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REVIEW

Current progress on the 3D printing of thermosets

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Abstract

3D printing has attracted increasing attention as it exhibits excellent potential in the fabrication of 3D complex structures, which are very difficult to make using conventional techniques, with low cost, less energy, and material consumption. Thermosets are integral to today's aerospace, automotive, marine, and energy industries and will be vital to the next generation of lightweight, energy-efficient structures, owing to their excellent specific strength, thermal stability, and chemical resistance. Manufacturing with thermosets using innovative 3D printing techniques has the potential to revolutionize composite manufacturing. However, thermosets are highly crosslinked and irreversibly cured, and it is challenging to integrate the printing process with curing process at high rate and high quality. This review will address current effort and future direction in 3D printing of thermosets.

Keywords 3D printing · Thermosets · Additive manufacturing

1 Introduction

Thermosets have increasing importance in recent decades due to many advantages, including thermal stability, chemical resistance, solvent resistance, environmental stability, and mechanical strength [1, 2]. In addition, they are also lightweight, inexpensive, and faster to manufacture in comparison with other materials; in fact, they have been primarily used to replace metals and alloys in a multitude of industries and become especially desirable for a wide range of applications, like medical, engineering, aerospace, robotics, marine, energy, and more [1–3]. They can be found practically everywhere and have become increasingly vital to modern-day society. Unlike thermoplastics, thermosets cannot be easily reshaped after their initial heat-forming due to the high-density crosslinkages during the manufacturing process thus make the formed polymers irreversible. This property makes thermosets well suited to the production of permanent components and large solid shapes.

The first commercial thermoset, Bakelite, was developed by Dr. Leo Baekeland in 1909 [4]. Since then, many manufacturing techniques have been developed, including hand lay-up or wet lay-up, spray-up, or chopping, injection molding [5], vacuum bag molding [6], resin transfer molding (RTM or liquid molding) [7], compression molding [8], etc. Each of these methods has its advantages and disadvantages. They are typically produced by heating liquid or powder within a mold, allowing the material to cure into its hardened form. The reaction used to create thermosetting products is not always the result of heating and is sometimes performed by chemical interaction between specialized materials. Current manufacturing methods of producing large, complex thermosetting parts take place in big autoclaves that are around the same size as the component [2]. It can take several hours of heating oligomers at elevated temperatures [9], and the oligomers are usually heated to around 180 °C and undergo both external pressure and internal vacuum. The mechanical strength, thermal stability, and ductility of thermosets rely heavily on this curing process: as crosslink density changes, all of these properties change accordingly [9]. These conventionally manufacturing techniques require a significant amount of time, energy, and monetary investment [2], and it is difficult to manage design changes when the manufacturing process is already underway [10].

3D printing has emerged as one of the most promising routes for fabricating the next generation, high-performance

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composites [11]. The main advantage of 3D printing techniques is the precise control that is enabled over the microstructure of the printed material, which results in the significant flexibility in design and a novel or improved properties compared with parts made via traditional techniques [10]. Besides, additive manufacturing has several other advantages over conventional methods, such as the simplification of the production process, significantly improved cost efficiency by reduced energy consumption and manufacturing time, and dramatically decreased material consumption. In some particular scenarios, such as innovative and lightweight parts to aircraft, 3D printing could be the only way to create complex parts, while in the other cases, 3D printing can serve to reduce the number of different components required for a project [12].

Paired with innovative 3D printing techniques, manufacturing with thermosets has the potential to become more productive, cost-effective, and material efficient. Furthermore, the 3D-printed thermoset parts could have the same or better mechanical properties while having extended the usually limited rheological profiles and pot-life [13]. With some newly formulated 3D printing inks, such as (dicyclopentadiene) DCPD-based ink [2], the in situ curing process can be completed in the order of seconds via frontal polymerization, compared with many hours or days by the conventional method.

In this review, we focus on the current research on 3D printing of thermosets and composites, including the preparation of thermosets and composite inks, different 3D printing techniques for thermosets, and their composites, in situ curing, and ex situ curing process. In the meantime, we highlight several emerging applications of 3D printing of thermosets and composites, such as aerospace, sensors, and robots. Opportunities and the challenges of 3D printing thermosets are also discussed.

2 3D printing techniques for thermosets

3D printing technologies create 3D objects by curing layer-upon-layer of material and cured either by irradiation (UV, laser or E-beam) or heat. Thermosetting polymers are the build materials for thermoset 3D printer; most of them are a viscous liquid. In this article, we will only discuss the 3D printing techniques that deal with a liquid form of thermosetting polymers. These techniques mainly based on VAT photopolymerization and material extrusion, as listed in Table 1.

VAT photopolymerization uses a VAT of liquid photopolymer resin, and an ultraviolet (UV) light is used to cure or harden the resin where required, while a platform moves the object being made downwards after each new layer is cured, some methods including stereolithography (SLA) and digital light processing (DLP), continuous liquid interface production (CLIP), and continuous digital light processing (CDLP). Stereolithography (SLA) is the first type of VAT photopolymerization 3D printing method. It deals with a laser beam following a designated pattern and curing a photocurable resin inside the VAT. SLA techniques possess many advantages like high accuracy that may be controlled by the laser spot size and the z-axis step increase of each layer [8]. However, brittleness and poor impact resistance due to inhomogeneous polymer architecture and high crosslink density are serious drawbacks[20]. Filled resins are one of the leading solutions, but they are usually not suitable for VAT photopolymerization techniques due to a substantial increase of viscosity derived from the presence of rigid particles within the reactive suspension [12] and the possible sedimentation phenomena, which further limits the available resins for SLA. Nonetheless, Taormina et al. developed a new technique that in situ generates silver nanoparticles (AgNPs) starting from a homogeneous liquid system containing a well-dispersed silver salt, which is subsequently reduced to metallic silver during stereolithographic process[12]; they reported that the thermal-mechanical properties of filled thermoset resin have significantly enhanced compared with the unfilled resin.

Digital light processing (DLP) is somewhat like SLA, as it is another type of VAT photopolymerization method. It is a fast process, but also only has limited materials to use since the resins need to be photocurable. The increase of viscosity and the possible sedimentation phenomena are another drawback shared with the SLA process. In the DLP, light cured a thin layer of photocurable resin that lies between the bottom of the printed piece and an optically transparent window. A projector dictates the shape of each level with a digital mirror. The printed piece is moved up by a layer of thickness after each level is printed. A severe issue that may occur is adhesion between the bottom of the printed piece and the optically transparent window. Adhesion may damage the part as it moves up. A solution called CLIP has been engineered to overcome this problem. It involves making the window to be oxygen permeable since oxygen serves an inhibitor for photopolymerization. This process creates a thin layer of uncured liquid resin, often referred to as the dead zone that allows the part to separate from the window quickly. 2D light projection improves DLP's speed tremendously.

In the past, DLP struggled with relatively low glass transition temperature, the high cost of a cationic photoinitiator, poor mechanical properties, and low curing rate when it came to producing thermoset products because it used photoinduced cationic polymerization. Recently, however, a hybrid ink was crafted for the DLP technique that includes a two-stage curing process [9]. As shown in Fig. 1, this hybrid ink contains both photocurable resin and thermally curable epoxy resin. There are a few seconds interval between two printed layers for retaining the printed structures. Afterward, the prints are

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Table 1 Recent AM researches, technologies, materials, and characterizations

AM Technique	Printing material	Addition (catalyst/curing agent/ photoinitiator inhibitor, etc.)	Viscosity (Pa.s)	*T* (°C)	*E* (GPa)	Ref.
SLA	Acrylic resin (Ebecryl 7100 and PETIA)	BAPOs (Ir 819), silver acrylate (AgAcr) and silver methacrylate (AgMAcr),		90	< 0.2	[12]
DLP	PEGDA	GO, BAPOs (Ir 819), UV-In, methyl red dye, water		70	< 0.02	[14]
Two-step DLP	A mixture of photocurable resin ETT and thermal curable epoxy resin Epon 828	BAPOs (Ir 819), Epikure 3253, Sudan I dye, etc.	< 0.6	100, 160	2	[9]
FFF	IPOX ER 1010 (DGEBA-based epoxy resin)	IPOX MH 3124, carbon fiber		80	57.9	[15]
FFF	Epoxy resin (E-54(616))	Carbon fiber bundle	5–10		161.4	[16]
FFF	DART polymers		2–30	90–150	< 0.1	[17]
DIW	BPF	DETDA, silica, carbon fiber	8000	80, 150–200	240	[13]
DIW	Cyanate ester	Cu(acac)2, silica nanoparticles	1	250	17	[11]
DIW	Epoxy resin Epon 862	NdFeB magnet particles, Cloisite 15A nanoclay platelets, Basionics VS03		100		[18]
UV- DIW	A mixture of UV curable resin acrylate with thermal curing Epon resin 862	DMP-30, BAPOs, fumed silica nanoparticle	100–20,000	100, 150	1	[19]

transferred to an oven. The second stage of curing dramatically improves the mechanical properties of the 3D-printed object.

Thermal induced 3D printing technologies use heat as curing resources. In material extrusion-based 3D printing technologies, the material is drawn through a nozzle and is then deposited layer by layer to build the 3D structure, then thermally cured. Material extrusion is currently the most widely used 3D printing technique; fused filament fabrication (FFF), also called fused deposition modeling (FDM), and direct ink writing (DIW) fall into this category. The difference between FFF and DIW is the ink extruded from the small nozzle. FFF manufacturing uses an extruder, also known as the liquefier, to melt the continuous thermoplastic polymer filament and push it through a heated nozzle to form the bead. The extruded bead is applied and fuses to the preliminary layer, and subsequently, it cools down and solidifies again [21]. In general, FFF is only compatible with thermoplastics, since the relatively higher melting temperature and irreversible curing process of thermoset make it hard to apply to conventional 3D printing processes such as FFF [8]. Scientists have developed two research directions to overcome this challenge: reversible thermoset and continuous fiber-reinforced thermosetting composites. Continuous fiber-reinforced thermosetting composite technique uses a fiber bundle from the fiber supply coil; it proceeded through the epoxy resin pool and entered the printing head [16]. The reversible thermoset has been discussed previously.

DIW is a low-cost material extrusion technique, it uses liquid ink as writing materials, and the ink extrudes the nozzle in a liquid-like state but maintains its shape by rapid solidification. DIW has been widely used to fabricate fiber-reinforced composites, epoxy composites, graphene-based composites, energetic materials, and cellular elastomeric architectures [7]. Most of the current 3D printing methods that are compatible with thermosets are DIW [2, 11, 18], as shown in Fig. 2.

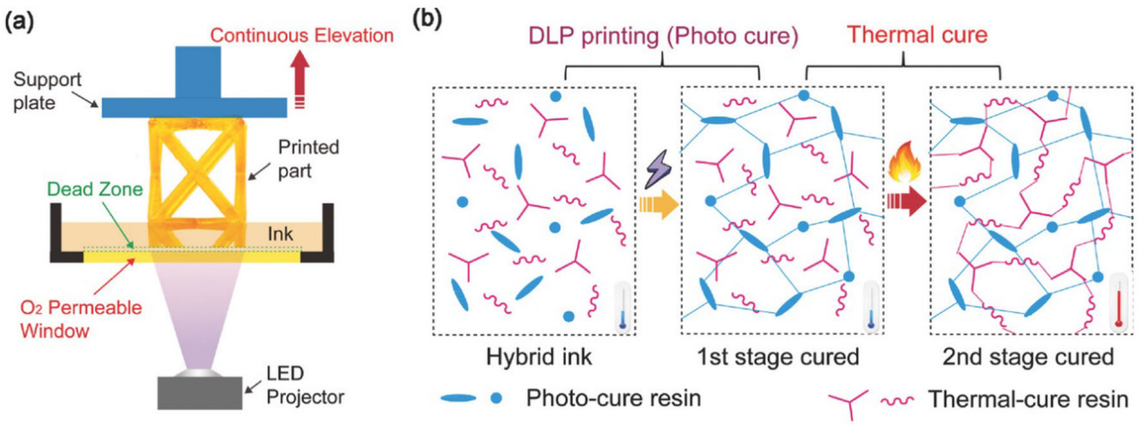

Fig. 1 Two-stage curing process of DLP 3D printing of thermoset composites. **a** Schematic of CLIP-based DLP printing. **b** Schematic of the two-stage curing process. Reproduced with permission from [9]

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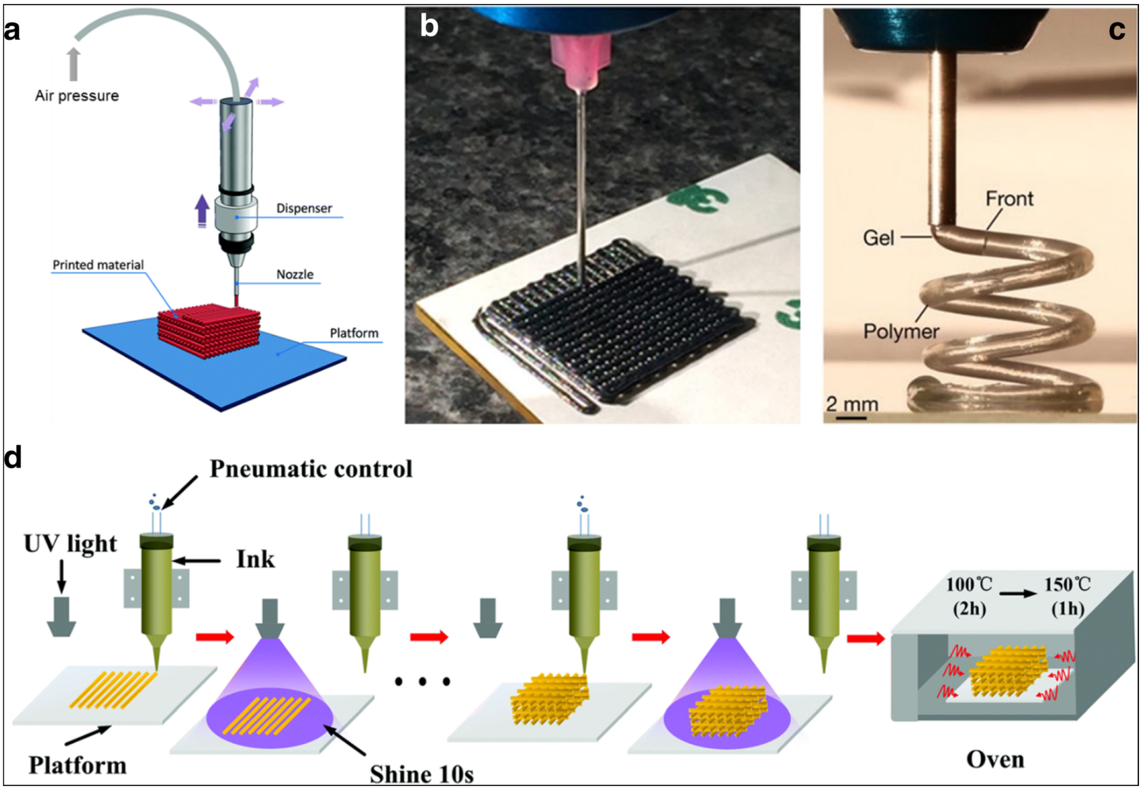

Fig. 2 **a** Schematic diagram of direct ink writing (DIW). **b** DIW of carbon fiber-loaded bisphenol-F resin ink (**d**), **b** DIW of DCPD based ink. **c** Printing of thermosets through frontal polymerization. **d** Schematic illustration of UV-assisted DIW printing epoxy composite material. Reproduced with permission from [2, 13, 19, 22]

One of the main challenges for DIW is in the design and formulation of the feedstock inks, which must be rheologically tailored to form self-supporting layers required for DIW parts to be successful. Some of the parameters must be considered, including the viscosity and density of the ink, the particle size within the ink, the type of dispenser, the nozzle size, the air pressure, the bed temperature, and other specific factors that can also be adjusted to obtain optimal deposition. Even though the created object is usually freestanding, a post-fabrication process may be necessary to harden it and improve its mechanical properties via steps of drying, heating, or sintering[22].

3 Inks for 3D printing of thermosets

3.1 Thermal curing inks

Epoxy resins are among the most commonly used thermosetting polymers due to their availability, cost, and ease of processing. They are a class of synthetic thermosetting polymers. Many types of epoxy resin have been studied in the 3D printing process for different purposes, such as high-performance structure materials [23], fast-curing materials [24], recyclable materials [1], etc.

Generally, epoxy resins are light-colored liquid with low viscosity and can remain in low reactivity at room temperature. Thus, the addition of the curing agent will not solidify the resin before reaching the threshold of activation energy [23]. This extended pot life is crucial since it enables the epoxy ink to be stored in the printer cartridge and cured separately. Once the resins are well cured, they often exhibit superior mechanical performance and chemical/heat resistance. One of the most commercially available types of epoxy resins is diglycidylether, including bisphenol-A, bisphenol-F, or other phenolic compounds [26]. Bisphenol A-based epoxy resins account for about 90% of the total output of epoxy resins, and it has been widely used in casting, bonding, coatings, paints, composite materials, etc. [27]. In the year of 2014, Compton et al. first demonstrated the capability of extrusion printing of epoxy paste, which contains a concentration of nano-fillers up to 31 vol% [14]. The printing process and printed structure are shown in Fig. 3, with the addition of oriented carbon nano-fillers as well as SiC fillers in the BFDE-based cellulose composites; exceptional mechanical properties were obtained [23]. As shown in Fig. 3, the alignment of the fiber fillers was tuned along the print direction. Other research regarding epoxy-based printing was also explored. For example, Zhu et al. fabricated carbon fiber/polyimide/epoxy composites with improved mechanical performance using a powder-based selective laser sintering method [28].

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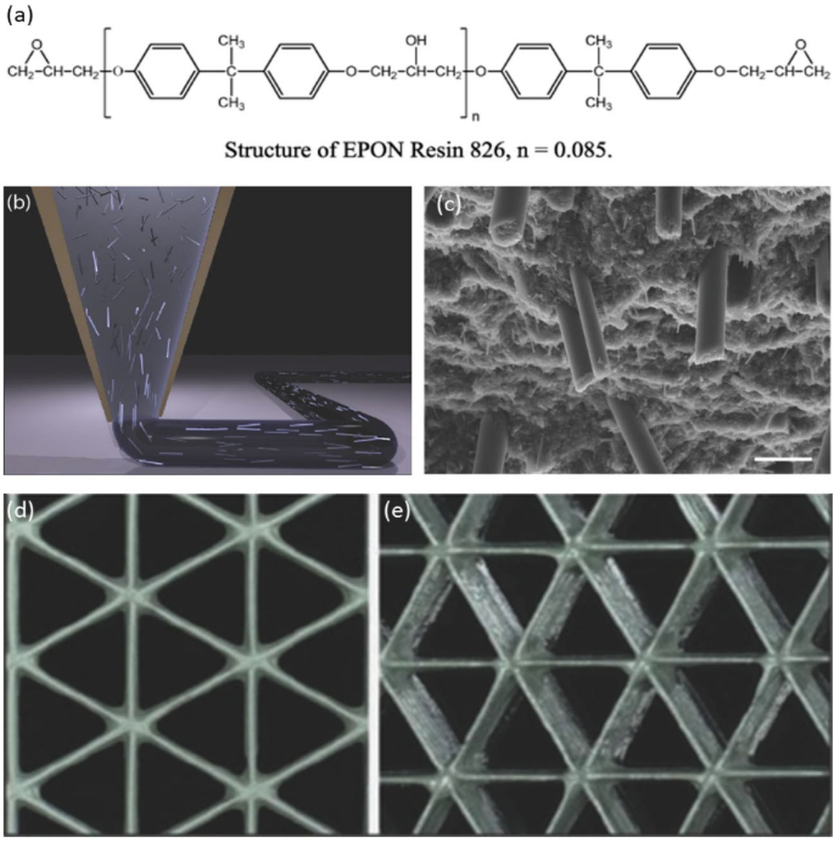

Fig. 3 Epoxy-based composites ink. **a** Chemical structure of EPON resin 826. **b** Schematic illustration of composite ink deposition. **c** SEM image of the fracture surfaces. **d**, **e** Triangular honeycomb structures composed of SiC-filled epoxy. Reproduced with permission from [23, 25]

Later, Compton et al. reported the magnetic functionalized epoxy composites via direct ink writing (DIW) [19, p.]. Moreover, Hao et al. are successfully prepared and characterized the 3D-printed continuous carbon fiber reinforced epoxy composites [16].

Cyanate ester is another class of thermosetting polymers with extremely high thermal stability, chemical resistance, low moisture absorption, and excellent mechanical performance [11]. Unlike the epoxy resins, only a few studies were reported regarding 3D printing cyanate esters. Chandrasekaran et al. recently explored a 'pure' thermal cure cyanate ester for 3D printing [11]. The thermosetting network was formed via cyclotrimerization, where a triazine ring is formed during the chemical reaction. The polymerization mechanism is demonstrated in Fig. 4a. The designed cyanate ester ink was printed on a glass slide coated with PTFE spray and was then subjected to thermal curing. The resulted structures, as shown in Fig. 4b, were able to withstand high temperature up to 400 °C and exhibited exceptional Young's modulus reached 17 GPa, which shows their potential in many industrial applications.

In addition to epoxy and cyanate ester, other types of thermosets have also been successfully studied. For instance, Robertson et al. reported in situ print and cure of high-performance polydicyclopentadiene (pDCPD) with reduced energy based on the frontal polymerization mechanism [2]. Frontal polymerizations (FPs) are a class of autocatalytic reaction that rapidly transform monomer to polymer upon a small thermal stimulus [29]. Researchers used the dicyclopentadiene (DCPD) as the monomers, as shown in Fig. 5a**,** Grubbs' 2nd generation ruthenium catalyst, and an alkyl phosphite as an inhibitor. With the control of polymer kinetics via adjusting the ratio of catalyst and inhibitor, the pot life could be increased by up to 140 times, while still allowing frontal polymerization at relatively high frontal velocities.

Free-form 3D printing, such as spiral structure, is easily achievable, as shown in Fig. 5b. The resulting pDCPD is a cross-linked thermoset polymer that is suitable for the fabrication of durable resin and fiber-reinforced polymer composite (FRPC) parts, as shown in Fig. 5c, owing to its high fracture toughness, impact resistance, stiffness, and chemical resistance [30, 31].

Thermosets, by definition, is a polymer which becomes irreversibly hardened upon being cured. However, science is the art of making the impossible, possible. Some specific thermosets can be reversibly crosslinked by making use of semimanual dynamic covalent networks [32] or by reversible network topology freezing [33, 34]. Diels–Alder (DA) reactions are also thermo-reversible and can be applied to a broader range of thermosets. One of the most iconic examples of the DA reaction is that between a furan and a maleimide. Chen et al. firstly reported furans and maleimides based on highly crosslinked remendable materials [35], which shows the possibility of thermally reversible reactions for 3D printing recyclable

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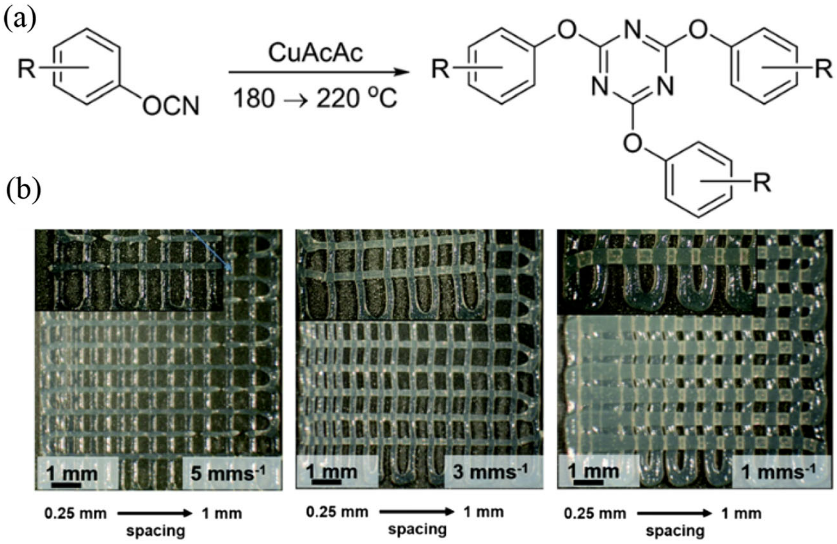

Fig. 4 **a** Mechanism of cyanate ester polymerization and the formation of triazine ring. **b** Printed 3D structure. Reproduced with permission from [11]

thermosets. Yang et al. reported the first generation of printable DART resins based on reversible furan-maleimide Diels–Alder (fmDA) linkages, which exhibit thermoset properties at use temperatures, ultra-low melt viscosity at print temperatures between 90 and 150 °C, and as-printed, isotropic mechanical properties [17]. The reversible crosslinking mechanism is illustrated in Fig. 6. The printed structure exhibits improved interlayer bonding after reformation which helps to obtain the isotropic toughness and robustness.

3.2 Photocuring inks

Photopolymerization is another possible way to crosslink the thermosetting polymer network with the aid of light in the visible or UV region [36]. This technique eliminates the high-temperature curing process that often involved during thermal cure. Thermosetting photopolymers claim almost half of all 3D printing materials and have been widely applied in various fields owing to good compatibility with high-resolution 3D printing technologies [37]. Compatibility with UV/visible light curing makes thermosetting photopolymers capable of forming at different dimensions, including micro-scale, submicron-scale, and even nano-scales. The mechanism of photopolymerization is that photoinitiators generate radicals under light irradiation, and the generated radicals further attack the electron-deprived sites for covalent bond formation. Functional thermosets such as shape memory polymers (SMP) are popular among 3D printing of photocurable thermosets. Because of the involvement of time, the fourth dimension, as the printed structure self-transform in the reaction of

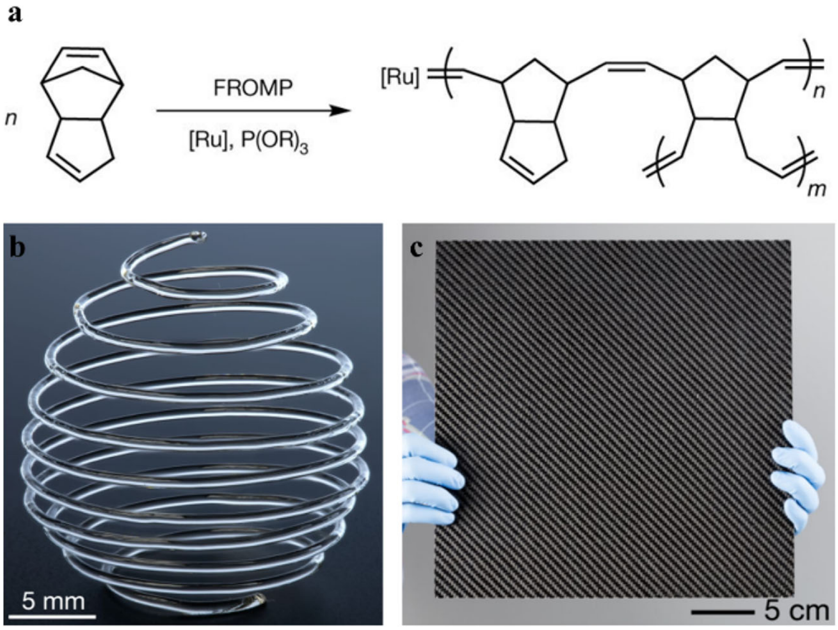

Fig. 5 Frontal polymerization of dicyclopentadiene (DCPD). **a** Frontal polymerization reaction, using a ruthenium catalyst ([Ru]) and an alkyl phosphite inhibitor (P(OR)3). **b** 3D printing spiral structure. **c** 3D-printed fiber-reinforced polymer composite (FRPC) parts. Reproduced with permission from [2]

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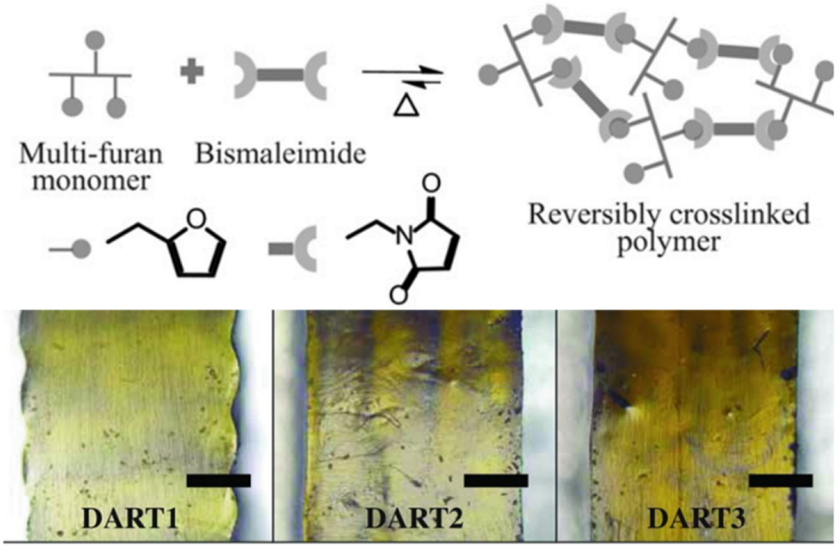

Fig. 6 Illustration of reversible printing of bismaleimides and printed structure. Reproduced with permission from [17]

pressure, heat, current, UV light, or other energy sources, it is named as four-dimensional (4D) printing [38]. Choong et al. used tert-butyl acrylate (tBA)-co-di(ethylene glycol) diacrylate (tBA-co-DEGDA) network and designed a dual-component phase switchable functional group. The built parts exhibited shape memory behavior [39]. Zarek et al. fabricated polycaprolactone (PCL)-based shape memory thermosets with electron transport ability used in flexible electronic devices [40], as shown in Fig. 7.

3.3 Two-step cross-linking inks

Though the high resolution is achievable using a photopolymerization-based curing process, obtaining enough mechanical properties and multi-functionalities of prints are also explored. Sometimes, the printed pieces are brittle and unable to adapt to the targeted applications. To improve the mechanical property, a secondary thermally induced crosslinking is introduced to the polymer network [37]. Different from stable and irreversible covalent bonds formed in photoinduced crosslinking, a thermally crosslinked network with physical bonding is dissociable. The secondary network is formed via dynamic covalent bonds (DCB) of a typical type of reversible polymer named vitrimer. Shi et al. demonstrated the possibility of printing vitrimer epoxy adopting the two-step crosslinking method, which was achieved through bond exchange reactions at elevated temperature [1].

Recently, Zhang et al. used a similar idea by introducing functional groups containing esters and hydroxyl functional groups for the first network [37]. Transesterification occurs, and the formation of dynamic bonds evolved between the ester and hydroxyl groups when temperature elevated above 180 °C, as shown in Fig. 8. After the heat treatment, Young's modulus significantly increased from 7.4 to ~ 900 MPa. Moreover, the designed secondary crosslinking impacts reshapeability, repairability, and recyclability to the

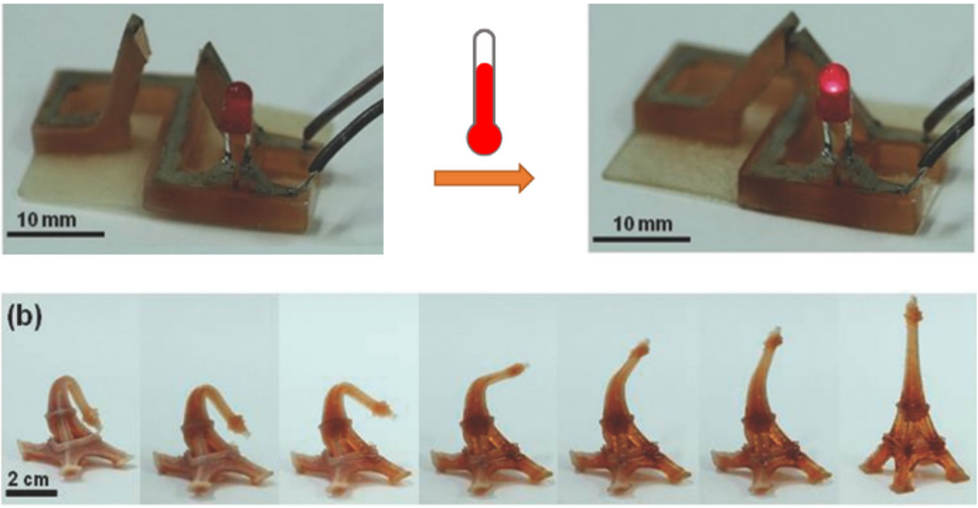

Fig. 7 3D-printed photocurable thermoset, shape memory polymer (SMP). **a** Temporary shape is an open electrical circuit, and when heated above the melting temperature (Tm), the circuit closes and lights an LED. **b** An Eiffel Tower model, 6 cm tall, reverting to its original shape at 70 °C. Reproduced with permission from [39]

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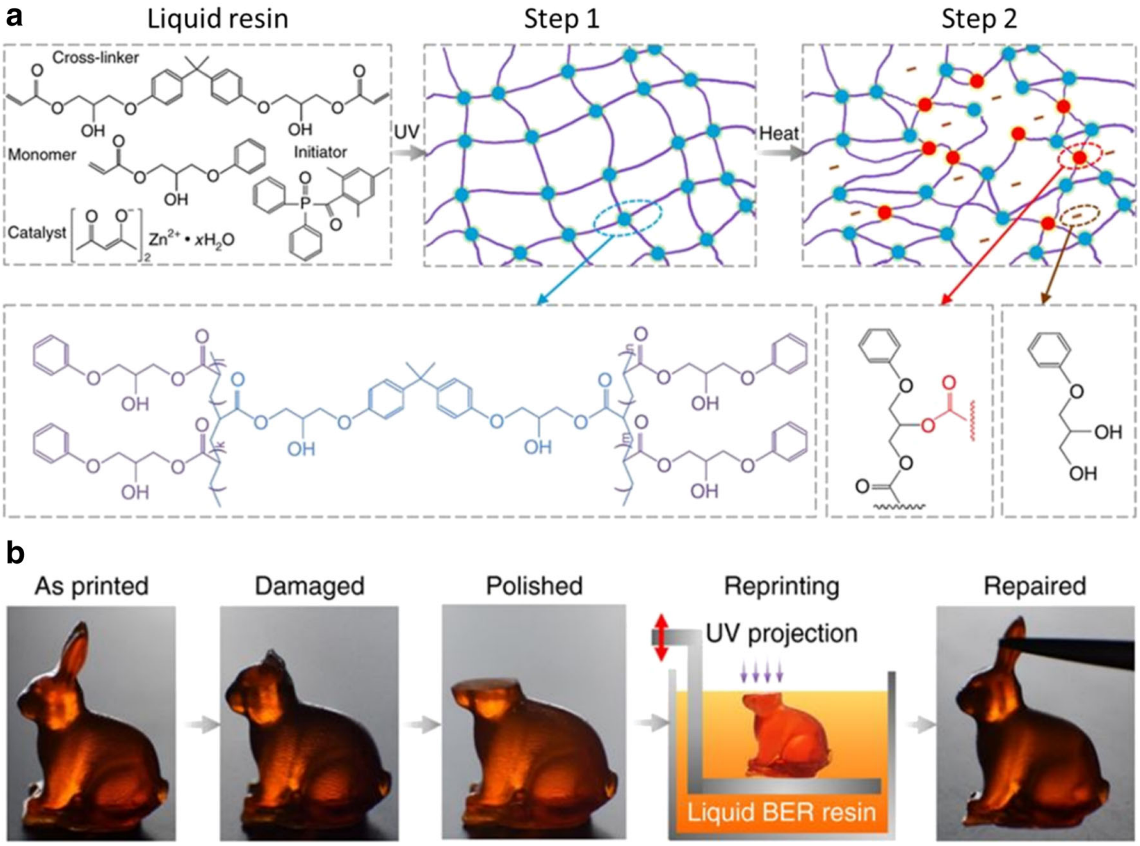

Fig. 8 Two-step reprocessable thermosets. **a** Chemical structures of monomer, crosslinker, initiator, and catalyst in the photopolymer solution, reprocessable thermosetting polymer solution (step 1), heating then imparts the reprocessability into the printed structures (step 2). UV curing forms the permanent covalent bonds (blue dots); d thermal-triggered transesterification leads to the formation of DCBs (red dots). Chemical structures of the resultant permanent crosslinked network of step 1 and DCBs of stage 2 after heating. **b** Demonstration of the reprocessability: surgery on a damaged rabbit. Reproduced with permission from [37]

thermosetting polymer. Surprisingly, the repaired parts exhibited similar mechanical stress to the undamaged ones. More importantly, by introducing this secondary crosslinking, thermosetting polymers able to become reprocessed and reprocessability is relevant to thermosetting polymers because of the severe environmental implications for the growing consumption and vast production waste of production industry [41, 42].

4 Emerging high-rate printing of thermosets

Traditional printing of thermosets are at slow rate and low scale. Recently, three significant efforts have been made in addressing these challenges toward high-rate printing of thermosets. Prof. Joseph DeSimone's group[43] firstly creates high-rate printing of thermosets through interfacial selective chemical reaction, and achieving 100-times faster than traditional printing process. This ground-breaking technology also leads to a startup company, Carbon 3D, for further commercialization. Currently, Carbon 3D has been reported with a value of $2.4 billions. It uses a stage submerged in a VAT of resin. A digital projector irradiates and quickly photocures a computer-designed layer up at the stage via a clear windows in the bottom of the resin pool. As-designed window is oxygen permeable and thus prevents curing reaction to form an ultra-thin 'dead zone' just above the window's surface. As a consequence, thermosetting resin is not adhesive to the VAT bottom once a layer is photocured (printed). The building platform continually moves up, pulling the cured layers up from the uncured resin pool when new layers continuously photocured due to photo projection. Inspired by this oxygen-induced interfacial reaction, Mirkin's group [44] invented oil-induced interfacial reaction for even much faster printing, and also makes more choices of the thermoset resins. For example, any thermoset resin that is not sensitive to oxygen can also be used for high-rate printing. The mechanism is illustrated in Fig. 9a.

Prof. Christopher Spadaccini's group invented a "replication" method for high-rate printing of thermosets[45]. As shown in Fig. 9b, when a glass of resin pool rotates, a projector irradiates a loop of video onto it that represents a 2D structure programmed by computer. Within seconds, the final object solidifies inside the liquid resin—no layers necessary.

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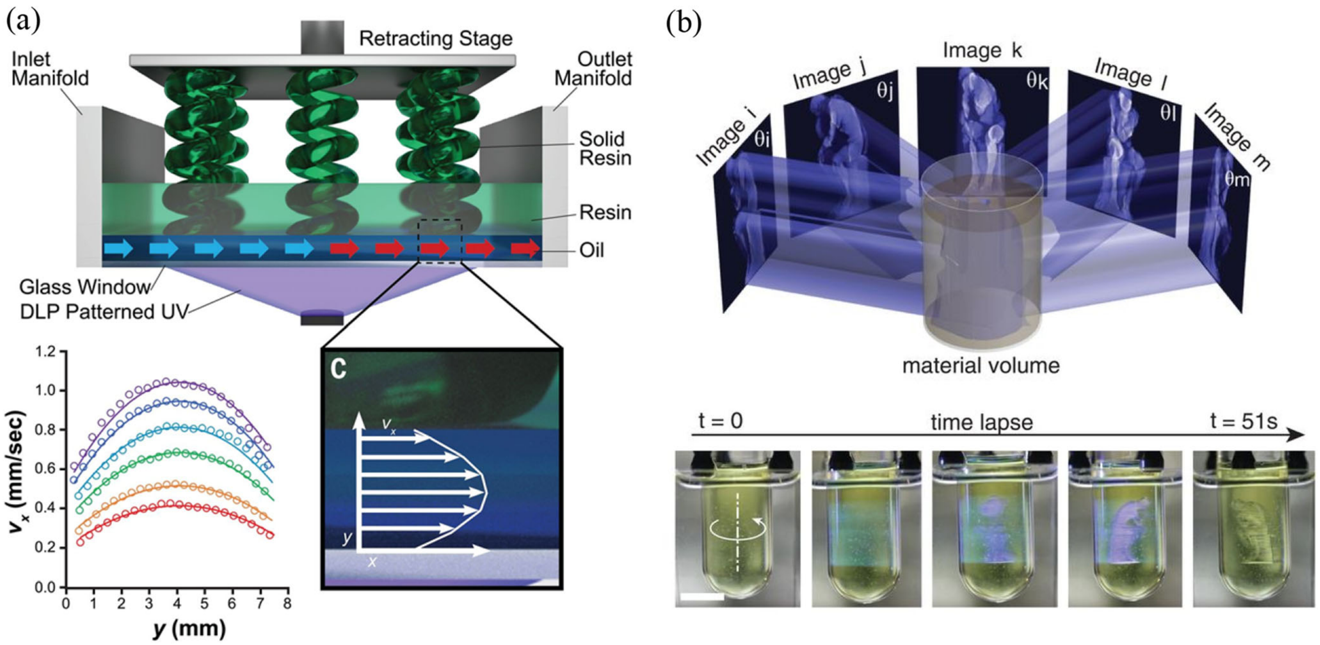

Fig. 9 **a** Mechanism of selective interfacial chemistry-enabled high-rate printing [44]. **b** Illustration of printing via rotating replication skills [45]. Reproduced with permission from [44, 45]

5 Concluding remarks and prospects

Thermosets are regarded as potential substitutes in aerospace [46], protective coating [47], civil constructions [48], as well as biomedical applications [49], owing to their lightweight, inexpensive, biocompatibility, high strength, and high-temperature resistance [23]. However, 3D printing of thermosets also faces a set of challenges for the massive manufacturing. Firstly, the availability of high-performance 3D printing ink materials is very limited. Most of the photocurable thermosets are suffering from brittleness and poor impact resistance due to inhomogeneous polymer architecture [20]. In addition, most of those thermocurable inks lack shear-thinning characteristics and are not suitable for 3D printing. High-through 3D printing is still challenging although recent emerging progress. Future research direction could focus on developing high speed, large-volume 3D printing techniques while exceptional properties are maintained. Another challenge that arises with additive manufacturing is how 3D-printed thermoset parts are inherently unrecyclable due to the permanently crosslinked networks in the polymers. Thermoset recycling is a growing concern as additive manufacturing becomes more popular, and especially as large-scale manufacturing becomes more feasible. Last but not least, although the thermomechanical properties of thermoset products have been greatly improved, shape shrinkage is still a big challenge. It occurs during curing, which usually displays as hollow of overhanging features on the printed object. Some attempts have been made to improve the fracture toughness and the strength of thermosets, through modifying thermoset resins with integration of various nanomaterials, such as carbon nanotube [50], glass fibers [2], and nanoclay [51], etc. Printing continuous reinforced thermosets at high rate is another major research direction in this field.

Overall, additive manufacturing has proven to be considerably more efficient than conventional manufacturing and can print precise structures with great flexibility and customizability that conventional methods cannot match with their molds. As new materials and techniques are continuously developing for 3D printing, a significant difference between 3D printing and conventional methods will be emerging.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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