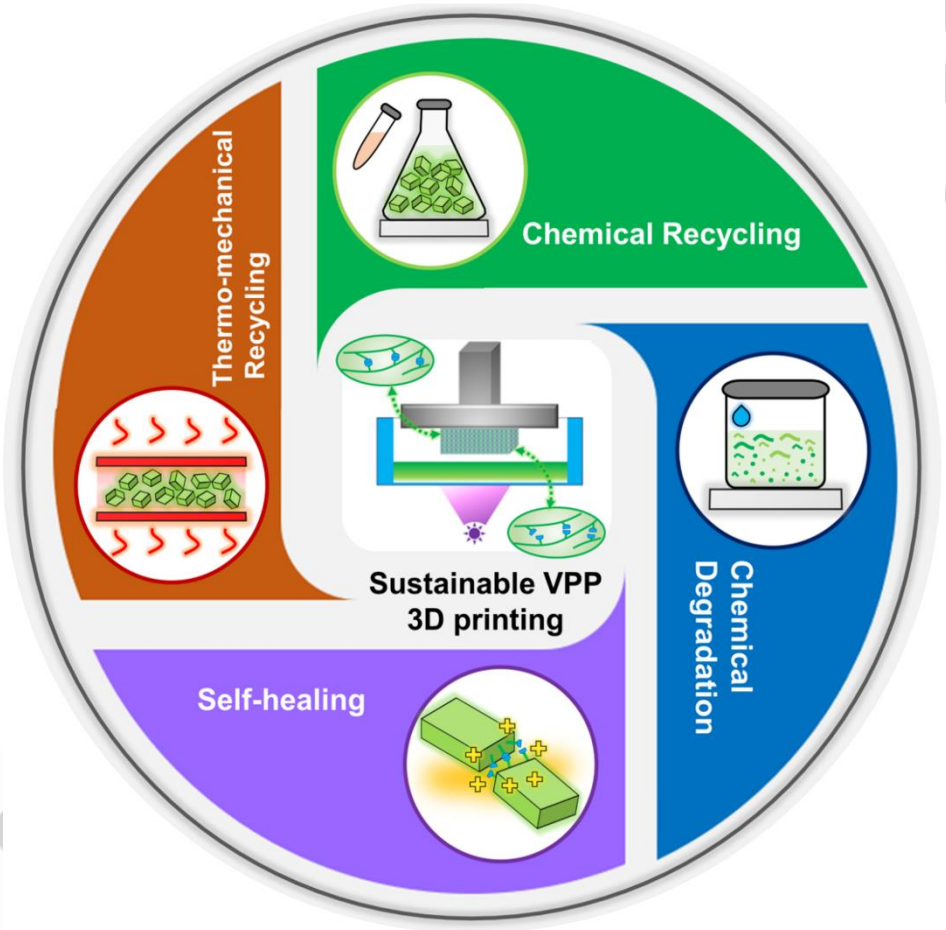
Sustainable Vat Photopolymerization-Based 3D-Printing through Dynamic Covalent Network Photopolymers

Sirawit Pruksawan[a], Yi Ting Chong[a], Wylma Zen[a,b], Terence Jun En Loh[a,c], and FuKe Wang*[a]



[a] Dr. S. Pruksawan, Y.T. Chong, W. Zen, T. J. E. Loh, Dr. FK Wang
Institute of Materials Research and Engineering (IMRE)
2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Republic of Singapore
E-mail: wangf@imre.a-star.edu.sg
[b] W. Zen
College of Design and Engineering
National University of Singapore (NUS)
4 Engineering Drive 3, Singapore 117583, Republic of Singapore
[c] T. J. E. Loh
Nanyang Polytechnic
180 Ang Mo Kio Avenue 8, Singapore 569830, Republic of Singapore

Abstract: Vat photopolymerization (VPP) based three-dimensional (3D) printing, including stereolithography (SLA) and digital light projection (DLP), is known for producing intricate, high-precision prototypes with superior mechanical properties. However, the challenge lies in the non-recyclability of covalently crosslinked thermosets used in these printing processes, limiting the sustainable utilization of printed prototypes. This review paper examines the recently explored avenue of VPP 3D-printed dynamic covalent network (DCN) polymers, which enable reversible crosslinks and allow for the reprocessing of printed prototypes, promoting sustainability. These reversible crosslinks facilitate the rearrangement of crosslinked polymers, providing printed polymers with chemical/physical recyclability, self-healing capabilities, and degradability. While various mechanisms for DCN polymer systems are explored, this paper focuses solely on photocurable polymers to highlight their potential to revolutionize the sustainability of VPP 3D printing.

1. 3D-Printed Dynamic Covalent Network Polymers

Vat photopolymerization (VPP) three-dimensional (3D) printing technologies, such as stereolithography (SLA) and digital light projection (DLP), are widely acclaimed for their ability to produce high-accuracy, isotropic, and watertight products with fine features, contributing to high mechanical performance.[1] These technologies utilize ultraviolet (UV) light to photopolymerize acrylate resins into thermosets, incorporating bifunctional or multifunctional monomers. The irreversible photcrosslinking of these monomers during 3D printing forms covalently crosslinked polymer chains within the thermosets. Although covalent crosslinking provides superior mechanical, thermal, and chemical stability, the reprocessability of these thermosets remains a challenge due to their crosslinked structures.[2] The inherent strength of covalent bonds requires a significant amount of energy to break, rendering these thermosets to be typically non-processable and single-use, raising environmental concerns.[3] The environmental impact of plastic pollution is substantial, with approximately 44 million tons of thermoset waste that cannot be melted and reclaimed for reuse.[4] This inability to recycle or reprocess thermosets contributes to increased waste generation and pollution, posing threats to ecosystems, including oceans and landfills. Furthermore, the energy-intensive processes involved in thermosetting polymers, including 3D printing with UV-curable materials, add to the environmental footprint.[5]

Addressing these challenges, dynamic covalent networks (DCNs) have emerged as a promising solution. DCNs are polymers with reversible crosslinks, featuring dynamic covalent bonds.[6] This distinctive property allows DCNs to undergo rearrangement within their network through reversible bond exchange processes, providing benefits like recyclability and reprocessability. Moreover, the reversible bond exchange process facilitates self-healing and degradation capabilities. Various mechanisms, both associative and dissociative, are explored for covalent dynamic bond materials to enhance their recyclability.[7] Associative bond exchanges, exemplified by transesterification and disulfide metathesis, maintain a constant crosslinking density during the exchange, resulting in materials known as vitrimers.[8] On the other hand, dissociative mechanisms, such as Diels-Alder cycloadditions and thiol-/aza-Michael additions, lead to a reduced crosslinking density upon bond activation.[6a, 7c] In recent years, DCN polymers have emerged as versatile materials with numerous advantages and potential applications, spanning from tissue adhesives and regeneration to drug delivery, sensors, and 3D printing.[9] This field has seen significant progress on multiple fronts: (1) the development of new dynamic covalent chemistries, (2) a deeper understanding of network recycling and self-healing mechanisms inherent to DCN polymers, (3) efforts to enhance the reversibility of reactions, even after multiple uses, (4) exploration of the intricate relationships between structure, reactivity, and properties of DCN polymers, and (5) expansion of applications beyond the current scope.[10] However, despite these advancements, a significant challenge highlighted in several studies revolves around the conflict between mechanical properties and dynamic reversibility.[7a, 11] Although several DCN polymer systems have been reported, the majority are not specifically tailored for photopolymerization-based 3D printing. Only a limited number of DCN polymers optimized for VPP 3D printing have been explored and developed thus far, owing to the challenges in controlling the photopolymerization kinetics.[7a, 12] Notably, 3D printing is an energy-intensive field, impacting the environment and demonstrating limited sustainability.[13] Achieving sustainability in 3D printing can be realized through various reprocessing methods applied to 3D-printed DCN polymers.[14] Therefore, the development of VPP 3D-printed DCN polymers plays a crucial role in enhancing sustainability by addressing challenges associated with the end-of-life disposal of 3D printed parts.[15] Their reprocessability supports sustainable practices by encouraging the reuse of 3D printing materials and minimizing waste generation. This capability not only contributes to environmental conservation but also provides a practical solution to the growing concerns of plastic waste, promoting the sustainability of VPP 3D printing.[16]

This review exclusively focuses on VPP 3D-printed dynamic covalent bond polymers and their functional aspects for sustainability. The subsequent sections will systematically explore recent methodologies for employing 3D-printed polymers within dynamic covalent network (DCN) polymers, utilizing diverse reprocessing techniques, including chemical recycling, thermo-mechanical recycling, self-healing, and controlled degradation. The review also discusses recent advancements in dynamic covalent photopolymers and concludes with a summary and an outlook on upcoming perspectives.

2. Chemical Recycling of 3D Printed Thermosets with Dynamic Covalent Bonds

Traditional thermosets are typically insoluble in all solvents due to their 3D crosslinked network structure. However, through chemical treatment, these crosslinks may be broken under elevated temperatures, pressure, and catalysis to form soluble chemical products, which subsequently serve as building blocks for creating new polymers.[17] While the degradation product from chemical recycling is miscible with the fresh resin, the chemical recycling process usually takes a relatively longer time than physical recycling.[18] This process is typically more facile in DCNs due to their inherently dynamic crosslinks.[19] Various 3D-printed thermoset systems, utilizing different dynamic covalent reactions and recycling methods, have been reported in studies on chemical recyclability, as summarized in Table 1.

Table 1. 3D printed chemical recyclable thermosets with dynamic covalent bonds

No.	Material	Dynamic covalent reaction	Printing technology	Recycling solution	Advantage	Limitation	Ref
1	Epoxy-anhydride stiff vitrimer, epoxy-acid soft vitrimer, and other transesterification-based vitrimers	Transesterification reaction	DLP	Various combinations of monomers and crosslinkers	Simple recycling procedures	Limited to transesterification-based vitrimers	[20]
2	Aliphatic dithiol 1,10-decanedithiol, tetrathiol crosslinker, and thioester diallyl ether monomer	Thiol−thioester exchange reaction	SLA	Pentaerythritol tetrakis(3-mercaptopropionate) and triethylamine	Easily repolymerized recycled products	Decreased mechanical toughness as a result of simultaneous photopolymerization and crystallization processes introducing defects.	[21]
3	Tetrahydro-furfuryl acrylate	Ester exchange reactions	SLA	Ethylene glycol	Enhanced mechanical properties through β-hydroxyl esters while allowing for reprocessing	High temperatures required for remolding, impacting mechanical properties	[22]
4	Methacrylated isosorbide, methacrylated vanillin, and Schiff-base resin	Imine/ester exchange reaction	DLP	Sodium hydroxide	Potential of methacrylated isosorbide to confer rigidity to thermosets	Deterioration of mechanical properties due to damage of nondynamic covalent bonds during the reprocessing procedure	[23]
5	2-hydroxyethyl acrylate, isobornyl acrylate, and diglycidyl ether of bisphenol A	Transimination reaction	DLP	Ethylene glycol	Modulus and strength of recycled samples comparable to original samples	Differences in polymer network evolution during reprinting	[24]
6	Isocyanate, and thiol	Thiol-isocyanate exchange reaction	DLP	Isocyanate functional monomer	Achieved zero waste closed-loop photoprinting	Slightly reduced mechanical properties after recycling	[25]
7	Isocyanate, and thiol	Thiourethane exchange reaction	SLA	Thiol monomer	Mechanical properties of reprocessed samples close to original after first recycle	Differences in polymer network evolution during reprinting	[26]
8	Castor oil, and isophorone diisocyanate	Amine/urea exchange reaction	DLP	2-(*tert*-butylamino)ethyl methyacrylate	Non-destructive recycling of thermochromic microcapsules from 3D printed materials	Limited solvent choice for achieving thermochromic abilities	[27]

One of the most prevalent dynamic covalent exchange reactions for chemically recyclable thermosets is transesterification. For instance, Li and colleagues have undertaken a remarkable effort to develop a method for upcycling universal vitrimer wastes. They introduced a UV-curable recycling system specifically designed for DLP 3D printing (Figure 1)[20] This system incorporates thermosets comprising epoxy-anhydride stiff vitrimer, epoxy-acid soft vitrimer, and other transesterification-based vitrimers. A UV-curable precursor solution was created by combining vitrimer powders with a UV-curable recycling solution. The UV-curable recycling solution includes acrylate functional groups for photopolymerization during DLP-based 3D printing, as well as hydroxy and ester functional groups for transesterification-based bond exchange reactions. This enables the creation of detailed 3D structures with high resolutions and intricate geometric complexity. Heat treatment activates bond exchange reactions in the 3D printed structures, enhancing their mechanical properties significantly. This method allows for the repetitive cyclic printing of vitrimer wastes.

Researchers have introduced another approach to the chemical recycling of thermosets, which involves thiol-thioester exchange reactions.[21] This method involves utilizing a thermoset containing dynamic covalent bonds formed through the photopolymerization of (1) aliphatic dithiol 1,10-decanedithiol, (2) a tetrathiol crosslinker, and (3) a thioester diallyl ether monomer. The process employs a 2,4,6-trimethylbenzoyldi-phenyl phosphine oxide (TPO) photoinitiator.

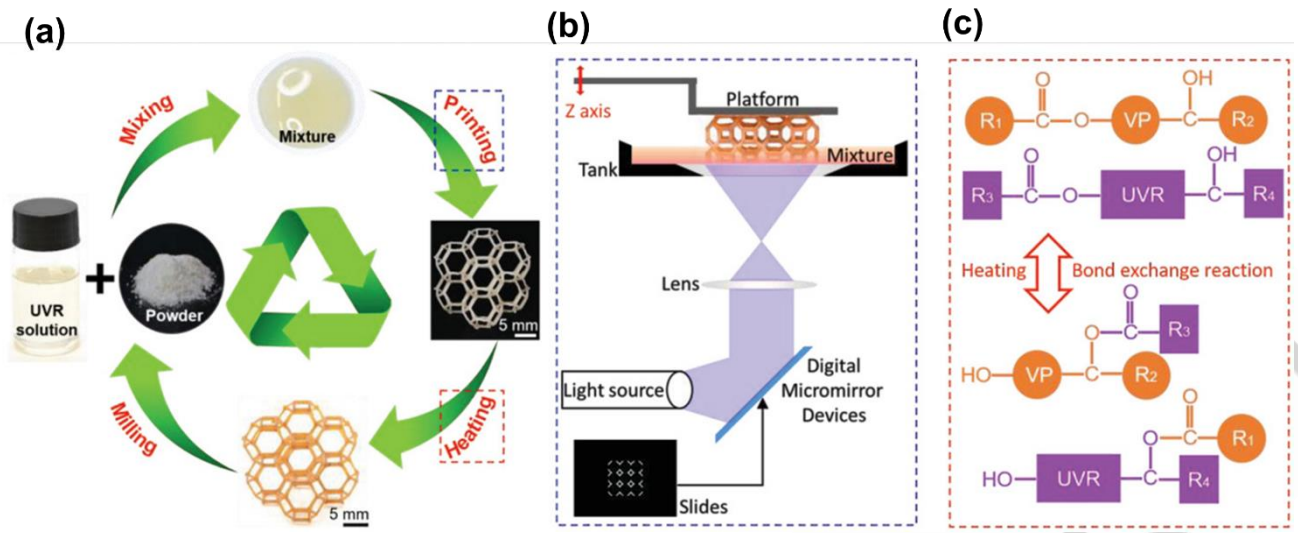


Figure 1. (a) Schematic illustrating a complete cycle for reprocessing transesterification-based vitrimers into intricate 3D geometries through DLP-based 3D printing and bond exchange reactions. (b) DLP-based 3D printing schematic. (c) Bond exchange reaction between UV-curable recycling resin (UVR) and vitrimer powder (VP) during heat treatment. R1, R2, R3, and R4 denote potential middle chains in acrylate polymer. Reproduced with permission.[20]

In this study, the complete degelation of the polymer network arises from exchange reactions between thiols and thioesters, catalyzed by nucleophilic or basic catalysts, with an excess of thiols exceeding twice the molar ratio. The chemical functionality of the original monomers, preserved within the oligomeric products (i.e., thiols), enables prompt repolymerization into fresh networks. This attribute distinguishes it from alternative techniques, like photodegradation, commonly employed to break down polymer backbones, wherein the resulting products are challenging to integrate into new materials, potentially leading to the persistence of various species as pollutants. However, recycled polymers experience diminished mechanical toughness resulting from simultaneous photopolymerization and crystallization processes, which introduce flaws into the material.

Gao and his colleagues presented a solution for chemical recycling thermoplastics (Figure 2).[22] They combined hydrogen bonds and exchangeable β-hydroxyl esters into acrylate-based vitrimers. The synthetic acrylate prepolymer is derived from glycidyl methacrylate, and suberic acid. Tetrahydro-furfuryl acrylate acts as a monomer, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst, acrylamide as a hydrogen-bond supplier, and diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide as a photoinitiator, with ethylene glycol and acetone as solvents. The SLA 3D printed materials exhibit reprocessability due to the presence of exchangeable β-hydroxyl esters in the acrylate vitrimers, enabling dynamic ester exchange reactions and rearrangement of crosslinked networks at elevated temperatures. This method and material provide a combination of mechanical robustness, and reprocessability in 3D printing applications, enhancing mechanical properties through β-hydroxyl esters while allowing for reprocessing via dynamic ester exchange reactions. As the temperature increases, the hydrogen bonds gradually break, but the synthetic vitrimers maintain their dynamic properties, enabling reprocessing of the sturdy 3D printed structures. However, mechanical strengths of the synthetic acrylate prepolymer with 20% acrylamide after thermal reprocessing and chemical recycling decreased from 15.3 MPa to 9.31 and 11.33 MPa respectively. One potential limitation is the requirement for high temperatures for remolding, as β-hydroxyl ester exchange reactions occur more rapidly at elevated temperatures.

Moreover, the incorporation of ester and imine functionalities in thermosets holds the potential to enhance processability, facilitated by the formation of associative dynamic covalent bonds. Liguori and her research team have introduced a novel material involving isosorbide-based resins and thermosets.[23] The materials employed comprise methacrylated isosorbide, methacrylated vanillin, and Schiff-base resin. The Schiff-base resin is derived from 2,2′-(ethylenedioxy)-bis(ethylamine) through an imination reaction with the methacrylated vanillin monomer. The composition of the resins significantly imparts rigidity to thermosets. Imine-based thermosets can undergo reprocessing through the metathesis pathway, which involves imine exchange, an associative mechanism. The thermoset was dissolved in 1 M sodium hydroxide (NaOH) at high temperature, acidified with aqueous hydrochloric acid (HCl) to a pH of about 2, and then underwent water evaporation. After adding ethanol, the mixture was stirred overnight. The resulting solution was then filtered to remove the salt, and the filtrate was dried under reduced pressure to form powders. These powders were further collected and hot-pressed. Despite having successful reprocessing methods, challenges still remain, primarily stemming from the deterioration of mechanical properties caused by damage to covalent bonds that are not dynamic during the reprocessing procedure.

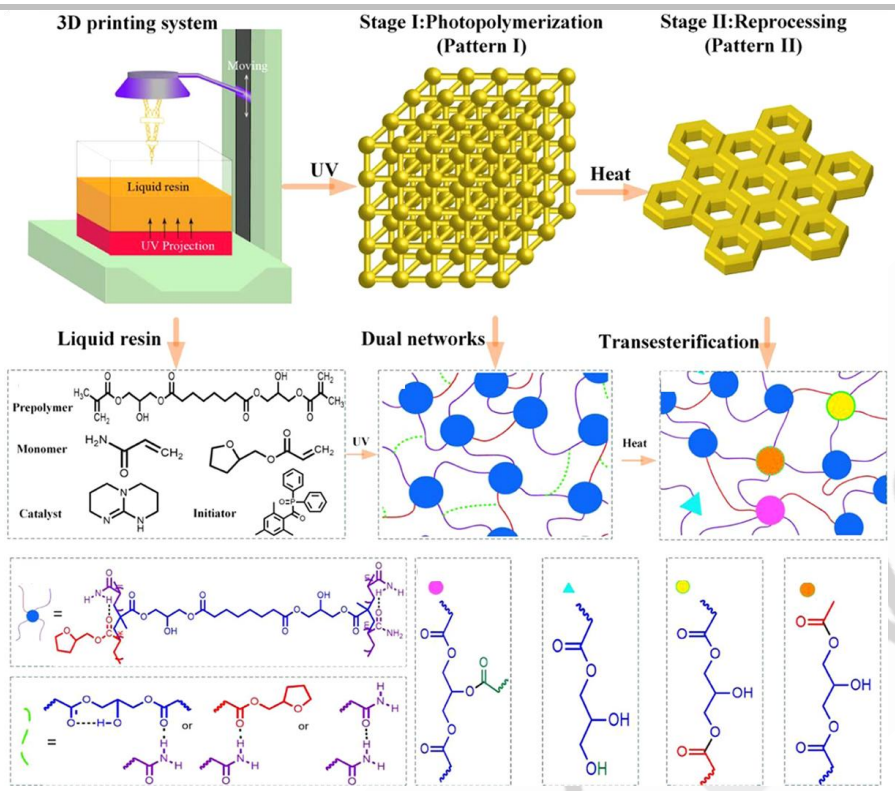


Figure 2. Schematic illustrating the 3D printing process and reprocessing of mechanically robust acrylate vitrimers. The system employs photocurable materials with permanent chemical crosslinks and dynamic hydrogen bonds. Reprocessability, facilitated by dynamic ester exchange through thermal-activated transesterification, enables dynamic covalent bond recombination. Reproduced with permission.[22]

Chen and colleagues proposed another successful chemical recycling approach, utilizing a transimination reaction to convert DLP 3D-printed thermosets into thermoplastics (Figure 3).[24] They utilized 2-hydroxyethyl acrylate and isobornyl acrylate in the photo-curable resin, and diglycidyl ether of bisphenol A in the thermally reactive resin for copolymerization via DLP 3D printing, followed by thermal polymerization. This technique allows for a small-molecule-assisted bond exchange reaction for the depolymerization of the thermoset. Printed parts would undergo recycling via the bond exchange reaction method, involving reprocessing solvent diffusion, ester bond cleavage, and depolymerization, facilitating their reuse in 3D printing. The recycling solvent consisted of ethylene glycol and transesterification catalyst. Concurrently, the integrity of the acrylate network is maintained, contributing to the strength and stability of the printed thermoset. Despite the recycled thermoset having a slight decrease in elongation and stress after reprocessing, this method shows potential for using hybrid resins to develop reprocessable thermosets without the need for a crosslinker in future 3D printing applications. Other potential dynamic reactions for chemical recycling of photopolymers include thiol-isocyanate exchange reactions[25], thiourethane exchange reaction[26], and amine/urea exchange reactions[27].

The chemical recycling of 3D printed thermosets presents significant potential for sustainable and efficient material reuse, offering a pathway for high-quality recycled materials within closed-loop systems. Ongoing research aims to enhance the recyclability and mechanical properties of recycled materials by investigating dynamic covalent reactions like transesterification, thiol-thioester exchange, and ester exchange reactions. While these approaches have shown successes, certain challenges still persist. A notable challenge involves the introduction of chemicals or catalysts during the recycling processes, giving rise to concerns regarding environmental impact and necessitating meticulous management of these inputs. Particularly, certain catalysts may deactivate or migrate during recycling, leading to loss of reversibility. Thus, the development of catalyst-free dynamic covalent bonds for UV-curable resin is highly desirable to achieve high performance comparable to recent achievements in non-UV sensitive resins.[28] Furthermore, the difficulty in reobtaining the monomers, particularly due to the characteristics of acrylate/methacrylate type structures, remains a significant challenge. Future research efforts are positioned to tackle these challenges and refine recycling conditions. In addition to dynamic covalent bonds, alternative techniques can also be employed to reprint polymers, utilizing methods similar to recycling dynamic covalent polymers. For instance, one approach involves using monofunctional photosensitive polymers to print dissolvable linear polymer parts[29], while another method entails employing polymerizable deep eutectic solvents for printing solvent-dissolvable polymers[30]. Additionally, the upcycling of printed structures through aminolysis presents another potential avenue for achieving this goal[31]. The ultimate goal is to establish a complete closed-loop system for additive manufacturing of high-performance functional photopolymers, ensuring sustainability and minimizing the environmental footprint of 3D printing processes.[32]

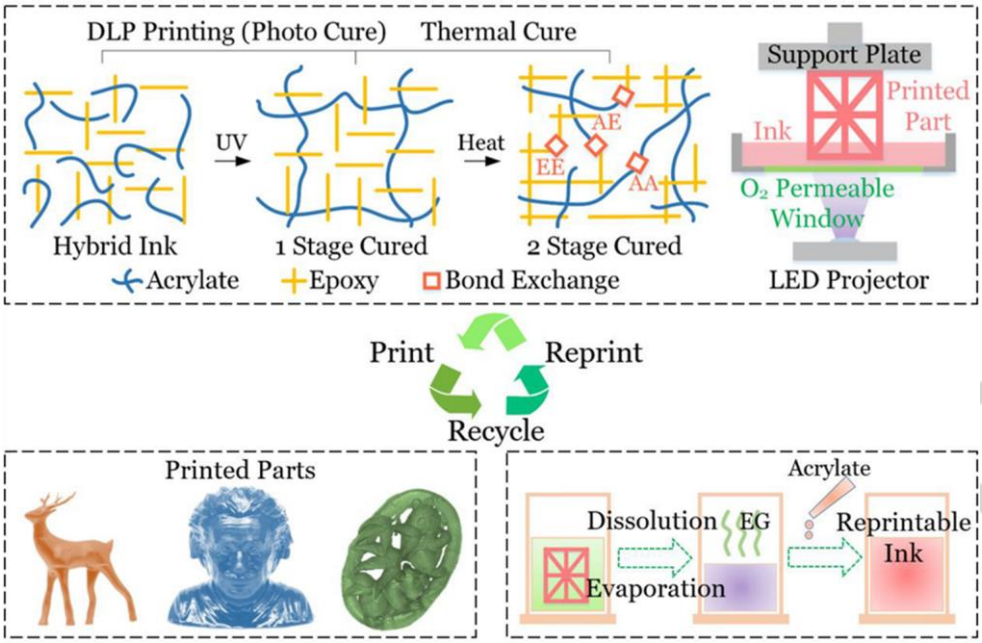


Figure 3. Schematic illustrating the DLP 3D printing, thermal curing, and reprocessing of 2-hydroxyethyl acrylate and isobornyl acrylate in the photo-curable resin, and diglycidyl ether of bisphenol A in the thermally reactive resin through dynamic transimination reaction. The process involves a two-stage curing process, including photopolymerization and thermal curing steps. Reprocessability of 3D printed parts is achieved through dynamic transimination reactions, enabling the reprinting of the ink while maintaining the acrylate network. Reproduced with permission.[24]

3. Thermo-mechanical Recycling of 3D Printed Thermosets with Dynamic Covalent Bonds

Thermo-mechanical recycling methods involve physical techniques such as hot pressing and hydraulic pressing at elevated temperatures and pressures.[33] Thermosets with dynamic/reversible properties are typically cut or ground into pieces, then pressed using a hot press or hydraulic press to create recycled materials, with properties influenced by parameters such as temperature, pressure, and particle size.[34] In comparison to chemical recycling, thermo-mechanical recycling is considered more energy-consuming, potentially leading to thermal degradation or oxidation during sustained heating. However, it does not require the addition of chemicals during the recycling process. Table 2 displays various studies reporting the thermo-mechanical recycling of 3D-printed thermosets.

For instance, Zhang and colleagues utilize the concept of transesterification reactions, with a focus on 2-hydroxy-3-phenoxypropyl acrylate, to create a 3D-printed thermoset with thermo-mechanical recyclability (Figure 4).[35] The utilized DLP-based 3D printing method through a two-step polymerization strategy involves photopolymerization (Stage I) and transesterification (Stage II). During 3D printing photopolymerization, permanent covalent bonds were formed. Upon heating the thermoset to an elevated temperature, a faster transesterification reaction occurs between the ester and hydroxyl groups, leading to the formation of dynamic covalent bonds. While the presence of permanent covalent networks limits full recycling of acrylate polymers, the resulting thermosets incorporated dynamic covalent bonds through transesterification reactions, facilitating controlled depolymerization and repolymerization. The recycling process involves heating samples under a hydraulic press at 500 MPa and 200 °C for 2 hours. Remarkably, even after multiple reprocessing cycles, the material displayed no significant deterioration in its properties. Slight mechanical degradation was observed after each reprocess treatment, but overall mechanical properties are still suitable for further use.

Additionally, Cui and colleagues introduced a transesterification method applied to a photo-curable mixture comprising 2-hydroxyethyl acrylate (HEA)/2-hydroxyethyl methacrylate (HEMA), a bis(2-acryloyloxyethyl) malonate crosslinker, and a diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) photoinitiator (Figure 5).[36] Because of the presence of an electron-withdrawing carbonyl group at the β position of the ester group, reversible transesterification occurs between hydroxyl and ester groups without the need for the addition of a catalyst/chemical, but it does require hot pressing. Following the first recycling cycle, recycled samples exhibit mechanical properties, including stress and strain, close to the initial state, with the recycled sample's Young's Modulus surpassing that of the original. After the second recycling cycle, there are slight decreases in mechanical properties. The recycling process involves exposing the material to high temperatures and pressures, potentially leading to the dehydration of hydroxyl groups into ether groups. This, in turn, may have a negative impact on ester exchange and overall mechanical properties.

Table 2. 3D printed thermo-mechanical recyclable thermosets with dynamic covalent bonds

No.	Material	Dynamic covalent reaction	Printing technology	Thermo/mechanical recycling condition	Advantage	Limitation	Ref
1	2-hydroxy-3-phenoxypropyl acrylate	Transesterification reaction	DLP	Hydraulic press with 500 MPa at 200 °C for 2 hours	High ability to reprocess multiple times	Slight mechanical degradation after each recycling treatment	[35]
2	2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate with bis(2-acryloyloxyethyl) malonate crosslinker	Transesterification reaction	DLP	Hot press with 6 MPa at 150 °C for 2 hours	Mechanical properties of reprocessed samples close to original after first recycle	Reduction in hydroxyl groups due to high temperature and pressure during recycling process	[36]
3	Bisphenol-A-glycerolate dimethacrylate	Transesterification Reaction	DLP	Hot press with 9-12 MPa at 150-200 °C for 2 hours	High mechanical strength, shape memory effect, and recovery stress	High temperatures required for recycling due to higher reactivity of transesterification reactions and higher chain mobility	[37]
4	2-hydroxy-3-phenoxypropyl acrylate, acrylated epoxidized soybean oil, tetrahydrofurfuryl methacrylate	Transesterification Reaction	DLP	Hot press with 0.3 MPa at 200 °C for 1 hour	Improved mechanical properties after recycling	Limited content of tetrahydrofurfuryl methacrylate due to rapid UV polymerization process	[38]
5	Bisphenol A glycerolate dimethacrylate and 2-hydroxy-2-methylpropiophenone	Transesterification Reaction	UV curing	Hot press with 6-14 MPa at 130-175 °C for 2 hours	Maintains high mechanical properties of original thermosets	Efficiency and number of recycling cycles limited	[39]
6	Vanillin acrylate and, methacrylate-functionalized Jeffamine crosslinkers	Imine exchange reaction	DLP	Hydraulic press with 10 MPa at 140 °C for 3 hours	Simple synthetic procedures	Potential decrease in mechanical performance from grinding into a fine powder	[40]
7	Trifunctional vanillin-based crosslinker, bifunctional vanillin-based building block bridge, and isobornyl methacrylate	Imine exchange reaction	DLP	Hot press with 40 kN at 200 °C for 5 minutes	Biobased photopolymer resin used, allowing reprocessing within 5 minutes	Observed lower values for strain at break	[41]
8	Polyurethane acrylate	Diels-Alder reactions	DLP	Hot press with 10 MPa at 130 and 80 °C for 1 and 25 hours, respectively	Achieves remarkable shape memory performance and high shape recovery stress	Significant reduction in elongation at break after recycling due to incomplete reverse of Diels-Alder-bonding causing microstructural defects	[42]

Various other thermo-chemical recycling methods based on transesterification reactions have been reported. For instance, Li and colleagues introduce a novel cubic microlattice, a multifunctional lightweight architecture, with mechanical strength comparable to metallic microlattices.[37] The polymer, composed of bis-phenol-A-glycerolate dimethacrylate (BPAGMA) and 1,4-butanediol dimethacrylate (BDDMA), demonstrates good recyclability due to the 1:1 ratio of hydroxyl groups to ester groups in BPAGMA. Thermo-chemical recycling can be achieved by applying a hot press with 9-12 MPa at 150-200 °C for 2 hours through the transesterification reaction, despite a reduction in tensile strength in recycled samples caused by BDDMA. Other examples include biobased vitrimers with 2-hydroxy-3-phenoxypropyl acrylate, tetrahydrofurfuryl methacrylate, and acrylated epoxidized soybean oil[38], or epoxy-based vitrimers[39].

Another promising thermo-mechanical recycling method explored by Cortés-Guzmán and colleagues involves the inclusion of vanillin acrylate as part of a dynamic imine covalent bond system.[40] Alongside this, they incorporated various vanillin methacrylate-functionalized Jeffamine crosslinkers and a diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (DPPO) photoinitiator for the development of DLP 3D-printed thermosets. By employing a hydraulic press under specific conditions—about 10 MPa pressure at 140 °C for 3 hours—they induce the formation of dynamic imine covalent bonds through transimination. The inclusion of imine moieties enables the materials to undergo remolding or reprocessing, facilitated by heat activation.

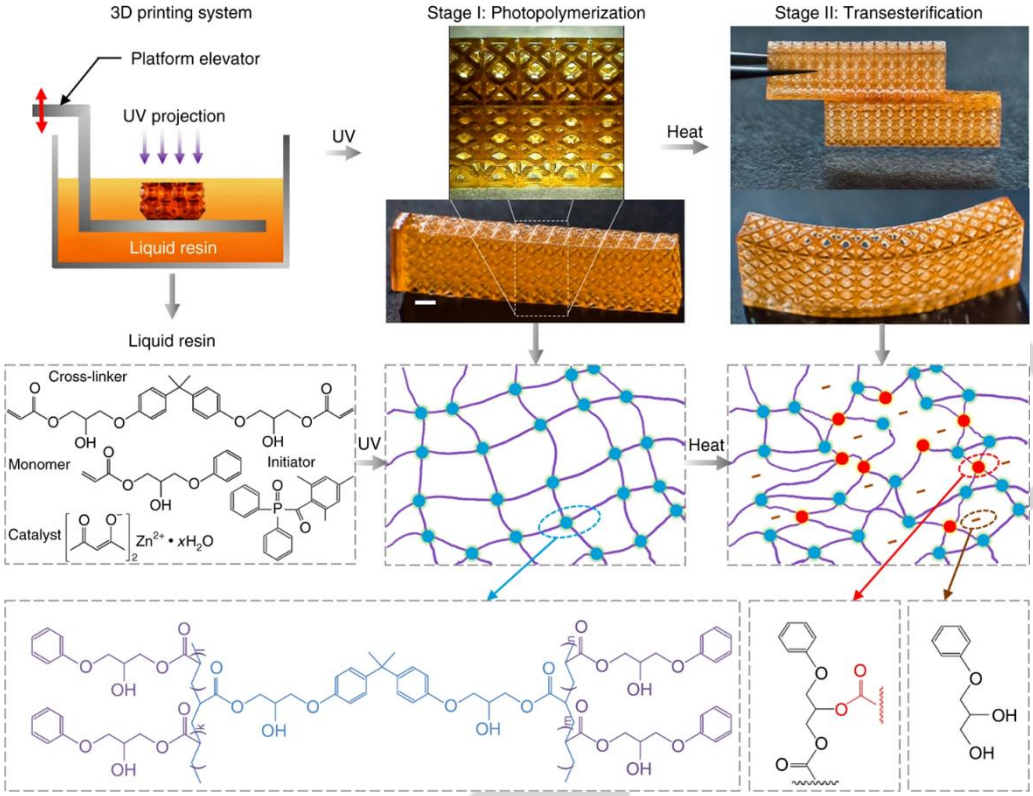


Figure 4. Schematic illustrating the DLP 3D printing and reprocessing of 2-hydroxy-3-phenoxypropyl acrylate through dynamic transesterification reaction. The process involves a two-stage curing process, including photopolymerization and transesterification steps. Recyclability of 3D printed parts is achieved through depolymerization and repolymerization, enabling the reprinting of the ink after recycling. Reproduced with permission.[35]

The approach stands out for its simplicity in synthetic procedures and the use of readily available Jeffamines. It should be noted that grinding into a fine powder may impact crosslinking and lead to a decrease in mechanical performance. This work presents novel resins incorporating different Jeffamines modified with vanillin methacrylate, providing a promising avenue for the development of reprocessable thermosets in the realm of 3D printing applications.

Besides, Stouten and colleagues have introduced a thermo-mechanical recyclable biobased photopolymer resin, synthesized from trifunctional vanillin-based crosslinker (CROSS), bifunctional vanillin-based building block bridge (BDG), and isobornyl methacrylate (IBOMA), incorporating a phenylbis(2,4,6-trimethylbenzoyl)phospine oxide photoinitiator (BAPO).[41] The resin's reprocessing capability is facilitated by dynamic imine covalent bonds, allowing efficient reprocessing within a brief 5-minute timeframe under hot pressing with 40 kN. Primarily utilized in 3D printing, the incorporation of a building block with a higher concentration of imine bonds accelerates stress relaxation, contributing to enhanced mechanical rigidity in the vitrimer. This study signifies a notable progress in biobased photopolymer resins, highlighting their potential in 3D printing applications by enhancing mechanical properties and enabling rapid reprocessing.

Exploring the application of polyurethane acrylate, Li and the team incorporated a Diels-Alder adduct.[42] This formulation incorporated hydroxyethyl acrylate as a reactive diluent and utilized different photoinitiators—2-hydroxy-2-methylpropiophenone and bis(2,4,6-trimethylbenzoyl) phenyl phosphine oxide. To create a recycled sheet, the original sheet was cut into small pieces, placed in a rectangular mold, and subjected to hot pressing at 130 °C for 1 hour, followed by 80 °C for 24 hours under 10 MPa pressure. The presence of the Diels-Alder adduct adds reversibility to the Diels-Alder reactions within the cured samples. Notably, the printed samples exhibit impressive shape memory performance, with shape fixity and recovery ratios of 96% and 99%, respectively, and a high shape recovery stress of 10.1 MPa—a noteworthy achievement for shape memory polymers. The cured samples demonstrate high mechanical properties, with a tensile strength exceeding 30 MPa. Post-recycling, the tensile strength of the samples nearly recovers to that of the original samples, although there is a notable reduction in elongation at break. This reduction is attributed to microstructural defects caused by the incomplete reversal of Diels-Alder bonding during recycling. The study represents a significant advancement in the development of high-strength and recyclable shape memory polyurethanes, leveraging the distinctive features of Diels-Alder chemistry.

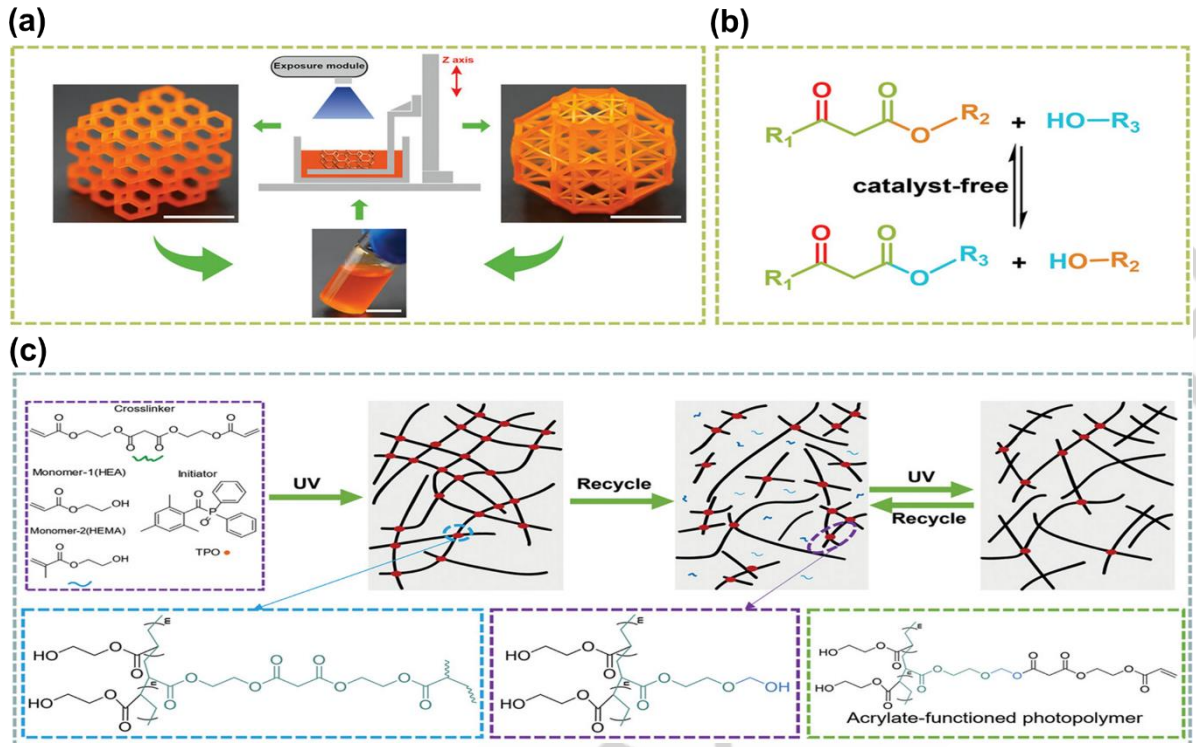


Figure 5. (a) Schematic illustrating the DLP 3D printing and recycling process of acrylate-functioned photopolymers through transesterification. (b) catalyst-free transesterification between the β-carbonyl ester and the hydroxyl groups. (c) Polymer crosslinked networks from 3D printing, capable of dissolution for chemical modification. Reproduced with permission.[36]

The future of thermo-mechanical recycling in 3D printed thermosets appears promising, with several key areas poised for development. Given the demanding conditions of elevated temperature and pressure during the recycling process, preserving structural integrity emerges as a critical consideration. The exploration of diverse dynamic covalent bond systems, extending beyond established methods like transesterification and imine exchange, is anticipated to broaden the scope of recyclable thermosets. This not only expands the range of recyclable materials but also introduces functionalities that simultaneously enhance both recyclability and material performance. Continued concerns about the environmental impact require ongoing efforts to improve assessments, focusing on reducing energy consumption and conducting thorough life cycle evaluations. Additionally, the intentional use of versatile materials, such as lightweight architectures and biobased compositions, is anticipated to become more prevalent.[37] This combination should allow for finding a careful balance between mechanical strength and recyclability, contributing to the progress of sustainable practices in thermo-mechanical recycling.

4. Self-Healing of 3D Printed Thermosets with Dynamic Covalent Bonds

Self-healing materials through dynamic bonds are another application that takes advantage of the reversibility of dynamic covalent bonds to govern self-repairing behaviors and promote their reuse. Polymers crosslinked through dynamic covalent bonding undergo the breakage of existing bonds and the formation of new ones, absorbing energy from sources such as light, heat, magnetic, or electric fields.[43] This capability for repair and reuse reduces the need to discard damaged items, aligning with sustainability goals and minimizing material waste. However, the development of dynamic covalent-based self-healing materials faces numerous challenges and deficiencies, requiring optimization of synthesis methods for various types of dynamic molecules, which can be complex and laborious.[44] This is particularly notable in photopolymer systems where the constraints of photopolymerization add further complexity. Despite these challenges, the development of dynamic materials offers exciting opportunities and potential for further advancements and discoveries. Table 3 showcases a range of studies highlighting the self-healing properties of 3D-printed thermosets incorporating dynamic covalent bonds.

Table 3. 3D printed self-healable thermosets with dynamic covalent bonds

No.	Material	Dynamic covalent reaction	Printing technology	Self-healing method	Advantage	Limitation	Ref
1	Vanillin glycidyl ether, Eugenol glycidyl ether, Guaiacol glycidyl ether, Vanillyl alcohol diglycidyl ether of vanillyl alcohol	Transesterification reaction	DLP	Heat at 120 and 180 °C with applied pressure	Excellent healing capabilities without compromising mechanical performance	Relatively high temperature of at least 120°C required for healing	[45]
2	Mono- and bi-functional acrylate monomers with hydroxyl groups	Transesterification reaction	DLP	Heat at 180 °C for 4 hours	Triple-shape memory characteristic	High temperature of 180°C required for healing	[46]
3	Urethane monoacrylate, acrylic acid, zinc dimethacrylate	Reversible ionic bonding and hydrogen bonding	DLP	Heat at 130 °C under a pressure of 10 MPa for 3 hours	Tailorable mechanical properties with wide range	Slight mechanical degradation after each recycling round	[47]
4	2-(*tert*-butyl amino) ethyl methacrylate, *n*-butyl acrylate, hexamethylene diisocyanate crosslinker	Hindered urea bonding	LCD	Adding "nutrient solution" and soaking for 1.5 hours, followed by exposure to a UV lamp for 5 minutes	Rapid self-healing within 5 minutes	Requires a nutrient solution for self-healing	[48]
5	Iminated methacrylated extended vanillin, and ethylenediamine	Transimination reaction	DLP	Heat at 125 °C for 30 minutes	Accelerated stress relaxation and improved mechanical rigidity with addition of a building block with higher imine bond concentration	Slight decrease in elongation and stress at break	[49]
6	Polyurethane acrylate, and hydroxyethyl acrylate	Disulfide exchange reaction	DLP	Heat at 80 °C for 12 hours	Multiple-time healing capabilities without compromising mechanical strength	Surface defects on self-healed materials are caused by stress concentration	[50]
7	Thiocarbamate bonds-containing one-step synthetic dynamic crosslinker, and reactive diluent methyl methacrylate	Dynamic exchange reaction of thiocarbamate bonds	DLP	Heat at 150 °C under a pressure of 6 MPa for 2 hours	High mechanical properties of the recycled materials	High temperature and pressure required for healing	[51]
8	Aliphatic dithiol 1,10-decanedithiol, tetrathiol crosslinker, and thioester diallyl ether monomer	Thiol−thioester exchange reaction	SLA	Add triethylamine dropwise and heat at 100 °C for 2 hours	Excellent healing capabilities without compromising mechanical performance	Required a chemical to facilitate self-healing	[21]

One example of a self-healing photopolymer is based on the biobased printable polymer resin developed by Cortés-Guzmán and co-workers.[45] This work focuses on three different formulations of resin, incorporating vanillin glycidyl ether (VGEA), eugenol glycidyl ether (EGEA), guaiacol glycidyl ether (GuGEA), and vanillyl alcohol, with diglycidyl ether of vanillyl alcohol (DGEVA) serving as the bio-based crosslinker. In this formulation, zinc acetylacetonate ($Zn(acac)_2$) is introduced as an additive, designed to yield thermosets with the capability of self-healing and recycling through dynamic transesterification reactions. The exceptional self-healing and recyclability of the materials are attributed to the presence of free hydroxy groups and dynamic transesterification reactions catalyzed by $Zn(acac)_2$. The incorporation of acrylate moieties into the resin components facilitates photo-reactive polymerization during 3D printing, enabling the fabrication of intricate structures with outstanding printability. VGEA and EGEA thermosets demonstrate remarkable healing capabilities, evident in the complete disappearance of inflicted surface defects (Figure 6). While the GuGEA thermoset also displays the ability to heal scratches, a faint scar persists even after the 180 °C treatment, attributable to its denser packing in the polymer networks. This study additionally presents reprocessing experiments that underscore the materials' capacity for recycling without compromising mechanical performance, particularly noticeable in the VGEA with 20% DGEVDA crosslinker formulation.

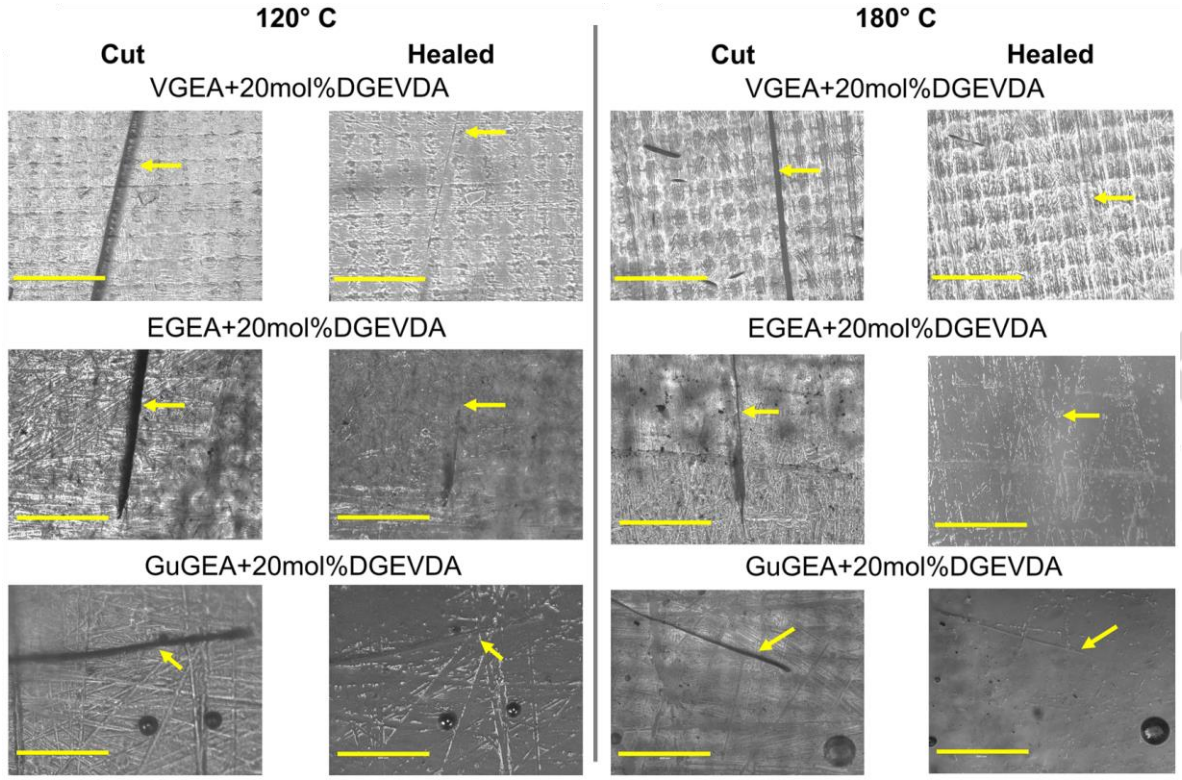


Figure 6. Optical microscopy images depicting scratches on the sample surface of vanillin glycidyl ether (VGEA), eugenol glycidyl ether (EGEA), guaiacol glycidyl ether (GuGEA), and vanillyl alcohol, with the diglycidyl ether of vanillyl alcohol (DGEVA) crosslinker. The outcomes subsequent to heat treatment at 120 °C and 180 °C for 16 hours are also demonstrated, with a scale bar of 400 µm. Reproduced with permission.[45]

Rossegger and colleagues have examined another transesterification-based 3D printed dynamic covalent thermoset. As commonly used transesterification catalysts are poorly soluble and compromise the cure rate of photocurable resins[46], they propose an efficient transesterification catalyst, oligomeric methacrylate phosphate, to enable the incorporation of the liquid and easily soluble substance into a wide range of acrylate monomers. A photocurable thiol-click formulation (resin-ER-1) was developed, comprising mono- and bi-functional acrylate monomers with hydroxyl groups. The addition of 25 mol% thiol as a crosslinker, along with 5 wt% catalyst and 2 wt% photoinitiator, resulted in a formulation with high storage stability and fast cure rates—essential for layer-by-layer 3D printing using DLP. The study explores the additional crosslink sites formed during thermal treatment, leading to self-healing and improved mechanical properties in 3D-printed specimens. This material exhibits remarkable triple-shape memory, allowing controlled and active macroscopic deformation upon heating. Broken parts of 3D-printed structures can be healed through thermal treatment at a high temperature of 180 °C, showcasing the potential for practical applications in soft robotics and actuator devices.

Additionally, Zhu and colleagues introduce a method that utilizes reversible ionic bonding and hydrogen bonding to facilitate DLP 3D printing with polymers that are both healable and recyclable.[47] The printable resins consist of monofunctional monomers including urethane monoacrylate (UMA) and acrylic acid (AA), with zinc dimethacrylate serving as the crosslinker, and camphorquinone. The materials printed in this study are composed of poly(urethane monoacrylate-co-acrylic acid) copolymers crosslinked through ionic bonding between Zn^{2+} and $-COO^-$, as well as hydrogen bonding between −NH or −OH and −C=O. The inclusion of both ionic and hydrogen bonding, which can be thermally reversibly broken and reformed in both soft and rigid materials, imparts a remarkable self-healing and recycling capability to the printed objects. 3D-printed structures with varying UMA/AA ratios were dissected into separate parts, subsequently brought together, and successfully healed at 90 °C for 12 hours (Figure 7). Notably, the 3D-printed part exhibited effective recovery, supporting a significant weight of 200 g without apparent deformation after the healing process. The self-healing efficiency demonstrated an increase with both heating time and temperature, owing to the outstanding self-healing capability resulting from the synergistic interaction of dynamic ionic bonding and hydrogen bonding. Furthermore, the 3D-printed part demonstrated the ability to be restored after recycling. Despite the repeatable nature of the recycling process, as seen in other studies, a slight mechanical degradation is observed after each recycling round, with more than 70% of the mechanical properties recovered.

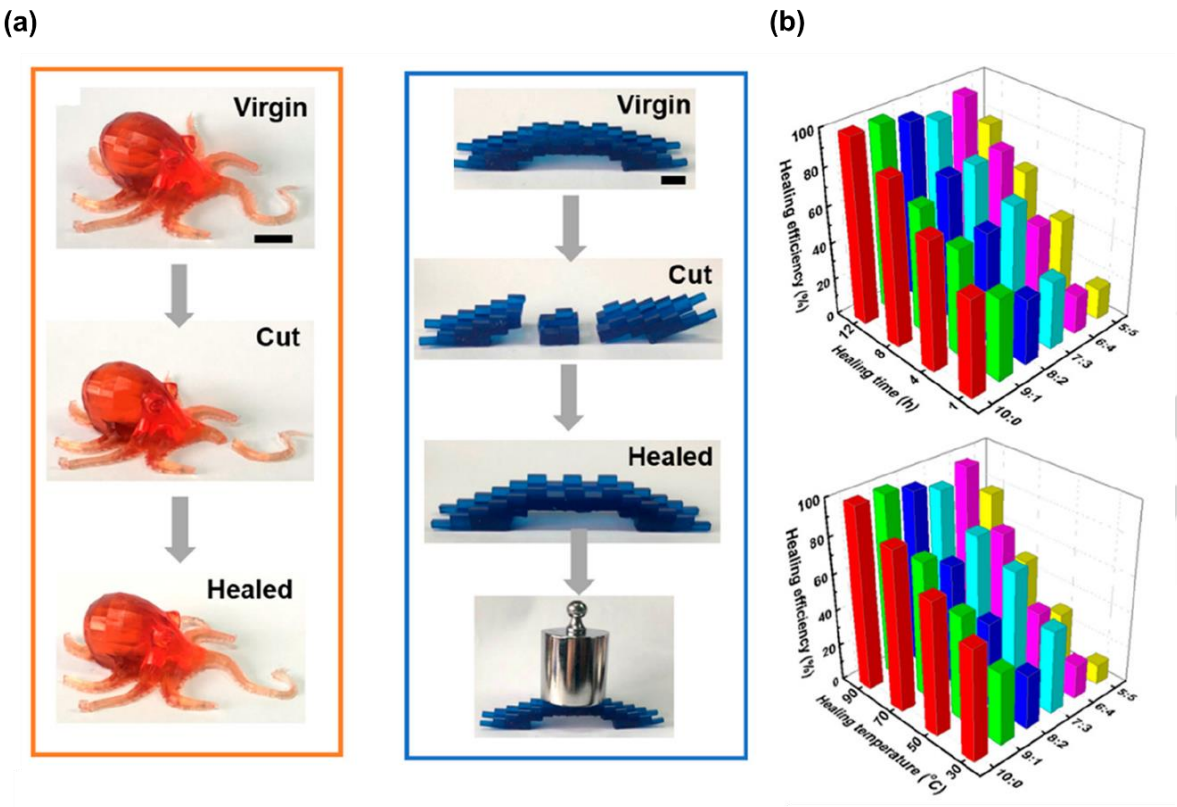


Figure 7. (a) Schematic illustrating the self-healing capability of the 3D-printed soft octopus with a urethane monoacrylate (UMA)/acrylic acid (AA) ratio of 9:1 and the 3D-printed rigid bridge with a UMA/AA ratio of 6:4. (b) Healing efficiencies of different UMA/AA ratios after healing at various times at 90 °C and various temperatures for 12 hours. Reproduced with permission.[47]

Furthermore, Jia and colleagues conducted a study focused on formulating a self-healable photocuring resin for 3D printing.[48] The formulation included key components such as 2-(*tert*-Butyl Amino) ethyl methacrylate, *n*-butyl acrylate, I819 photoinitiator, and hexamethylene diisocyanate as a crosslinker. Based on the dynamic nature of hindered urea bonds, this 3D-printed material demonstrates rapid self-healing properties, achieved by applying a "nutrient solution" to the damaged area and exposing it to UV light (405 nm) for just 5 minutes. Notably, the material exhibits an impressive capacity for swift self-healing. Additionally, a notable feature lies in a direct recycling process where the solid polymer is ground and blended with pure photocuring resin, enabling re-3D printing without the need for catalysts or solvents. During the recycling process, the reprinted material experiences minimal mechanical fatigue. Investigation into various crosslinker/monomer ratios revealed that elevated ratios lead to higher tensile strength and an increased glass transition temperature. Considering the challenges associated with traditional thermosets in terms of healing and reusability, this material offers fast damage-healing and direct recycling capabilities, addressing critical aspects in the realm of 3D printing.

Another work on self-healable and 3D printable vanillin-based photocurable resin has been developed by Liguori and her colleagues through the concept of dynamic imine covalent bonds through transimination.[49] This resin is derived from the reaction of iminated methacrylated extended vanillin and ethylenediamine in dichloromethane. Because of its crosslinked structure and imine linkages, the thermoset exhibited malleability, self-healing, and thermal reprocessability. As shown in Figure 8, the Schiff-base methacrylated extended vanillin thermoset (SH X-SB2) was cut into two pieces, overlapped, and heated at 125 °C for 30 minutes to initiate the imine exchange for self-healing. Successful healing of the specimens is observed, facilitated by the metathesis pathway. Furthermore, the study demonstrates recyclability through dynamic imine covalent bonds via transimination, achieved by hot pressing at 200°C for 5 minutes. However, this reprocessing step leads to a slight reduction in elongation and stress at break.

In addition, Li and colleagues explored the fabrication of self-healing polyurethane elastomers through DLP 3D printing, employing a novel material synthesis and a distinctive self-healing method via disulfide metathesis.[50] The material, polyurethane acrylate, is synthesized with a two-step process, incorporating disulfide bonds into the network. The photopolymer resin exhibits notable properties such as high fluidity, rapid UV curing, and a self-healing mechanism primarily attributed to disulfide metathesis. The polymer is cut into 2 pieces, and the damaged surfaces of the samples are carefully connected and aligned to facilitate healing. They are then placed in an oven at 80 °C for 12 hours. Qualitatively, the material's remarkable self-healing properties are observed through optical microscopy, demonstrating the disappearance of scratches and the reassembly of complex structures with repeated healing cycles.

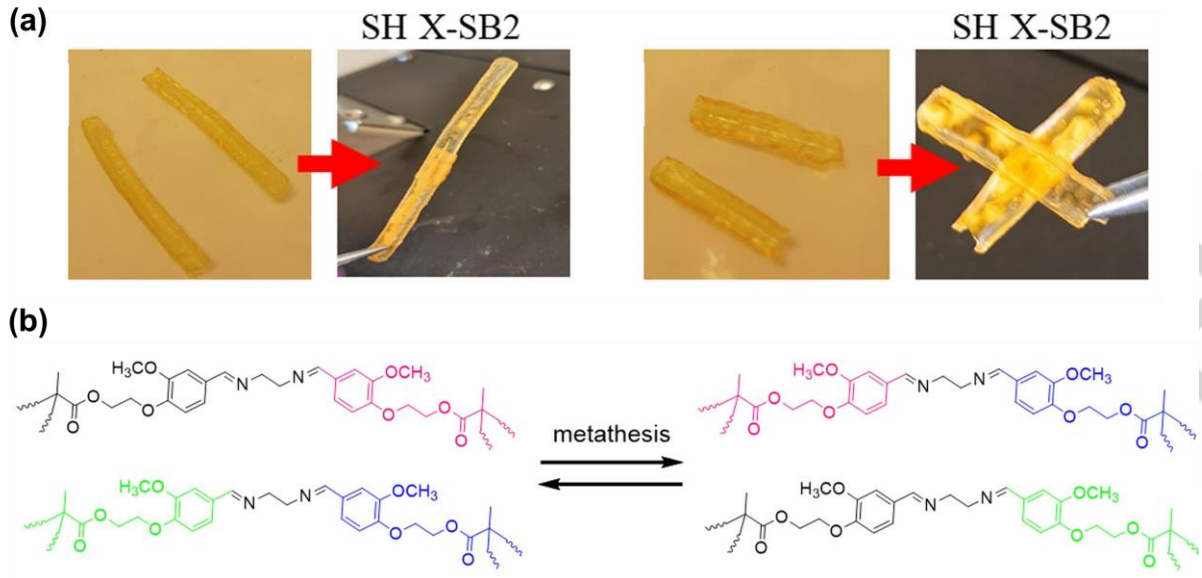


Figure 8. (a) Schematic illustrating the self-healing capability of cut photocured specimen samples of methacrylated extended vanillin-based thermoset (SH X-SB2). (b) Metathesis pathway contributing to their self-healing and mechanical recyclability. Reproduced with permission.[49]

This self-healing process is quantitatively evaluated through tensile tests, revealing a significant healing efficiency after the first cycle and a gradual decrease with subsequent cycles primarily attributable to stress-concentrated induced cracks on the sample surfaces. The self-healing ability is further visually demonstrated through scratch healing and the reassembly of cut cylindrical samples, showcasing the material's capability to support both stretchability and weight after healing. The study highlights the material's potential for applications in 3D printing, where the photopolymer resin demonstrates high accuracy and exceptional self-healing abilities with disulfide bonds. This material, coupled with its tailored self-healing method, presents promising avenues for applications in flexible electronics, soft robotics, and sensors, providing a robust foundation for future advancements in functional materials and 3D printing technologies.[52] Moreover, other possible dynamic covalent reactions for 3D printed self-healing materials include the dynamic exchange of thiocarbamate bonds[51] and thiol−thioester exchange bonds[21], offering the potential for high mechanical performance of healed materials.

The ongoing research into 3D printed self-healing materials, based on dynamic covalent bonds, offers exciting prospects for future advancements and applications. A critical area for further exploration involves simplifying synthesis to facilitate easier access to monomers and enhancing the properties of healed materials. This includes investigating innovative ways to control the formation and breakdown of dynamic covalent bonds precisely, and exploring new strategies to integrate dynamic functionalities into a broader range of materials. Additionally, it's important to delve deeper into the various dynamic covalent reactions and their potential applications in material design. By expanding the understanding of these reactions and their impact on material properties, new avenues for tailoring materials with specific functionalities and improved performance characteristics can be uncovered.

5. Degradation of 3D Printed Thermosets with Dynamic Covalent Bonds

The degradable thermoset method enables the incorporation of reversible bonds within the polymer network, ensuring controlled degradability after post-photopolymerization.[53] This involves integrating specific chemical components, such as crosslinking agents and reactive functional groups, into the polymer matrix. The outcome is a network structure with reversible covalent bonds, facilitating controlled degradation. Unlike chemical recycling, the primary objective of degradation is to break down the polymer structure, facilitating its disposal in a more environmentally friendly manner. The method aligns with circular economy principles by introducing DCNs that promote degradability, providing a sustainable solution to polymer end-of-life scenarios and minimizing environmental impact.[54] This sets it apart from other reprocessable thermoset methods that entail more environmentally burdensome processes due to additional material usage. Despite these merits, the degradable thermoset method may encounter limitations, including challenges in mechanical properties and processing complexities. There is a limited number of developed 3D printed photopolymers that exhibit good degradability (Table 4).

Table 4. 3D printed degradable thermosets with dynamic covalent bonds

No.	Material	Dynamic covalent reaction	Printing technology	Degradation solution	Advantage	Limitation	Ref
1	Thioester monomer	Thiol–Thioester exchange reaction	SLA	Triethylamine	Room temperature degradation within hours, no extensive temperatures and pressurized conditions.	Inconsistent degradation for structures thicker than 3 mm	[55]
2	Tetra-thiol and di-ene monomers	Thiol–Thioester exchange reaction	UV curing	Tetra-thiol (PETMP)	Tunable degradation time with respect to either the rate of the thiol–thioester exchange reaction and/or the diffusivity of the thiolates	Potential issues with initiators and catalysts used after multiple rounds of decomposition	[56]
3	Aliphatic dithiol 1,10-decanedithiol, tetrathiol crosslinker pentaerythritol tetrakis(3-mercaptopropionate), and thioester diallyl ether monomer	Thiol−thioester exchange reaction	SLA	Thiols and nucleophilic or basic catalysts	Achieve full degradation	Require optimization of the degradation solution to achieve the desired oligomer products	[21]
4	Vanillin acrylate and, methacrylate-functionalized Jeffamine crosslinkers	Imine exchange reaction	DLP	Hexylamine/ THF	Tunable and wide-ranging mechanical properties	Long degradation time up to 3 days	[40]

Hernandez and colleagues successfully achieved controlled degradation in 3D printed photocurable thioester networks.[55] This degradation method relies on dynamic bond rearrangement within thioester-containing covalent adaptable networks, facilitated by thiol-thioester exchange reactions through a base- or nucleophile-mediated pathway (Figure 9). The approach stands out for its high selectivity with thiols, efficient use of mild bases, stability in aqueous solutions, and inherent biocompatibility. Utilizing butyl 3-mercaptopropionate (BMP) and triethylamine (TEA) to cleave thiol-thioester networks, structural mass changes were systematically recorded and analyzed to examine the degradation rate of this polymer. The degradation rate exhibited a notable shift when the structure's wall thickness exceeded 3 mm, indicating that diffusion rates through increasing wall thickness become non-negligible. This method has demonstrated remarkable success, with 91% of the composite recoverable and reusable. Noteworthy features of this approach include its rapid degradation at room temperature within hours, absence of the need for extensive or high-temperature/pressurized conditions. However, for structures with thicknesses above 3 mm, the degradation time exhibits inconsistency compared to thinner structures. The potential applications of this thiol-thioester degradation method on an industrial scale for degradable thermoset composites are promising for the future.

Another work utilizing the dynamic covalent bonding concept for degradation of photopolymers is proposed by Wang and co-workers (Figure 10).[56] This research incorporates thioesters into the backbone of rapidly photopolymerizable step-growth crosslinked networks, aiming to construct a degradable and recyclable material with minimal changes in handling or polymerization methods. They utilize bi-functional reactive tetra-thiol (PETMP)/di-ene (TEDAE) polymers that efficiently participate in polymerization and subsequent dynamic exchange reactions, facilitating material degradation and the formation of oligomers. The introduction of acetone as a solvent enhances mass transfer between solid and liquid phases. The film completely degraded within 3 hours, resulting in a clear, non-viscous solution of dissolved oligomers. The degradation time is adjustable, depending on either the rate of the thiol–thioester exchange reaction or the diffusivity of the thiolates. In addition, these degraded oligomers can undergo polymerization again, allowing for the recovery of the pristine polymer. Results indicate that the material can be reprocessed up to 3 times without noticeable changes in detectable properties, particularly in terms of mechanical strength. Material characteristics remain consistent between different recycled rounds and batches compared to the pristine polymer. This research highlights the potential applications of the degradable and recyclable polymer in composite materials and 3D printing. However, ongoing work is necessary to optimize reaction conditions, understand degradation/stability behaviors, and implement this recycling scheme with a broader range of properties for specific photopolymer applications.

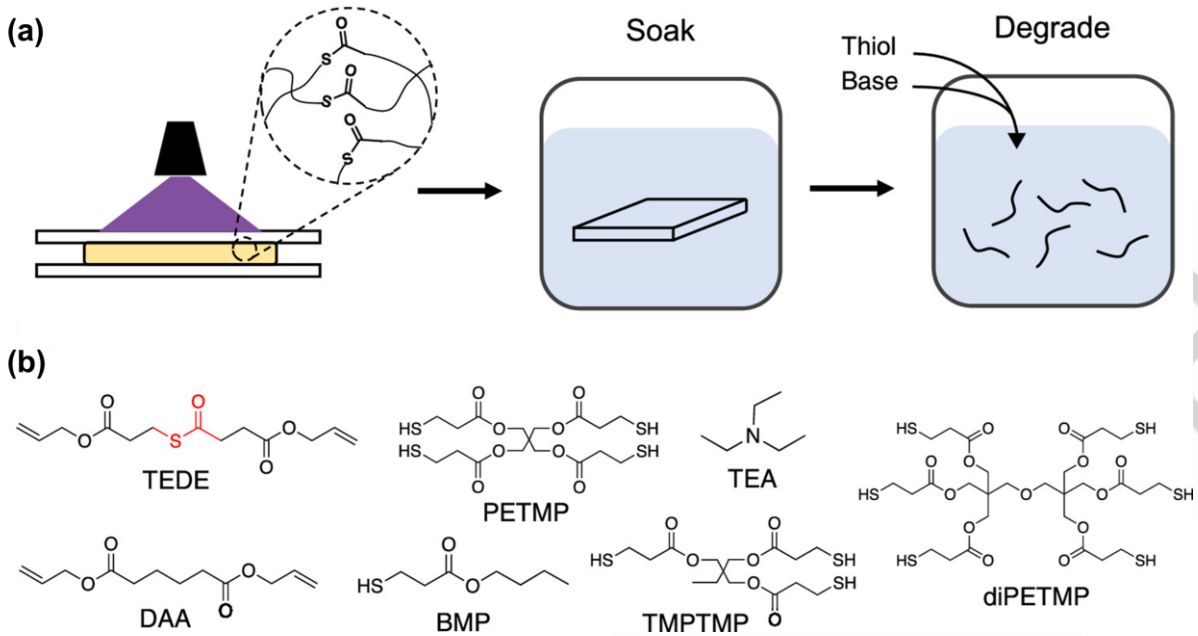


Figure 9. (a) Schematic illustrating the degradation of thioester-containing thermosets via thiol-thioester exchange triggered by the addition of thiol and base catalyst. (b) The chemical structures of monomers, free thiol, and base catalyst used to create networks and trigger thiol–thioester exchange are shown: thioester monomer (TEDE), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), triethylamine (TEA), diallyl adipate (DAA), butyl 3-mercaptopropionate (BMP), trimethylpropane tris(3-mercaptopropionate) (TMPTMP), dipentaerythritol hexakis(3-mercaptopropionate) (diPETMP). Reproduced with permission.[55]

Another promising dynamic covalent thermoset resin is formed through the photopolymerization of aliphatic dithiol 1,10-decanedithiol, the tetrathiol crosslinker, and a thioester diallyl ether monomer, as reported by Kuenstler and colleagues mentioned earlier.[21] The thermoset offers the capability of chemical recycling, self-healing, and controlled degradation under specified conditions and processes. Size-exclusion chromatography results demonstrate complete degelation of the polymer network in the presence of a molar excess of thiols, along with nucleophilic or basic catalysts, leading to exchange reactions between thiols and thioesters and the formation of low-molecular-weight oligomers with a molecular weight range of approximately 800–2700 g/mol. Crucially, the thiol–thioester exchange maintains the chemical functionality of the original monomers within the oligomeric products, enabling prompt repolymerization into new networks. This feature distinguishes it from methods such as catalysis[57] and photodegradation[58], where the collected products cannot be easily integrated into new materials. Moreover, the incorporation of thioester groups into other structured polymer systems, including those with nanoscale ordering or mesophases, offers opportunities to simultaneously control polymer assembly at small scales, enhance macroscopic performance, and improve recyclability.

In addition to thiol−thioester exchange reactions, 3D-printed chemically degradable thermosets have been achieved through dynamic imine exchange.[40] Formulations based on biobased vanillin-derived resins, comprising vanillin acrylate and vanillin methacrylate-functionalized Jeffamines, were fabricated using DLP 3D printing technology and demonstrated favorable characteristics such as recyclability, self-healing, and degradability. As previously stated, the dynamic imine moieties confer recyclability to the polymers through heat-triggered transimination reactions. Specifically addressing chemical degradability, the 3D-printed thermoset was immersed in a 1 M solution of hexylamine in tetrahydrofuran (THF) for 3 days to break the imine crosslinks and dissolve the polymer. Complete dissolution was confirmed through evaluation using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The NMR spectra revealed characteristic peaks of vanillin along with a peak at 8 ppm, corresponding to an imine, resulting from the transimination of hexylamine with the imine crosslinks within the polymer network. Due to its simple synthetic procedures, this biobased thermoset holds promise for advancing the adoption of materials primarily derived from renewable sources, contributing to a gradual shift away from polymers derived from non-renewable resources.

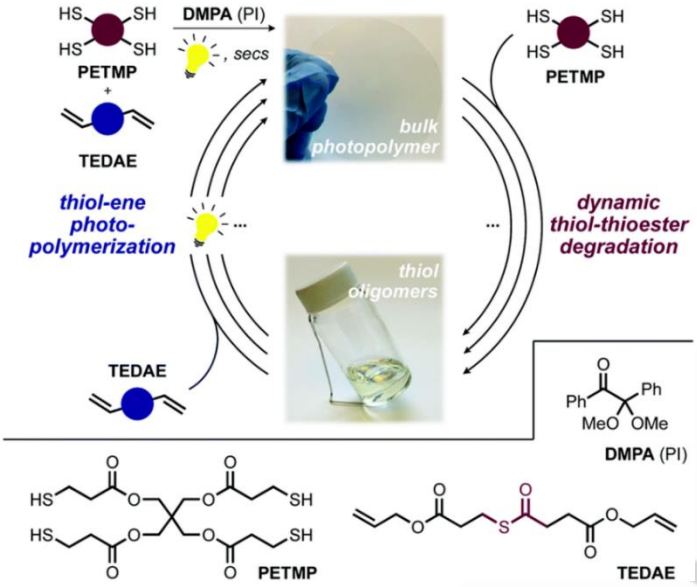


Figure 10. Schematic illustrating the degradation and repolymerization of crosslinked tetra-thiol (PETMP)/di-ene (TEDAE) photopolymers through a free radical thiol–ene polymerization and an anionic thiol–thioester dynamic degradation. The chemical structures of monomers and photoinitiator are shown: tetra-thiol (PETMP), di-ene (TEDAE), and 2,2-dimethoxy-2-phenylacetophenone photoinitiator (DMPA). Reproduced with permission.[56]

The development of 3D printable degradable thermosets with dynamic covalent bonds shows significant potential in addressing environmental concerns associated with conventional non-degradable thermosets. However, due to the limited number of reported resins and reactions for chemical degradability of photopolymers, further research is crucial to refine the dynamic covalent mechanism and thoroughly understand their degradation and stability behaviors. In addition to dynamic covalent polymers, other promising pathways for achieving degradable photopolymers include hydrolytic degradation[59] and enzymatic degradation[60]. In hydrolytic degradation, water molecules catalyze the breakdown of polymer chains into smaller, degradable fragments, while enzymatic degradation involves specific enzymes catalyzing similar breakdown processes. This entails exploring a wider range of properties and applications for specific photopolymer formulations, as well as optimizing reaction conditions to consistently achieve desired outcomes. Future studies should prioritize research on controllable degradation, rapid and straightforward degradation methods, as well as degradation at room temperature.

6. Summary and Outlook

Developing sustainable materials for vat photopolymerization (VPP) three-dimensional (3D) printing is crucial for making this technology more attractive for future sustainable industries. In this review paper, we provide a brief summary of recent developments in VPP 3D printable and reprocessable polymers with dynamic covalent bonds. These materials exhibit chemical recyclability, thermo-mechanical recyclability, self-healing capabilities, and chemical degradability by integrating dynamic reversible bonds into photopolymer networks. Various dynamic covalent reactions, such as transesterification, transamination, or thiol-thioester exchange, have been utilized to realize these properties, showcasing their adaptability in design and application. These findings suggest the potential of photopolymers to achieve high reprocessable efficiency with broad functionalities. To realize the full potential of these materials, several avenues of exploration can be pursued:

- Chemical recycling methods necessitate further research to enhance their versatility in broader photopolymer resins, focusing on optimizing the incorporation of specific chemicals to promote targeted dynamic covalent reactions while minimizing the degradation of mechanical properties over multiple recycling cycles. A closed-loop photoprinting platform with zero waste and free of catalysts is highly desirable.
- Themo-mechanical recycling methods demands investigations into refining process parameters such as temperature and pressure to mitigate any adverse effects on the properties of recycled materials. Furthermore, advancements in dynamic covalent design can customize thermoset properties to meet a wider range of application requirements.
- Self-healing methods should aim to achieve high healing efficiency without the need for added chemicals, which can be realized through the exploration of novel dynamic covalent reactions or the optimization of existing ones. Furthermore, exploring other external stimuli, such as light, pH, or electric fields, holds promise for advancing self-healing applications.
- The degradation method should expand the range of dynamic covalent reactions beyond thiol-thioester exchange, striving for controlled degradation to yield desired oligomer products.

Another challenge lies in the low bonding energy of dynamic covalent bonds, which results in limited mechanical properties of polymers, particularly affecting applications requiring hardness. Identifying stronger dynamic covalent polymers, particularly for photopolymers, can be pursued through the utilization of the high bonding energy of dynamic bonds. One potential avenue is via reversible Si–O–Si networks.[61]

Overall, progress has been notable across various fronts, including the exploration of new dynamic covalent chemistries and strategies for network reprocessing, while ongoing efforts continue to extend these advancements to practical device applications. This collective progress represents a crucial step forward in unlocking the full capabilities of sustainable functional 3D printing technologies.

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Contributions

S.P. and F.W. conceived the idea and developed the outline. S.P., Y.T.C., W.Z., T.J.E.L., and F.W. collected and analyzed data and drafted the manuscript. S.P. and F.W. compiled all sections and reorganized the writing with contributions from all authors. W.Z., Y.T.C. and T.J.E.L. proofread the drafted manuscript.

Keywords: VPP 3D printing • Photocurable polymer • Recyclability • Dynamic covalent network • Sustainability

Dr. Sirawit Pruksawan earned his Ph.D. in Materials Science and Engineering from the University of Tsukuba, Japan, in 2020. From 2018 to 2020, he served as a junior researcher at the National Institute for Materials Science (NIMS) in Japan. In 2021, he joined the Institute of Materials Research and Engineering (IMRE) at the Agency for Science, Technology, and Research (A*STAR) in Singapore as a research scientist, where he continues his work. His research focuses on polymer composites, 3D printing, and material toughening.



Dr. FuKe Wang earned his Ph.D. degree in 2003 from the National University of Singapore (NUS) and served as a research associate at IMRE, A*STAR until 2005. Subsequently, he pursued post-doctoral research positions at the University of California and Oklahoma University before rejoining IMRE in 2010. Presently, he holds the positions of group leader and principal scientist at IMRE, A*STAR. His research expertise includes 3D/4D printing, functional polymers, and polymer nanocomposites.



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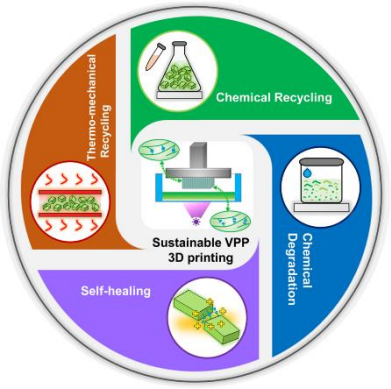
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This review paper focuses on sustainable materials for vat photopolymerization (VPP) based 3D printing. Recent developments in VPP 3D printable polymers with dynamic covalent bonds are summarized, showcasing their chemical recyclability, thermo-mechanical recyclability, self-healing capabilities, and chemical degradability. Various dynamic covalent reactions and processes have been utilized, demonstrating adaptability in design and application.

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