such as aerospace, solar cell sealants, and windmills. However, the insoluble nature of thermosets makes them impossible or difficult to recycle. Therefore, addressing the recycling of thermosets has become an important topic for the sustainable development of society.

Dynamic covalent bonds (DCBs) [9–11] are reversible covalent bonds that have lower bond energies compared to traditional carbon-carbon and carbon-nitrogen bonds [12,13]. They can undergo reversible bond breaking and recombing processes under certain conditions (e.g. heat, pH and UV light). Polymer networks containing dynamic covalent bonds are called covalent adaptable networks (CANs) [14,15]. CANs show similar stability to thermoset materials at working temperature, but the network topology is rearranged by reversible exchange reactions of dynamic covalent bonds under external stimuli, enabling the recycling or reprocessing of such materials. Nowadays, typical dynamic covalent bonds, including disulfide, imine, silicon-oxygen, boron-oxygen bonds, and so on, have been widely used in the design and preparation of polymeric materials.

Depending on the mechanism of reversible chemical bond exchange, CANs can be divided into dissociative covalent adaptive networks and associative covalent adaptive networks [16]. The exchange mechanism of a dissociative covalent adaptable network is similar to the depolymerization of a polymer network, which involves a process of breaking followed by re-forming [16,17]. When the temperature rises, the chemical bonds within the entire dissociative covalent adaptable network break faster than they can be joined, and a reverse decomposition reaction occurs due to the decreasing equilibrium constant with increasing temperature, resulting in a reduction in the density of the crosslinking point and an increase in the mobility of the polymer, enabling the material to be processed and shaped [18]. When the temperature drops, the crosslink density of dissociative CANs increases and eventually reach the same level of the initial state, leading to the recovery of mechanical properties [14].

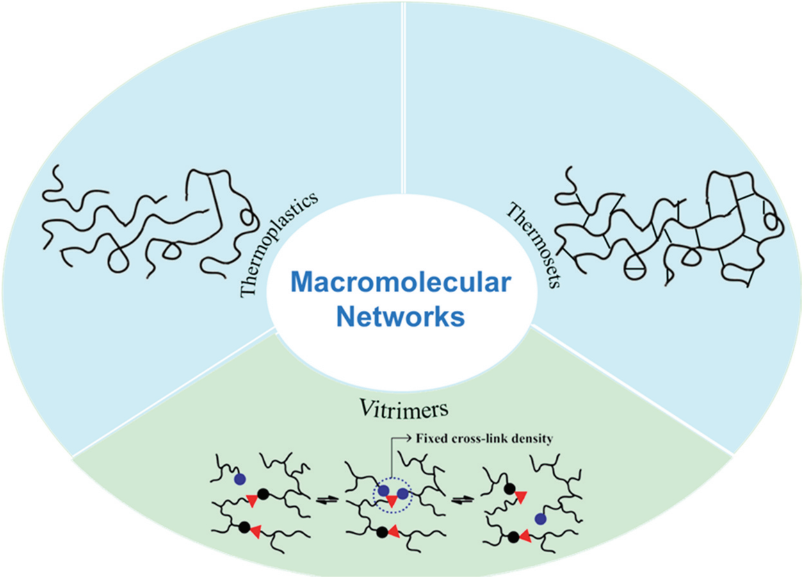

Figure 1. The macromolecular networks of thermoplastics, thermosets and vitrimers [16].

Unlike the dissociative type, the associative CANs have a constant crosslink density during the change, creating new bonds and breaking old ones occurring simultaneously. In 2011, Leibler and coworkers [19] identified this type of materials and named it as 'vitrimer' (*i.e.* glasslike polymer). The name 'vitrimer' was given to a polymer containing a dynamic cross-linked network which, under high-temperature, undergoes rapid rearrangement of the topology of the network, thus making the material 'fluid' [19], malleable and reprocessable (Figure 1). These properties give materials not only the high mechanical properties, chemical resistance and thermostability like traditional thermoset materials, but also the thermal ductility and reproducibility like thermoplastic materials [16,19].

A large amount of research works has been carried out on the development of various types of vitrimers [20–31]. Vitrimer materials have been reviewed and discussed in several review papers [13,32–36]. These reviews mainly presented and analyzed vitrimers from the aspects of different types of vitrimers. On the other side, the recycling strategies for vitrimers also affect the performance of the recovered materials and thus determine the potential applications of the recovered vitrimers. Therefore, it is an innovative and valuable perspective to discuss vitrimer materials according to their different recycling strategies.

In this review, we start with a brief overview of vitrimers, and then, focus on recycling strategies for vitrimers. Starting with the traditional physical and chemical recycling methods, we analyze the advantages and disadvantages of the two different recycling strategies. We then explore the feasibility of upcycling vitrimers using 3D printing technology. Finally, we discuss the impacts of recycling strategies on vitrimer materials and the prospects for maximizing the use of vitrimer materials.

2. General introduction of vitrimers

2.1 Glass transition temperature (T_g) and topological cooling transition temperature (T_v)

The main feature that distinguishes vitrimers from dissociative CANs is their unique viscoelastic behavior. Researchers generally use the topological cooling transition temperature (T_v), a temperature at which the material transits from a viscoelastic solid to a viscoelastic liquid, to describe the vitrimer's viscoelastic behavior [19,37]. The temperature of the second transition of vitrimer is T_v, which is the temperature at which the bond exchange reaction of the activated dynamic covalent bonds takes place [38]. T_v can be detected by means of a Thermal Power Analyzer (TMA). During the test, the test probe provides an oscillatory force on the specimen during heating. When the temperature reaches T_v, the sample undergoes plastic deformation by the force, which is due to thermally induced dynamic covalent bonds resulting in a reduction in specimen size [39]. In contrast, there are two main factors influencing T_v: the types of dynamic covalent bonds and the proportion of dynamic covalent bonds in the vitrimer system. Their viscosity behavior follows Arrhenius' law and they are considered to have undergone a topological cooling transition. The glass transition is an inherent property of polymer materials and is a macroscopic manifestation of the transformation of the polymer's form of motion. The relationship between these two transition temperatures (T_g and T_v) determines the properties of vitrimer materials. In the case of $T_g < T_v$ (Figure 2(a)), when the temperature is heated from below T_g to between T_g and T_v, the material first changes from the glassy to the rubbery state and exhibits elastomer-like behavior. The reaction rate is very slow and the network structure is essentially fixed. At temperatures above T_v, the material becomes fluid as a result of the exchange reaction and its viscosity is controlled by the kinetics of the exchange reaction in accordance with Arrhenius' law. If $T_g > T_v$ (Figure 2(b)), no chain segment movement occurs at temperatures below T_g. When further heated above T_g, chain segment movement occurs gradually, while the exchange reaction occurs rapidly. In this case, the viscosity of the network is first controlled by the law of diffusion (Williams Landel Ferry law, WLF law), and when heated further, the exchange kinetics change from a diffusion-controlled to exchange reaction controlled (obeys Arrhenius' law).

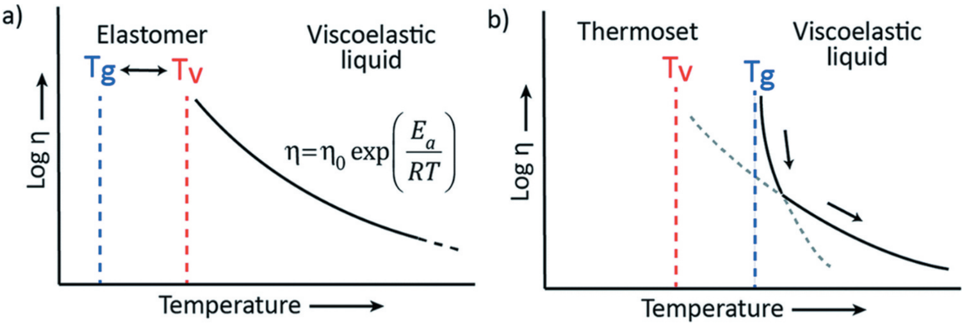

Figure 2. Two different viscoelastic behaviors of vitrimer materials [16].

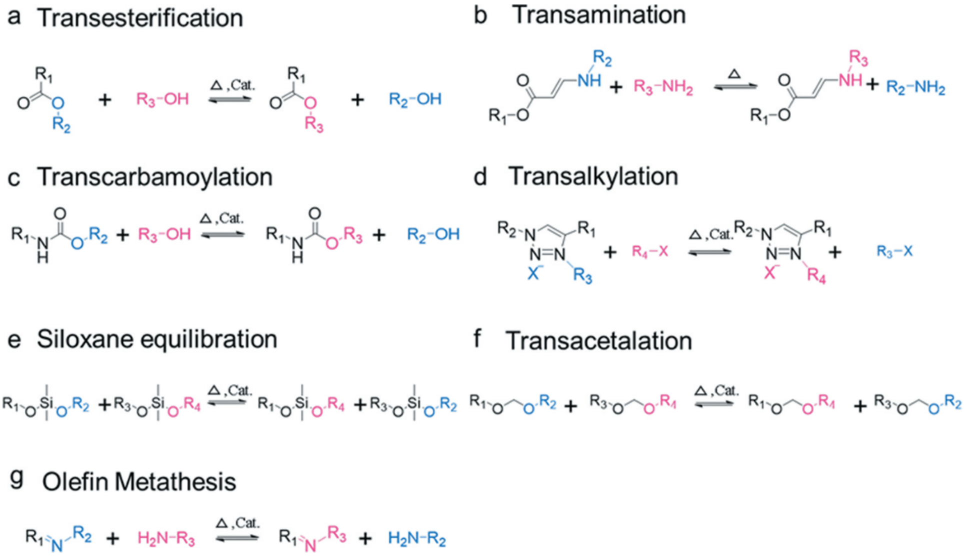

Figure 3. A variety of common covalent exchange reactions enable recycling in vitrimers [46].

2.2 Classification of vitrimers

In the last decade, there have been many types of vitrimers that have been developed (Figure 3). Depending on the types of bond exchange reaction introduced, they are broadly classified as vitrimers based on transesterification reactions [19], vitrimers based on transamination reactions [40], vitrimers based on transcarbamoylation reactions [41], vitrimers based on transalkylation reactions [42], vitrimers based on siloxane equilibration reactions [43], vitrimers based on transacetalation reactions [44], and vitrimers based on olefin metathesis reactions [45,46], and so on [13,47].

The transesterification-based vitrimers (Figure 3(a)) achieve the change of the cross-linking network through dehydration condensation and hydrolysis of both carboxyl and hydroxyl groups. At room temperature, the rate of transesterification is extremely slow, and this network shows similar properties to traditional chemical crosslinked networks, with good mechanical stability without creep. But after heating, the fast transesterification reaction enables such vitrimers to relax by rearranging the network structure [19]. The transamination based vitrimers (Figure 3(b)) conduct the exchange of urethane and ammonia through Michael addition at a high temperature. The reaction process does not require the participation of catalysts, but the stability of the amine in the network is a factor that must be considered, and the oxidative damage of the amine affects the durability of the material [40]. The transcarbamoylation based vitrimers (Figure 3(c)) achieve exchange via carbamate reaction, but the reaction is slow and has side reactions. A typical transalkylation based vitrimer (Figure 3(d)) is synthesized by addition polymerization of α-azide alkyne monomer and alkylating reagent with the bifunctional group. But transfer agents have poor scalability, high cost, and high toxicity of azide and alkylating agents, making it difficult to industrialize [41,42]. The siloxane equilibration-based vitrimers (Figure 3(e)) are prepared by addition/elimination of silanol groups or silanols on siloxane molecules, but side reactions such as hydrolysis degradation, thermal cyclization and depolymerization can destroy the topological network structure [43]. The transacetalation based vitrimers (Figure 3(f)) are prepared by the interaction of acetals with alcohols. The olefin metathesis based vitrimers (Figure 3(g)) are prepared by using imine-amine reversible exchange and imine reversible exchange to prepare vitrimer, but the polyimine network is sensitive to water, resulting in limited applications of this type of materials [45,46]. It should be noted that, beside the above discussed associative dynamic covalent bonds for vitrimers, other dissociative dynamic covalent bonds, such as disulfide bonds (S-S) and diselenide bonds (Se-Se), have been exploited in the synthesis of DCBs [48,49]. The exchange mechanism involves a process of conjugate exchange through the addition or elimination of substitution by free thiols [50]. The exchange mechanism of diselenide bonds is similar to that of disulfide bonds, as they both belong to the chalcogen group in the periodic table and exhibit similar chemical properties [51].

Due to their associative exchange mechanism, vitrimers can retain the integrity of the network during the exchange reaction process, and endow the material with the performance of repeated processing. Generally, recycling methods of vitrimers are similar to other polymeric materials, by physical or chemical recycling for secondary use. Furthermore, benefiting from cutting-edge technologies, such as 3D printing [52], researchers find that the upcycling of vitrimers can be realized.

3. Recycling strategies of vitrimers

In this section, the recycling strategies of vitrimers are discussed. First, the commonly used physical recycling method and the chemical recycling methods are introduced. And then, the advantages and disadvantages of these two methods are compared and discussed. Furthermore, a new method based on 3D printing technology is introduced, which provides a promising way to realize the upcycling of vitrimer materials.

3.1 Physical recycling

The physical recycling of vitrimers refer to a way of recycling materials by directly using traditional manufacturing methods or using materials as a filler by grinding vitrimers into powders or pellets [53]. The physical recycling methods mainly include hot pressing, injection molding, extrusion molding, and so on.

Hot press recycling involves cutting vitrimers into pieces and pressing them through a hot press to form a recycled material. The properties of recovered materials vary with the hot-pressing parameters, such as temperature, pressure and powder particle size [54–56]. Yu et al. [53] investigated the effects of reprocessing parameters on the transesterification based vitrimers. An epoxy resin containing a 5 mol% zinc catalyst mixed with carboxylic acid was cured to form a transesterification based vitrimer (Figure 4(a)). The used carboxylic acid consisted of 23% diacid and 77% triacid. Then, the vitrimer was ground with sandpaper, and the resulting powder's diameters ranged from 25 μm to 120 μm. After pressing at a pressure of 45 kPa under 180°C for 30 min, the recycled specimen exhibits tensile stress of 2.9 MPa, which was 76.7% of the original specimen. In 2019, Delahaye et al. [57] studied physically recycling of the catalyst-free polyester vitrimers (Figure 4(b)). Specimens were first ground into particles with diameters around 1 mm, and then the resulting particles were hot-pressed at 150°C for 60 min to obtain the transparent

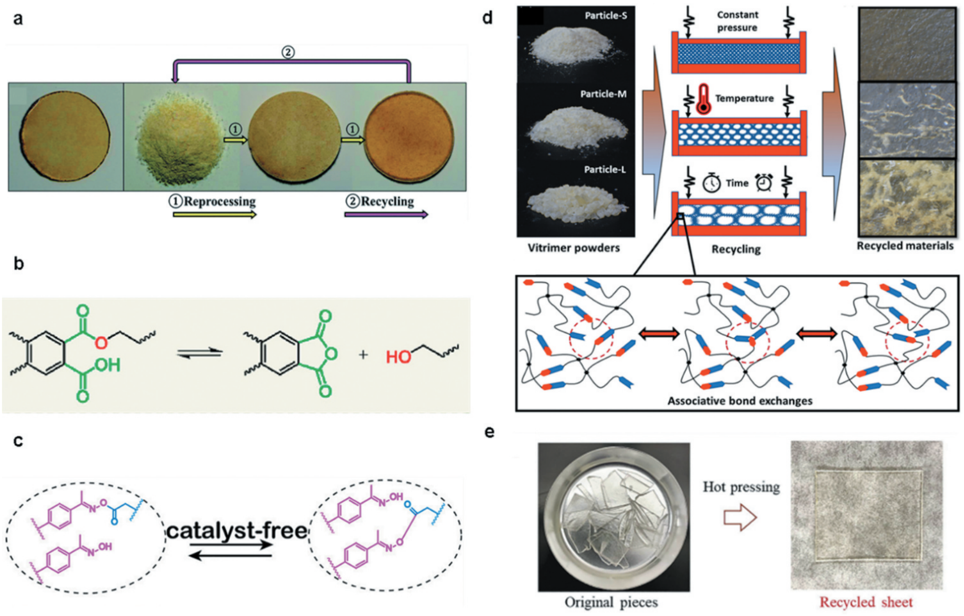

Figure 4. (a) The typical reprocessing and recycling routine of a fresh bulk thermoset polymer (180°C in temperature and 45 kPa in pressure). From left to right: pulverous polymer after milling, polymer powder after being heated for 10 min and 30 min respectively [53]. (b) The dynamic exchange of phthalate monoesters [57]. (c) Exchange process of poly(oxime ester) (POE) network via oxime transesterification in POEs [58]. (d) From left to right, from top to bottom: The resulting polymer powders (Particle-S, Particle-M, and Particle-L) from epoxy-anhydride vitrimers by using 0.5, 1.0 and 2.0 mm trapezoidal perforation sieve rings, respectively; The treating parameters for recycling materials; the resulting new shapes from epoxy-anhydride vitrimers powders with different particle sizes and the associative bond exchanges between carbonyl and hydroxyl groups [54]. (e) Recycling vitrimer sample from pieces to a reshaped transparent plate [61].

specimens. This cyclic process was repeated three times and the recovered materials exhibited tensile properties comparable to the raw material in each case. He et al. [58] used thiol-ene click chemistry achieving a catalyst-free poly(oxime ester) (POE) vitrimers with high stretching and ductility (Figure 4(c)). At high temperatures, the POE network exhibits excellent malleability and reprocessability due to the oxime ester exchange reaction. This dynamic network can be easily reprocessed and recycled many times without degradation of chemical and physical properties. Liu et al. [59] demonstrated that the integration of sacrificial bonds into vitrimer networks can significantly improve the overall mechanical properties by facilitating network rearrangement. By a chemical reaction between the epoxy and carboxyl groups to generate exchangeable β-hydroxy esters and introduce amide functional groups into the network, the prepared epoxidized natural rubber (ENR) can change their topology by esterification, which makes their recycling possible. The hydrogen bonding generated by the amide functional group acts as sacrificial and reversible factor where it breaks preferentially before the covalent framework and undergoes reversible fracture and reforming to dissipate mechanical energy under external loading, achieving a combination of high strength, high modulus and elongation. Topological rearrangement of the cross-linked network is accomplished by ester exchange at high temperatures. To demonstrate the reprocessability, samples are cut into small pieces after tensile testing and then reshaped at 180°C for 5 min to obtain a new coherent sample.

A series of experiments were conducted by Zhang [54–56] to investigate the effect of various processing conditions (including particle size distribution, particle size, temperature, time and pressure) on the properties of recycled vitrimers (Figure 4(d)). And the experiment results show that finer polymer powders can increase the contact surface of the recycled material, thus improving the quality of the recycled material. Debnath et al. [60] reported a set of β-activated ester-based vitreous polymers that can be used in the absence of catalyst-free conditions at about 150°C for thermal reprocessing. The relaxation temperature was reduced to 110°C in the presence of $Sn(Oct)_2$. In addition, the used malonate, a natural ester, can be extracted from a variety of fruit juices. Poly(hydroxyethyl methacrylate) was used as a hydroxyl precursor for the synthesis of vitrimers. These vitrimers show adequate tensile strength (11.3–33.0 MPa) and elongation (80–290%), which can be effectively self-repaired and reprocessed upon heating, exhibiting similar mechanical properties to fresh materials.

In 2021, Feng et al. [61] reported a covalent adaptive network (i.e. polyethylene (PE)-CAN) based on β-hydroxy phosphate that exhibits high strength, recyclability, shape memory and fire resistance properties (Figure 4(e)). At room temperature, the abundance of hydrogen bonds in PE-CAN contributes to the toughness (5.44 MJ/m^3). At around 100°C, the rapid exchange reaction between the phosphate ester and the adjacent β-hydroxyl group gives almost 100% recycling efficiency of the material. Lossada et al. [62] successfully combined vitrimers with a simulated pearl nanocomposite design to achieve functional synergy. The method starts with the preparation of an aqueous vitrimer prepolymer, which is assembled into a nanocomposite and cross-linked by thermal curing. The composite is ground into a fine powder, which can be reprocessed and recycled into a homogeneous film. Yue et al. [63] demonstrated a catalyst-free method to recycle cross-linked bio-based epoxy resin into high-performance nanocomposites with cellulose nanocrystals (CNCs). CNCs provide abundant free hydroxyl groups to facilitate the ester exchange reaction and also act as reinforcing fillers for the resulting nanocomposites. The cured epoxy resin and the cellulose nanocrystal composites were ground into powders using a ball mill respectively, and the recycled nanocomposites were obtained by hot pressing the mixture of the above two powders.

Injection molding is the process of melting plastic to ‘flow’ and injecting it into the mold at a certain speed. The mold is cooled by the watercourse and the plastic is solidified to give the same shape as the designed mold cavity. Extrusion molding is a method of processing where the material is thermal-treated by the action of the extruder barrel and screw. Then, the fluidic material is pushed forward by the screw and continuously passes through the head to make various cross-sectional products or semi-products. According to the general rule, materials are suitable for injection molding when the melt flow index (MFI) is greater than 10 g $(10\ \text{min})^{-1}$ at the processing temperature (measured by the ASTM D-1238 standard) [57]. Leibler and coworkers [19] demonstrated that epoxy/anhydride polymer networks containing a large number of hydroxyl/ester groups can be reprocessed in the presence of a suitable catalyst. Despite being permanently cross-linked past the gel point, the broken or ground samples can still be reprocessed by injection molding (Figure 5(a)). Shrinkage-free molding can be achieved by adjusting the

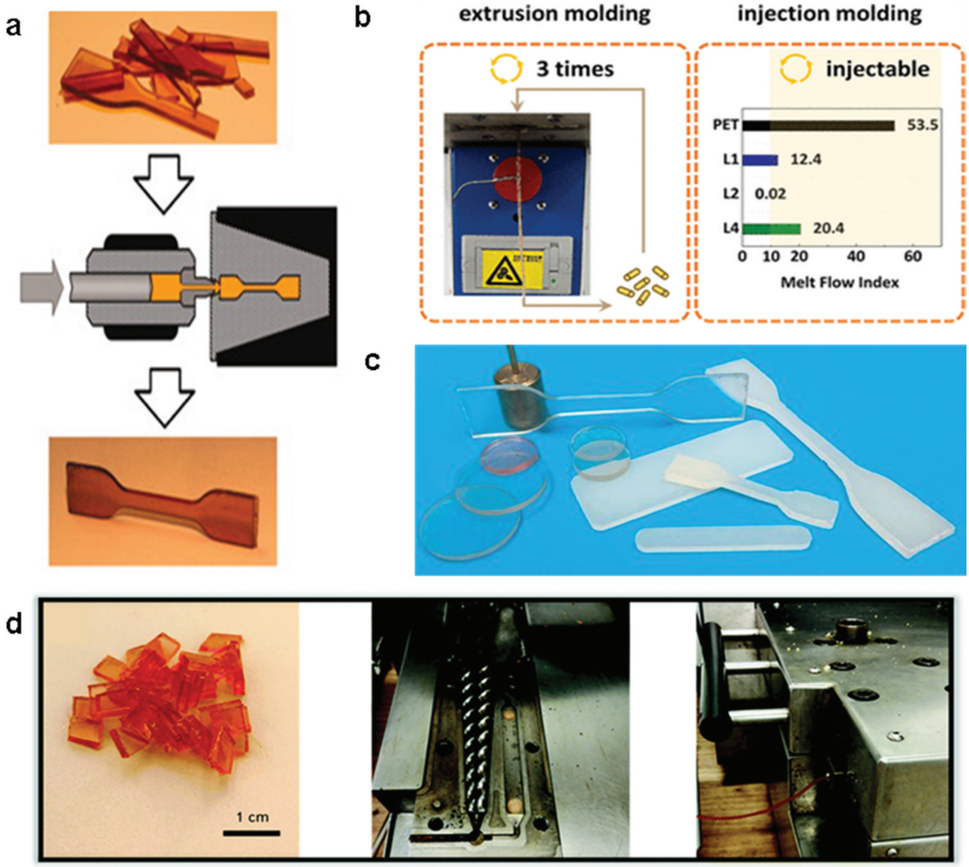

Figure 5. Injection and extrusion of vitrimers. (a) A cross-linked sample broken into pieces is reprocessed in an injection machine to recover its initial aspect and properties. No shrinkage is observed after demolding [19]. (b) Reprocessability of PET vitrimers via extrusion molding and injection molding [65]. (c) Injection- and compression-molded vitrimers. Injection-molded PMMA discs and dog bone samples (length, 6.6 cm) [66]. (d) Extrusion and recyclability assessment of vitrimer $N_{20}H_6$. Elastic vitrimer pellets and a double-twin screw extruder setup were used to create vitrimer extrudates [67].

molding temperature and dwell time. Zhou [64] et al. proposed a method to prepare polybutylene terephthalate (PBT) vitreous based on an ester exchange reaction. By adjusting the molding temperature and dwell time, the relatively long relaxation time and high viscosity of PBT vitreous can be overcome, and a high production rate of the finished product by injection molding can be maintained. Inspired by Zhou's work [64], Qiu et al. [65] introduced 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol (BIS-TRIS) with more reactive groups into the poly(ethylene terephthalate) (PET) chains. During the extrusion process, a commonly used double epoxy resin is also introduced to cross-link the activated PET chains through the reaction between hydroxyl and epoxy groups. The extra hydroxyl and tertiary amine structure accelerates the dynamic ester exchange reaction of the vitreous network and thus maintains the post-processing capability like a thermoplastic. The improved PET vitrimer retains its pre-processing properties after extrusion and injection molding (Figure 5(b)).

In 2021, Leibler and coworker [66] studied the decomposition reaction of dioxaborane that is fast and thermally stable, which is suitable for preparing vitrimers from different commodity polymers, such as poly(methyl methacrylate), polystyrene and high-density polyethylene. All these materials demonstrated the ability to be reprocessed by extrusion or injection molding (Figure 5(c)). Taplan et al. [67] investigated the effect of trace additives on the rearrangement of the macromolecular structure of the vitrimer networks. The synthesized $N_{20}H_6$ were dried thoroughly at 60°C for 48 h under vacuum (Figure 5(d)). A melt flow index (MFI) device was used to estimate the flow of this material at 170°C and was determined to be 0.75 g/10 min.

Besides, the vitrimer material also has a wide range of applications in foams. There are numerous works on recycling of vitrimer foams [68,69]. For example, Yu et al. [68] developed a vitrimer bead foam containing dynamic covalent bonds to solve the problem of non-reusability of traditional commercial foaming bead products. The bulk polyolefin elastomer (POE) vitrimers were recovered by completely destroying the foam structure at 130°C. The recovered POE vitrimers were extruded, blended and re-foamed. This recycled vitrimer bead foam still has a good closed cell structure and is comparable in all respects to the original one.

In this part, we first introduced the simple hot press recycling method. By following, the more diverse and efficient injection and extrusion molding methods are introduced. Currently, the physical recycling or reprocessing of vitrimers is based on limited compression moldings, which is an energy-consuming and time-consuming process that can be subject to thermal degradation or oxidation during prolonged heating. In addition, the recycled resin material usually has slightly lower properties than the original sample [56,57].

3.2 Chemical recycling

Chemical recycling is a recovery method that uses chemical solvents or monomers to dissolve or degrade vitrimers into oligomers [46]. Zhao et al. [70] reported the imine-embedded bisphenol (EN-VAN-AP) network, a vitrimer that derived from the synthesis of imine bond-bridged bisphenol monomers, the condensation of bisphenols and cross-linking with a hardener (Figure 6(a)). The result vitrimer was dissolved in DMF with the aid of HCl, which was removed from the solution, leaving the partially polymerized gel. By further heating, polymer gel can restore to the solid state. Kuang et al. [71] used ethylene glycol as a solvent to get the production of dicarboxylic acid esters by recycling epoxy based vitrimer (Figure 6(b)). Bowman and coworkers [72] demonstrated that the dynamic thioester network does not require the addition of foreign reactants, and using the original monomer can directly degrade the networks to a monomer mixture. As shown in Figure 6(c), the polymer was first obtained by photoinitiated thiol-ene polymerization. After the introduction of acetone as a solvent, an excess of tetrathiol monomer, and triethylamine as a catalyst, the dynamic thiol-thioester exchange reaction occurs rapidly and the polymeric network degrades to oligomers. These oligomers can be repolymerized upon the addition of

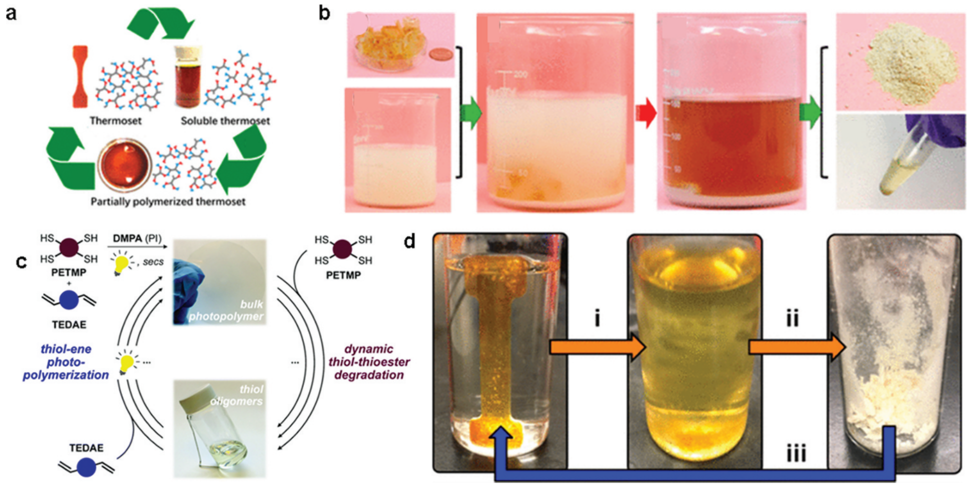

Figure 6. Chemical recycling of vitrimers. (a) Recycling steps of EN-VAN-AP [70]. (b) Pictures showing the dissolution of epoxy thermoset and extraction of DEHS as a biolubricant [71]. (c) Reaction scheme for recycling and repolymerizing cross-linked photopolymers by a free radical thiol-ene polymerization and an anionic thiol–thioester dynamic degradation. In particular, the pristine polymer is initially prepared by photo-initiated thiol-ene polymerization between a stoichiometric ratio of a tetra-thiol and a thioester-containing diallyl ether. The bulk photopolymer is degraded into thiol oligomers by thiol–thioester exchange with a defined amount of a tetra-thiol under basic conditions. Subsequently, these oligomers are polymerized with a thioester-containing diallyl ether by a photo-initiated thiol-ene reaction. Three complete cycles of this procedure are demonstrated here to indicate the capacity for full recovery of the initial polymer [72]. (d) Chemical recycling of vitrimers: (i) addition of excess monofunctional amine, (ii) precipitation of modified prepolymer, and (iii) reintroduction of tris (2-aminoethyl)amine (TREN) to yield rejuvenated networks [74].

a certain stoichiometric amount of prodiene. Without the use of any external reactants and organic solvents, Garcia et al. prepared a recyclable thermoset material obtained by the condensation reaction of paraformaldehyde and diamines, showing an ultra-high modulus (14.0 GPa) [73]. Sumerlin and coworkers [74] reported a strategy that could convert linear prepolymers obtained by controlled radical copolymerization of methyl methacrylate and (2-acetoacetoxy)ethyl methacrylate (Figure 6(d)) to vitrimer in one step by trifunctional amine treatment. An excess of a monofunctional amine with a low boiling point, such as n-butylamine, was added to the solvent during the chemical recovery process. The modified prepolymer is then recovered using a precipitation method. Eventually, tris(2-aminoethyl)amine (TREN) can be reintroduced into the modified prepolymer to produce the network again in a continuous curing cycle.

Unlike recycling of vitrimers by solvent, vitrimer based composites are separated into multiple materials during the recycling process. Yu and coworkers [75] demonstrated the full recycling of epoxy-based carbon fiber reinforced polymer (CFRP) composites. After immersing the composite in ethylene glycol (EG) and increasing the temperature, the epoxy matrix can be dissolved with the long polymer chains breaking into smaller segments. The carbon fibers can then be recycled with the same dimensions and mechanical properties are comparable to the fresh carbon fibers. Further heating of the dissolved solution leads to the repolymerization of the epoxy resin matrix. Therefore, the recycling of CFRP achieves a closed-loop model with near 100% recovery. Wang et al. [76,77] presented a fully recycling method for bio-based polyimide vitrimers and investigated the effect of the fine structure of the material on its thermal, mechanical, solvent resistance and degradation properties. They found the lightly degradable nature of the polyimide vitrimers and the easy recycling of carbon fibers (CFs) that can be used to develop environmentally-friendly composites. Polyimide vitrimers can be easily depolymerized into crude monomers by acid degradation. The CFs were recovered from the polyimine vitrimers/CF composites by acid degradation. The hydrolysis of the polyimine vitrimers left almost no residue and the chemical structure of the recovered CF was not destroyed. By using aromatic disulfide cross-linked epoxy resin as a matrix, Si and coworkers [78] prepared reprocessable, degradable carbon fiber thermoset composites (CFRP) with a glass transition temperature (T_g) of 147°C and tensile strength at 63.1 MPa (Figure 7(c)). As shown in Figure 7(c), the carbon fiber composites were immersed in a dilute

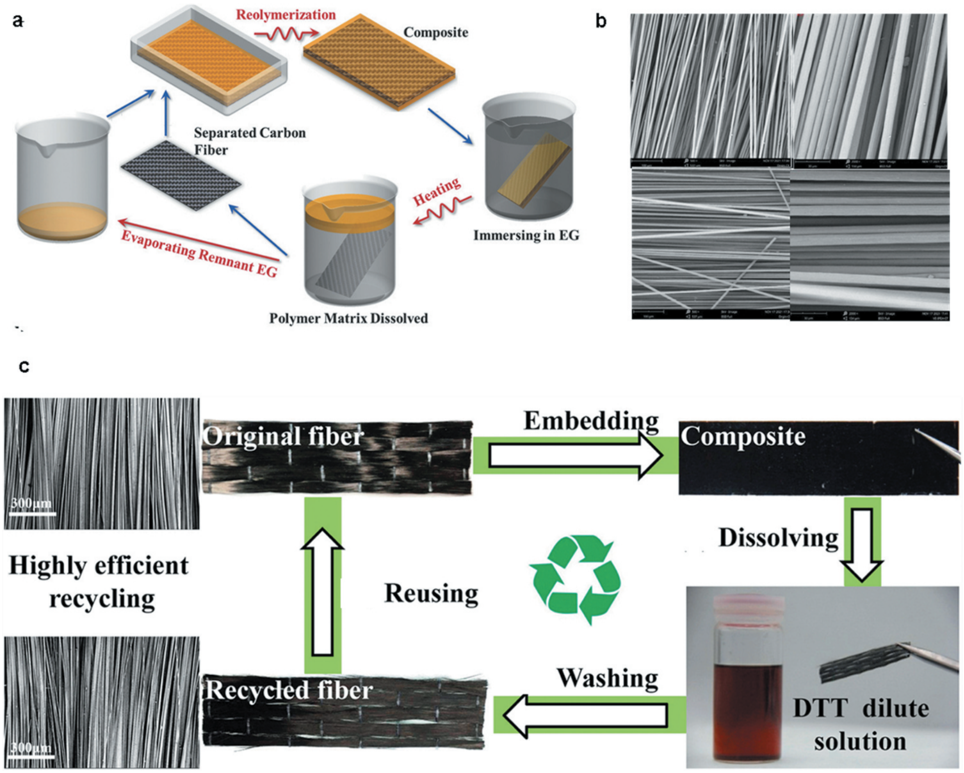

Figure 7. Recycling of fiber-reinforced vitrimer-based composites. (a) A schematic view of the closed-loop recycling paradigm for CFRP composites [75]. (b) The morphology of crude, recycling carbon fibers from DAV/DETA/CF, DAV/IPDA/CF and DAV/DDM/CF in 0.1 M HCl solution at 60°C for 24 h [76]. (c) The recycling process of CFRP composites is based on a dual disulfide vitrimer: embedding the carbon fibers in an epoxy matrix; dissolving the epoxy matrix at 90°C in 1 h; washing and drying the recovered carbon fibers; reusing the recycled carbon fibers to form new composites [78].

solution of dithiothreitol (DTT) for recovery. After washing and drying, the recovered carbon fibers can still be reused to prepare CFRP composites similar to the original carbon fibers.

Overall, we first discussed the pure solvent recovery of vitrimer as a single material, and then we presented the recovery of vitrimer composites, which enables the simultaneous recovery of the vitrimer and composites. When chemical recycling is used to recover fiber-reinforced vitrimer-based composites, the length of the fibers can be retained, facilitating the re-use of the recovered fibers and enhancing the residual value of the recovered material.

3.3 Comparison of the advantages and disadvantages of two traditional recycling methods

Both physical and chemical recycling methods have their advantages and disadvantages. A mandatory step in physical recycling is the pulverization of vitrimers, which is unfriendly to fiber-reinforced composites containing a large number of carbon or glass fibers. And this pulverization process will shorten the valuable long fibers and reduces the residual value of the material to be recycled [79]. For the hot press recycling strategy, a certain degree of fluidity is required for the topological transformation of the vitrimers. That means higher temperature and pressure are needed to ensure that the properties of the recovered vitrimers are close to the original ones [80,81]. In addition, the physical recycling methods of extrusion and injection molding are not used frequently because harsh processing conditions are usually needed [79]. Chemical recycling involves dissolving vitrimers in a solvent containing exchangeable functional groups of small molecules. This method can dissolve vitrimers into small molecules or glycopolymers that can be reused again. Chemical recycling of vitrimers is more efficient as it undergoes dynamic bond exchange reactions by simply putting the materials in the corresponding solvents at certain conditions. On the other hand, chemical recycling is a time-consuming and energy-consuming process. In comparison, physical recycling is simple and easy to operate. However, it can cause problems with thermal degradation. Therefore, each method has its advantages and disadvantages [79], which are presented in Table 1.

Table 1. Comparison of physical recycling and chemical recycling methods [79].

	Advantages	Disadvantages
Physical recycling	● Simple ● Easy to operate ● The vast majority of materials can be recycled in this way.	● Energy- consuming and time-consuming. ● Reprocessed samples are often dark in color and may undergo thermal degradation or oxidation. ● Some restrictions on using injection molding and extrusion molding ● Shorten the value of long fibers
Chemical recycling	● More efficient than physical recycling ● The length of the fibers can be retained, facilitating the re-use of the recovered fibers and enhancing the residual value of the recovered material.	● Time-consuming and energy-consuming

3.4. Vitrimers for 3D printing

3.4.1. 3D printing

3D printing [82–89], also known as additive manufacturing (AM), is used as a general technology platform for highly specialized model making and rapid prototyping. Different from traditional material processing technologies, 3D printing of structures based on a 3D CAD model is manufactured by adding materials layer by layer.

3D printing technology can be generally divided into Fused Deposition Modeling (FDM) [90–93], Digital Light Processing (DLP) [94,95], Stereo Lithography Apparatus (SLA) [96–98], Direct Ink Writing (DIW) [99–102], Laminated Object Manufacturing (LOM) [103,104], Electron Beam Melting (EBM) [105], Selective Laser Melting (SLM) [106], Laser Direct Melting Deposition (LDMD) [107], Electron Beam Freeform Fabrication (EBF) [108] and many others. These methods have been used in different fields due to their different process characteristics. FDM, DLP, and SLA are the most commonly used three printing methods. And the demand for 3D printing materials is growing rapidly. Especially, there are a wide range of vitrimers available for 3D printing, such as acrylic ester vitrimers [109], poly (ϵ-caprolactone) vitrimers [52], polyurea vitrimers [110], etc. Vitrimer materials used for 3D printing are not related to their reversible bond exchange rate but the viscosity of the matrix material. The vast majority of resins used in photocurable 3D printing are photosensitive acrylates [109]. To compromise a fluent printing process, the viscosity of photocurable acrylates ought to be kept within a range, which is below 1.3 Pa·s for most commercial DLP-based 3D printers [111]. The formation of covalent crosslinks during photopolymerization gives the material excellent mechanical properties but is not conducive to recycling and reprocessing. In 2018, Zhang et al. [52] developed a type of 3D printable vitrimer, which is ultraviolet (UV) curable and reprocessable. The UV curable property make it suitable for high resolution DLP printing. Joe et al. [110] expanded the concept of the reprocessable 3D printing vitrimer ink and reported a new class of a 4D printable poly(ε-caprolactone) based vitrimer. In 2021, Niu et al. [112] systematically investigated the application of a synthetic polyurea elastic vitrimer in 3D printing. The rational material design associated with the optimal printing process was demonstrated to turn this vitrimer ink into different 3D geometries.

3.4.2. Recycling of vitrimers by 3D printing

The rapid development of 3D printing technology has led to rapid growth in the demand for 3D printing materials, especially photosensitive resins. The photosensitive resin generally comes from the petrochemical industry, and the preparation of low yield, energy consumption and raw materials for nonrenewable resources is not conducive to environmental protection and sustainable development. The emergence of vitrimers provides a new direction for the recycling of 3D printing resins. By introducing dynamic covalent bonds into 3D printing inks, self-healable and re-processable 3D structures can be fabricated, which can achieve a multiple of recycling while maintaining the high strength of the materials.

The term ‘upcycling’ was first used to refer to any process that transforms by-products, undesired, unwanted or waste products into new materials of higher value [113]. The chemical recycled ink is then used for 3D printing to ‘upcycling’ the vitrimer. This approach seeks to reuse vitrimer into higher value products with wider economic value.

This new type of recycling offers a completely new way of thinking about recycling vitrimers. Based on the above discussion, we believe that 3D printing is a suitable recycling method in parallel with physical recycling and chemical recycling.

In 2017, Shi et al. [114] developed a recyclable 3D printing approach for thermally cured thermosetting vitrimer epoxy (Figure 8). This printing method use solvent-assisted transesterification type bond exchange reactions (BERs) of vitrimer epoxy to achieve 3D printing and recycling. By carefully tailoring the composition, pre-crosslinking temperature and time, vitrimer epoxy inks can be printed into complex architectures, and then recycled multiple times where the printed polymer parts are dissolved in ethylene glycol (EG) solvent and reused as ink for the next printing cycle. In this approach, no additional additive is needed, and the created thermosetting parts in each printing cycle exhibit almost equivalent thermomechanical properties. The recycled epoxy vitrimer from wastes is also used to repair damage or smooth the surfaces of printed polymer parts through EG participated BERs in the absence of welding pressure. However, the printed objects suffered from a rather low resolution and poor surface quality due to the applied filament extrusion printing technique.

In 2018, Zhang et al. [52] transferred the concept to photo-curable resins printable by Digital Light Processing (DLP). Compared to DIW, DLP offers several advantages as it enables the fabrication of 3D objects with high resolution and surface quality and comparably high throughput rates. They developed the first 3D printed reprocessable thermosets (3DPRTs) by combining vitrimers with DLP 3D printing technology (Figure 9

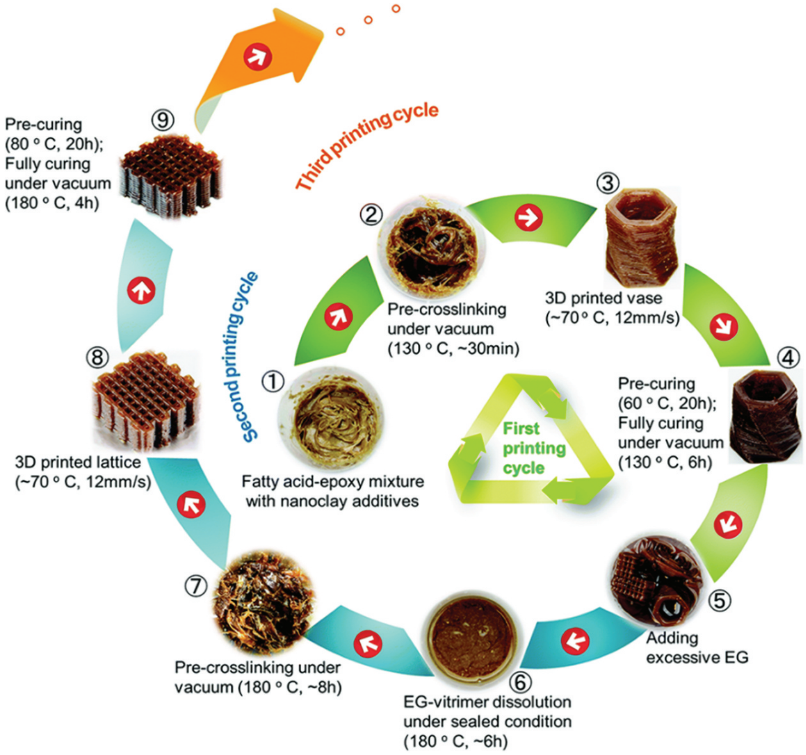

Figure 8. Recycling vitrimers by direct ink writing (DIW) [114].

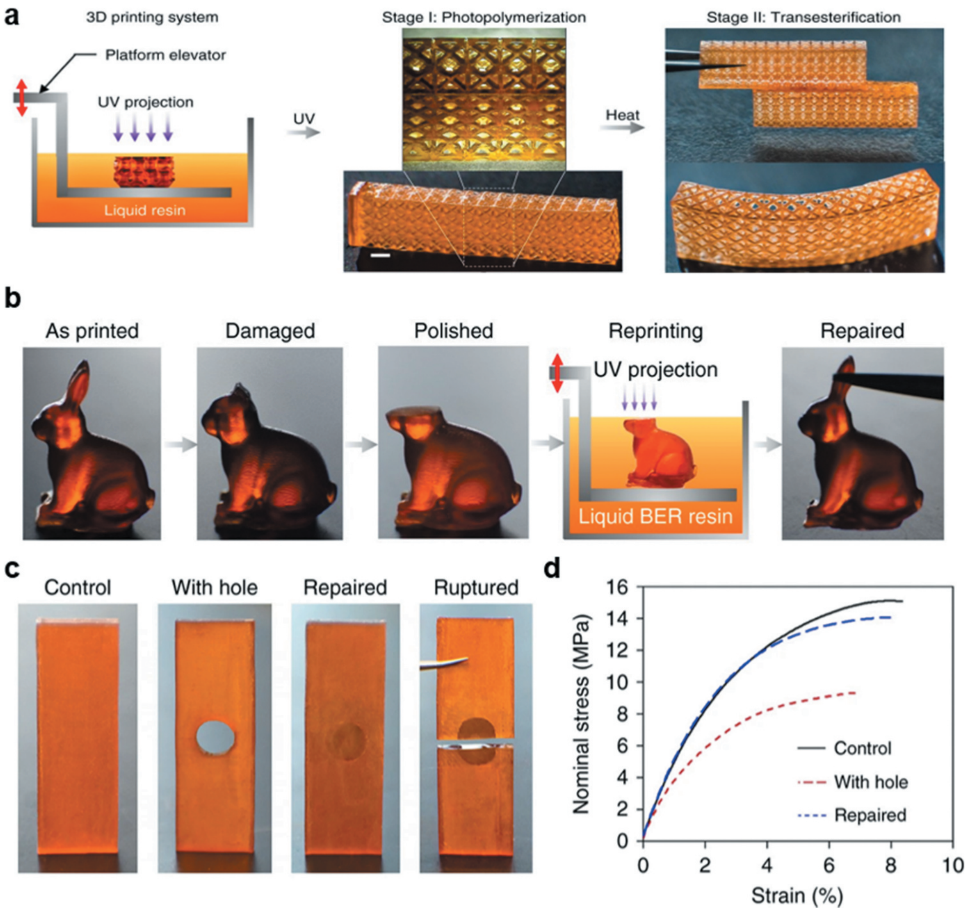

Figure 9. Recycling vitrimers by digital light processing (DLP) based 3D printing [52]. (a) Route of 3D printing structures with a UV curing-based 3D printing system using the reprocessable thermosetting polymer solution. (b) Demonstration of the ability of the material to repair flawed printed structures. (c) Photos of the control sample, a sample printed with a hole, a repaired sample, and a ruptured sample after repair. (d) Comparison of the nominal stress vs. strain for the samples in c.

(a)). They prepared a photosensitive resin precursor with 2-hydroxy-3-phenoxypropyl acrylate monomer, bisphenol A glycerolate (1 glycerol/phenol) diacrylate as a crosslinker, and diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide as a photoinitiator [115]. During the DLP 3D printing process, the double bonds of the acrylate open and form a permanent covalent cross-linked network with the cross-linker, allowing the liquid to cure, layer by layer, eventually forming a three-dimensional structure. By heating the 3D structure to a higher temperature, the ester exchange reaction between the ester and the hydroxyl group in the polymerized network is achieved in molding, repair or recycling. This material allows users to reform a printed 3D structure into a new arbitrary shape, repair a broken part by simply 3D printing new material on the damaged site (Figure 9(b)), and recycle unwanted printed parts (Figure 9(c,d)) so the material can be reused for other applications [88,89,114,116,117]. The recycling of vitrimer was achieved using the above methods, but repeated 3D printing could not be achieved. Gao et al. [118] demonstrated a new strategy for developing a kind of mechanically robust and reprocessable 3D printing thermosets by combining hydrogen bonds and exchangeable β-hydroxyl esters into acrylate vitrimers. To realize this purpose, diacrylate prepolymer containing β-hydroxyl esters was first synthesized from glycidyl methacrylate and suberic acid. Then, the resin formulations for 3D printing comprising the synthesized diacrylate prepolymer together with acrylamide generate exchanged β-hydroxyl ester and pendent amide in cross-linked networks. Here, hydrogen bonds resulting from the amide group as sacrificial bonds dissipate vast mechanical energy under an external load. The network rearrangement of cross-linked vitrimers can be achieved through the dynamic ester exchange reactions with the gradual disappearance of hydrogen bonds at elevated temperatures, imparting reprocessability into the printed structures. The network rearrangement of cross-linked vitrimers can be achieved through the dynamic ester exchange reactions with the gradual disappearance of hydrogen bonds at elevated temperatures, imparting reprocessability into the printed structures. Various photo-3D printing or UV irradiation shapes were successfully produced, and these shapes dissolved in EG could be remolded again. The recycling of vitrimer was achieved using the above methods, but repeated 3D printing was still an issue.

In 2021, Chen et al. [119] proposed a two-stage curing approach involving dynamic reactions by using the acrylate-epoxy hybrid resin for the recyclable DLP 3D printing of high-performance thermosetting polymers (Figure 10(a)). Bond exchange reactions (BERs) could establish covalent bonds between the acrylate network and the epoxy network, thus partially triggering the copolymerization. The resulting new polymers exhibited excellent mechanical properties. A small-molecule assisted BER method was then used to efficiently depolymerize the thermosetting printed parts into soluble oligomers, which were formulated with fresh photopolymers for the next round of printing. The reprinted samples still showed good mechanical properties comparable to the virgin ones. Very recently, Li and Zhang et al. [120] proposed a method for upcycling vitrimer through DLP 3D printing and bond exchange reactions. The crushed and ground vitrimer powder was miscible in a UV-curable recycling solution to create a low-viscosity recycling precursor solution suitable for DLP 3D printing (Figure 10(b)), and the powder was well dispersed without clustering or precipitation after the addition of a dispersant. Complex, high-precision structures can be printed using DLP, and the vitrimer powder is then heat-treated to complete a bond exchange reaction with 3DPRT to form an interfacial fusion. Upcycling of vitrimer is achieved by 3D printing and bond exchange reactions allowing waste vitrimer to be manufactured into highly accurate and complex products.

In general, the combination of the vitrimer-based resin systems with 3D printing technology complements each other and promotes the joint development of materials science and 3D printing technology. Now, the recycling of vitrimer resins for reprinting has been achieved to some extent, where the vitrimer resin is ground up and added to a solution of vitrimer resin precursors to be mixed for recycling and printing. This method brings a breakthrough in plastic upcycling, but the shape, particle size and dispersion uniformity of the ground vitrimer resin limits the accuracy of the print. Fully recycled printing of vitrimer resin remains a challenge.

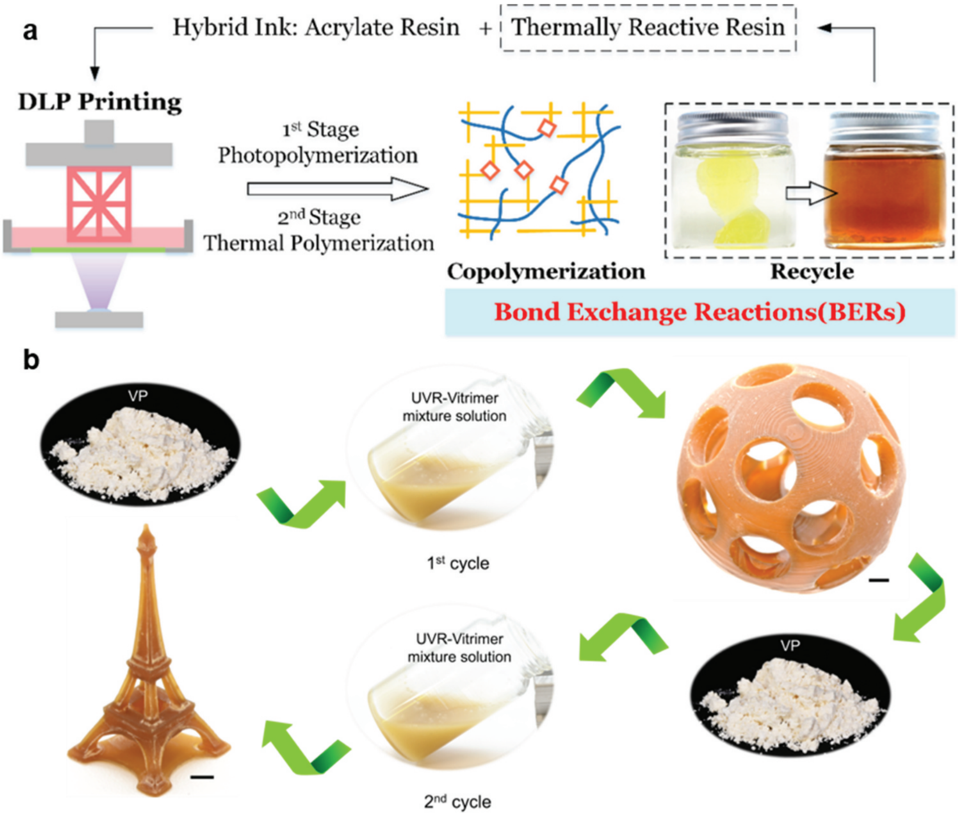

Figure 10. Upcycling of vitrimers by 3D printing. (a) 3D printing is based on a two-stage curing process with the first stage of photopolymerization followed by the second stage of the thermal curing step [119]. (b) Flow chart of twice upcycling vitrimer: UVR-vitrimer buckliball model (first cycle) and UVR-vitrimer tower model (second cycle) [120].

4. Conclusions and perspectives

In this review, we briefly summarize the definition and characteristics of vitrimers in nature and then emphasize the recycling strategies of vitrimers in details from both physical and chemical recycling methods. Importantly, we compare the advantages and disadvantages of the two different recycling strategies. The physical recycling method is simple but low-efficient and energy-consuming, while the chemical recycling method is high-yielding but time-consuming. In addition, with the advent of vitrimers, the variety and integrity of material systems for 3D printing have also been achieved. The introduction of special structures in vitrimers has increased the recycling time and profitability of 3D printing materials to a higher level. It means that vitrimers provide a highly viable solution to the recyclable problem of 3D printing materials. The benefits of working with raw materials for 3D printing have been expanded. However, there are too few vitrimer materials available for 3D printing. And there are still many issues that need to be addressed for commercializing the vitrimer materials in 3D printing, such as cost reduction, efficiency and sustainability.

It is expected that more recyclable vitrimer materials will be developed to replace traditional disposable printing materials, so that the pollution problems of consumables from a large amount of use of 3D printing materials could be solved efficiently, thereby providing a sustainable strategy for realizing the vision of 'emission peak and carbon neutrality.

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