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Sustainable Photopolymers in 3D Printing: A Review on Biobased, Biodegradable, and Recyclable Alternatives

Vincent S. D. Voet,* Jarno Guit, and Katja Loos

The global market for 3D printing materials has grown exponentially in the last decade. Today, photopolymers claim almost half of the material sales worldwide. The lack of sustainable resins, applicable in vat photopolymerization that can compete with commercial materials, however, limits the widespread adoption of this technology. The development of "green" alternatives is of great importance in order to reduce the environmental impact of additive manufacturing. This paper reviews the recent evolutions in the field of sustainable photopolymers for 3D printing. It highlights the synthesis and application of biobased resin components, such as photocurable monomers and oligomers, as well as reinforcing agents derived from natural resources. In addition, the design of biologically degradable and recyclable thermoset products in vat photopolymerization is discussed. Together, those strategies will promote the accurate and waste-free production of a new generation of 3D materials for a sustainable plastics economy in the near future.

1. Introduction

Additive manufacturing (AM), alias 3D printing, enables the fabrication of tailor-made products with complex three-dimensional shapes. In contrast to subtractive or formative techniques, a virtual model is digitally sliced and physically built layer by layer, without the need for molds or machining.[1] AM is preferred in applications that require a high level of individuality, like patient-specific implants and customized parts for vehicles. 3D printing technologies are considered as an essential ingredient in the latest industrial revolution, referred to as Industry 4.0, promoting the integration of smart production and information systems.[2,3] By 2029, the worldwide revenues for AM materials are forecast to grow to $23 billion, with the largest market shares for aerospace, defence, medical and dental industries.[4] Currently, the largest fraction of material sales belongs to polymers.

Leading 3D printing technologies based on material extrusion and powder bed fusion allow the use of biopolymers, such as polylactic acid (PLA) and thermoplastic starch (TPS).[5,6] Vat photopolymerization, however, relies on liquid photocurable polymers which greatly limits the choice of materials.[7] Commercially available photopolymer resins for 3D printing are generally based on epoxides or acrylates produced from fossil resources, having a relatively large carbon footprint.[8,9] Moreover, photopolymerization leads to thermosetting products that are intrinsically not recyclable or (biologically) degradable, due to their crosslinked macromolecular network.[10,11] Their unprocessable nature combined with the increasing demand for AM materials will result in serious waste management problems.

The limited availability of environmentally friendly photopolymers is a major barrier to the large-scale adoption of 3D printing. To address aforementioned concerns, the scientific community has made an effort to develop sustainable alternatives for current photopolymer print resins that reduce their environmental burden. The development of biobased, biodegradable and recyclable materials for vat photopolymerization will benefit the ongoing transition towards a circular economy.[12] This review strives to provide an overview of the recent advances in the field. After a short introduction to vat photopolymerization, we discuss the application of photopolymer resins (and resin components) based on renewable resources, e.g., vegetable oils, lignin and saccharides. Also, the incorporation of biobased additives is reviewed. A discussion on photoresins that show (potential) degradability follows thereafter. Finally, we explore the recent development of reprocessable thermosetting polymers, i.e., vitrimers, and their application in additive manufacturing. **Figure 1** captures the scope of this overview article schematically.

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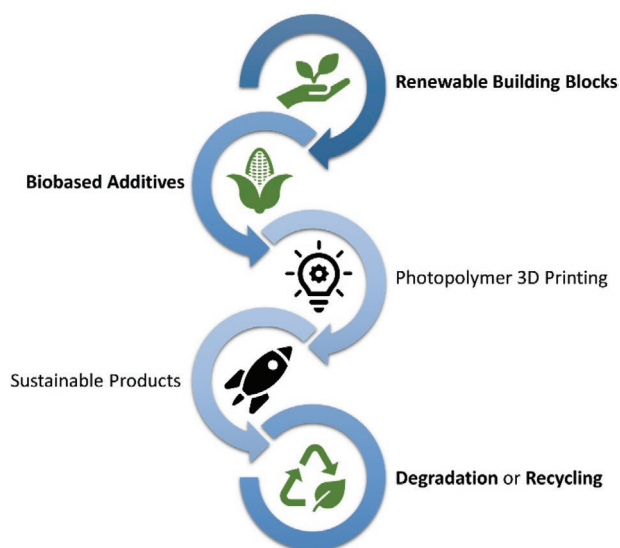Rapid Communications**

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Figure 1. Recent advances in the field of sustainable photopolymers for additive manufacturing. Replacement of fossil resources by renewable monomers, oligomers, and additives will reduce the carbon footprint of 3D printing materials. Moreover, design strategies that aim for (bio)degradability or recycling of manufactured products will facilitate a waste-free circular plastics economy.

2. Vat Photopolymerization

Additive manufacturing based on photopolymer chemistry is referred to as vat photopolymerization, according to the standard ASTM terminology.[13] In this process, a liquid photopolymer ink placed in a vat is cured via light-activated polymerization on a predetermined location.

In the 1980s, Chuck Hull introduced the stereolithography apparatus (SLA),[14] which became the first example of a 3D printer. Nowadays, the term SLA is used for both the equipment as well as the technique. In SLA, a coherent light source (e.g., a UV laser) activates photopolymerization of a liquid resin. When the laser beam scans the surface, the resin solidifies and one layer is formed. By repeating this process, a three-dimensional thermoset product can be printed layer by layer. The illuminated pattern originates from a sliced computer model designed by 3D drawing software. Hence, SLA provides 3D fabrication of complex structures with high resolution and a low feature size (on micrometer scale), related to the spot size of the laser beam.[15] The original stereolithography apparatus by Hull used light exposure from the top to build a construct in a bottom-up manner (**Figure 2**). Alternatively, exposure from the bottom can be employed to print an object top-down. This approach has recently become more popular, since it requires lower resin volumes.

Similar to SLA, digital light processing (DLP) utilizes light to selectively crosslink photocurable resin in a layer by layer fashion. In DLP, however, each layer is exposed at once by a digital mirror device (DMD), a technology used in overhead projectors as well (Figure 2). This significantly reduces the printing time with respect to SLA. More recently, a new generation of vat photopolymerization has been developed, named continuous liquid interface production (CLIP).[16] CLIP uses
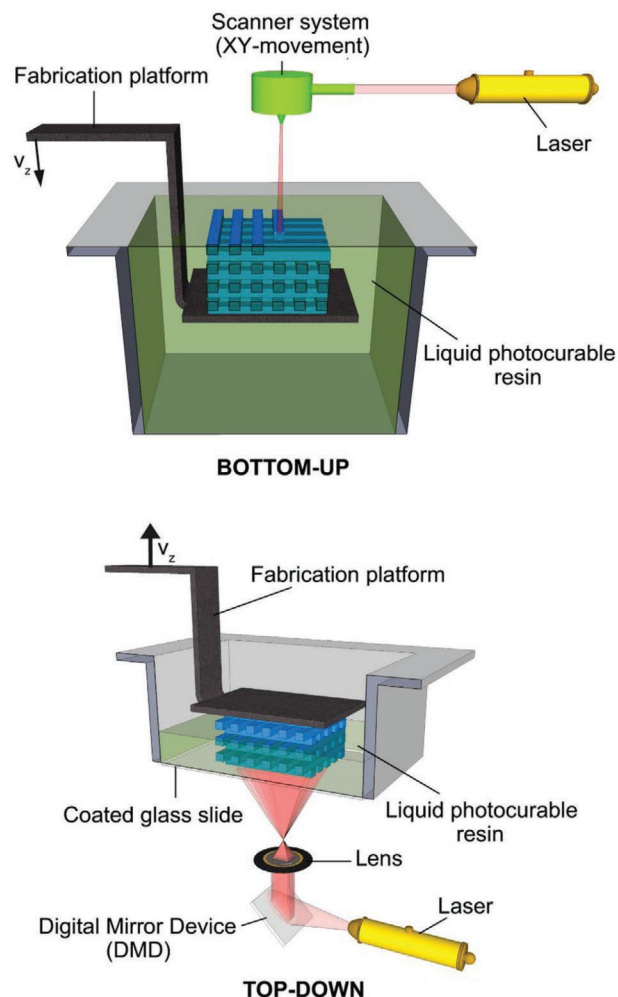

Figure 2. Scheme representing bottom-up and top-down vat photopolymerization. The bottom-up setup represents a system whereby the laser scans the surface for selective curing of photosensitive material. In the top-down setup, dynamic light projection technology is used to cure a complete 2D layer at once. Reproduced with permission.[89] Copyright 2012, Elsevier.

an oxygen permeable window to create an interfacial layer in which the photopolymerization process is inhibited. This so-called dead zone excludes the need for a time-consuming resin recoating step and enables fast and continuous fabrication of layerless objects.

An essential ingredient in vat photopolymerization is obviously the ink. 3D print resins require photocurable monomers and oligomers, that can undergo polymerization in the presence of photoinitiators to yield thermosets.[17,18] Commercial resins typically contain (meth)acrylates, epoxides or thiol-enes. Acrylate resins undergo radical photopolymerization, and are often based on bisphenol A diglycidyl ether (DGEBA) or urethane acrylates. To reduce viscosity, reactive diluents such as trimethylolpropane triacrylate (TTA) and dipropylene glycol diacrylate (DPGDA) can be added. Epoxy monomers, like commercially available DGEBA or 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ECC), are cured via a cationic mechanism.[19] Other components can be added in order to

tune resin properties by desire. For instance, radical inhibitors are often required to prevent premature polymerization of acrylate-based resins. Optical absorbers are used to control the penetration depth of the incident light, and color can be provided by the addition of dyes. Finally, fillers can be incorporated to obtain composite products with enhanced mechanical properties. Photopolymerization in 3D printing is extensively reviewed by Bagheri and Jin,[19] and Liska and co-workers.[1,7]

3. Biobased Photopolymers

The majority of resins for vat photopolymerization are derived from fossil resources. To accelerate the transition towards a circular economy, development of biobased resins for 3D printing is crucial. Common synthetic strategies used to impart photocuring functionality into naturally derived oligomers include epoxidation of unsaturated moieties, and conversion of epoxy-, acid- and hydroxyl groups into methacrylates by reaction with methacrylic acid, glycidyl methacrylate and methacrylic anhydride, respectively. Although research on the development of biobased resin (components) has increased in recent years, actual biobased content of the formulated resins is rarely reported.

Vegetable oils are among the most commonly reported resources for biobased resins. The C=C bonds in the fatty acids are chemically modified, generally with epoxides,[20] acrylates,[21] or methacrylates,[22] which enables the formation of a thermoset network by UV curing. Modified soybean oil was one of the first vegetable oils applied in SLA to produce shape memory bioscaffolds.[23] In following years, more reports of soybean oil in vat photopolymerization were published. Epoxidized soybean oil acrylate (ESOA) was applied in direct laser writing (DLW) to form microporous woodpile structures without use of a photoinitiator.[24] Guit et al.[25] used ESOA, and novel synthesized epoxidized soybean oil methacrylates (ESOMA) with varying functionalities, to create a library of biobased resins with a biobased content of 74–83%. ESOMA was synthesized via a "green" solvent-free synthesis route, incorporated in a resin with commercial biobased diluents and subsequently applied in DLP. The resulting polymers demonstrated good layer fusion with mechanical performance competitive to commercial counterparts (**Figure 3**). Prior to this development, solely commercial resin components were used to formulate resins with a biobased content ranging from 34% to 67% within the same research group.[26,27] Another soybean oil-based compound, epoxidized sucrose soyate, was (meth)acrylated and mixed for 42% with commercial monomers, and applied in vat photopolymerization. The resulting polymers demonstrated competitiveness with their commercial references regarding glass transition (T_g).[28] In another study, up to 30% of urethane epoxidized soybean oil was mixed with commercial acrylate compounds and applied as dual-curing resin in SLA to yield an interpenetrating network.[29] Other vegetable oils, such as modified linseed oil,[20] castor oil,[22] and cardanol oil[30] could potentially be applied in vat photopolymerization, since these were found to exhibit UV curable properties.

Another reported bio-source for photopolymers is lignin. Sutton et al.[31] functionalized lignin with methacrylates. The product was incorporated up to 15% w/w in a commercial resin

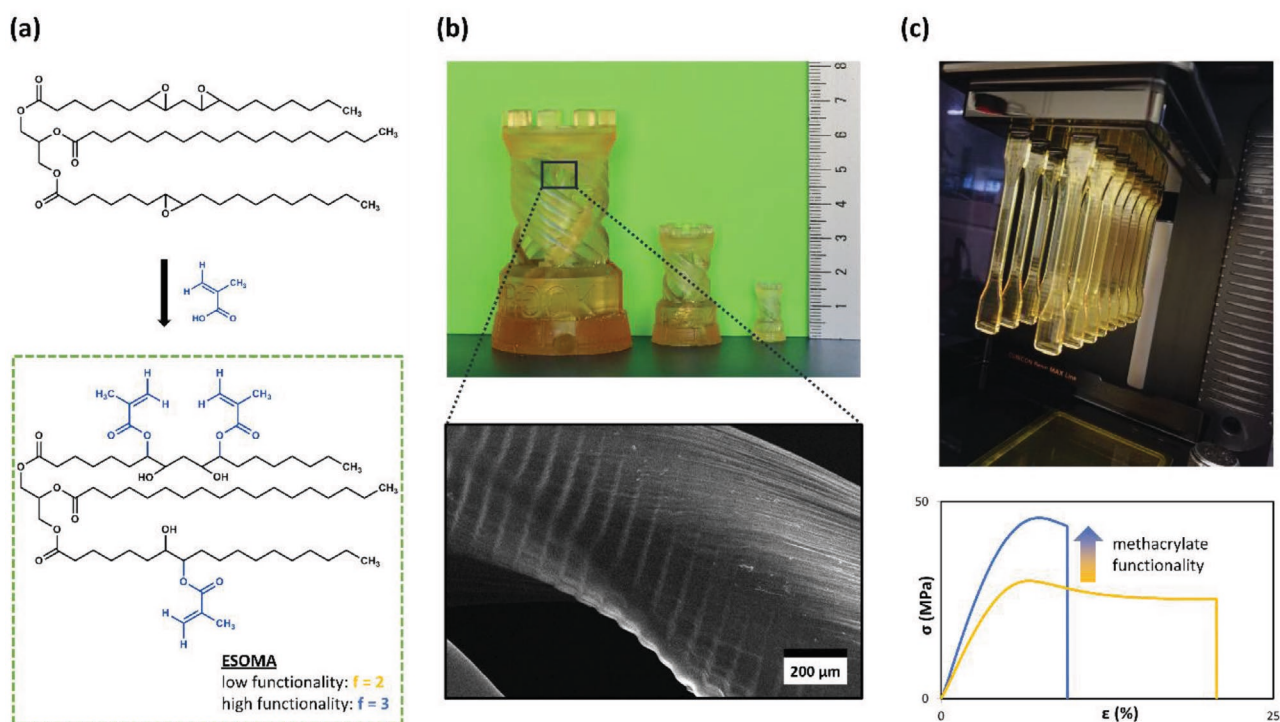**Figure 3.** Biobased photopolymers based on soybean oil for stereolithographic 3D printing.[25] a) Solvent-free synthesis of ESOMA with various functionalities. b) Picture of rook tower prototype printed with tri-functional ESOMA and SEM image of internal double helix structure on microscale. c) Picture of 3D printed tensile bars (top) and stress–strain curves demonstrating the mechanical properties (bottom).

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and subsequently applied in stereolithography. Lignin was found to act as a plasticizer; stiffness decreased with increasing lignin content, whereas ductility improved. Lignin derivates, such as vanillin, have been applied in SLA as well.[32] Vanillin was firstly methacrylated and mixed with glycerol dimethacrylate in an equimolar ratio. The resulting photopolymer resin exhibited a biobased content of only 35%. However, the 3D printed product demonstrated a high glass transition temperature (153 °C) and high Young's modulus (4900 MPa). Other lignin derivates, such as eugenol and guaiacol, were also incorporated in resins for SLA, resulting in polymers with mechanical properties competitive to commercial SLA resins.[33]

Recently, Miao et al.[34] reported the formulation and 3D printing of resins with exceptional mechanical properties. Both succinic acid and itaconic acid were functionalized with glycidyl methacrylate, resulting in BHMP2 and BHMP3, respectively. BHMP2 demonstrated a glass transition temperature of 147 °C and BHMP3 a T_g of 183 °C. Although both polymers demonstrated low ductility, their tensile moduli were high, i.e., 1563 MPa for BHMP2 and 4480 MPa for BHMP3. Moreover, both resins demonstrated great printability by DLP, resulting in well-defined models with good layer adhesion.

Cosola et al.[35] used acrylated γ-cyclodextrin (Ac-γ-CD) as biobased compound in DLP printing. Up to 30% of this oligosaccharide obtained from starch was mixed with monofunctional methacrylated poly(ethylene glycol) (PEG) as reactive diluent to formulate resins. Increasing Ac-γ-CD content resulted in stiffer networks, due to its crosslinking function. The resin containing 20% Ac-γ-CD was used to print high resolution models.

The use of biobased resins for biomedical applications such as tissue engineering has also been reported. Unsaturated polyesters, prepared by polycondensation of multiple bioacids with glycols, were applied in SLA. The 3D printed scaffold had a homogenous surface and demonstrated good cell viability.[36] Methacrylated gelatin was used to print detailed hydrogels with properties similar to liver tissue[37] and vascular-like constructs with good cell viability of the encapsulated fibroblasts.[38] Terpenes, such as linalool monomer and a prepolymer from limonene[39] and polymyrcene mixed with reactive diluent β-myrcene,[40] were used to print porous structures with high ductility following thiol-ene chemistry. Methacrylated chitosan,[41,42] starch[43] and carboxymethyl cellulose[44] have also been used to print hydrogels, and good biocompatibility has been reported. Moreover, silk fibroin modified with methacrylates was applied in DLP printing to fabricate scaffolds and mimicked organ shapes with excellent biocompatibility.[45]

The above-mentioned resins are generally derived from biomass, which could be used for other purposes, such as human consumption or medicinal applications. One of the most recent advances in the field of sustainable resins is the development of a photopolymer resin from McDonald's waste cooking oil by Simpson and co-workers.[21] The fatty acids of these oils were acrylated and the resulting resin was subsequently 3D printed. The prints demonstrated decent quality with slight over-exposure (**Figure 4**), however it should be noted that, other than a photoinitiator, no additional chemicals were added to the resin. Interestingly, the polymers were found to be biodegradable. After 14 days of incubation below the surface of soil under specified conditions, 18% weight loss was observed.

4. Biobased Fillers

Although the mechanical properties of thermoset polymer networks fabricated by vat photopolymerization have improved drastically in recent years, these networks often demonstrate brittleness due to their highly crosslinked structure. To overcome this drawback, photopolymer resins can be reinforced by incorporating fillers, or nanoparticles, resulting in composites with improved mechanical properties. A few studies report the use of additives based on renewable resources for stereolithography resins. Even though it hardly increases the overall biobased content of a resin system, in combination with renewable monomers it can potentially lead to a fully biobased composite.

Among the applied biobased reinforcers in photopolymers, cellulose is most often studied. Kumar et al.[46] reinforced a photopolymer resin by incorporating up to 5% w/w cellulose nanocrystals (CNC). A higher concentration of CNC resulted in aggregates, which negatively impacted mechanical properties. With incorporation of 5% CNC, resin viscosity moderately increased and the tensile modulus was found to increase by 1 GPa. Storage modulus and T_g improved as well, however, elongation decreased with increasing CNC content. Similar trends regarding mechanical properties were observed for lignin-coated CNC.[47] Incorporation of various concentrations CNC in PEG hydrogels resulted in indistinct trends regarding mechanical properties, but successful 3D printing of a high-resolution construct was demonstrated.[48] More recently, Wang et al.[49] incorporated up to 1.0% w/w CNC into a commercial methacrylate resin. Tensile strength was found to increase up to a CNC content of 0.5%, due to agglomeration at higher concentrations. Also, a compound additive was formulated with CNC, butane tetracarboxylic acid (BTCA) and sodium hypophosphite (SHP), to enhance connection between CNC and the resin. With respect to bare CNC, introduction of compound additive improved tensile strength, elongation and Young's modulus even further. Mohan et al.[50] tailored the surface hydrophobicity of cellulose nanofibrils (CNF) with PEG and reduced graphene oxide (rGO) to enhance dispersion of CNF in the photopolymer resin. Up to 5% w/w of surface-grafted CNF was incorporated into polyurethane resins, since aggregation occurred at higher concentrations. For both 5% PEG-CNF and 5% rGO-CNF, hardness and tensile properties other than elongation were found to improve.

Lignin has also been used as biobased filler in photopolymer resins. Zhang et al.[51] introduced up to 1% w/w of softwood kraft lignin into a commercial methacrylate resin. Incorporation of only 0.2% lignin increased tensile strength by 52% and tensile modulus by 26% to 2.2 GPa, compared to the nonreinforced reference. Further increase of lignin content did not demonstrate an improvement of similar magnitude, and eventually a decrease in mechanical properties was observed. A similar trend was observed by Ibrahim et al.[52] Organosolv lignin and lignin with 10% graphene (lignin-G) were used to reinforce a polyurethane resin. Tensile strength and stiffness improved with incorporation of lignin up to 0.6% w/w. Increasing the filler concentration further led to a decline of mechanical properties with respect to the neat polyurethane resin (**Figure 5**).
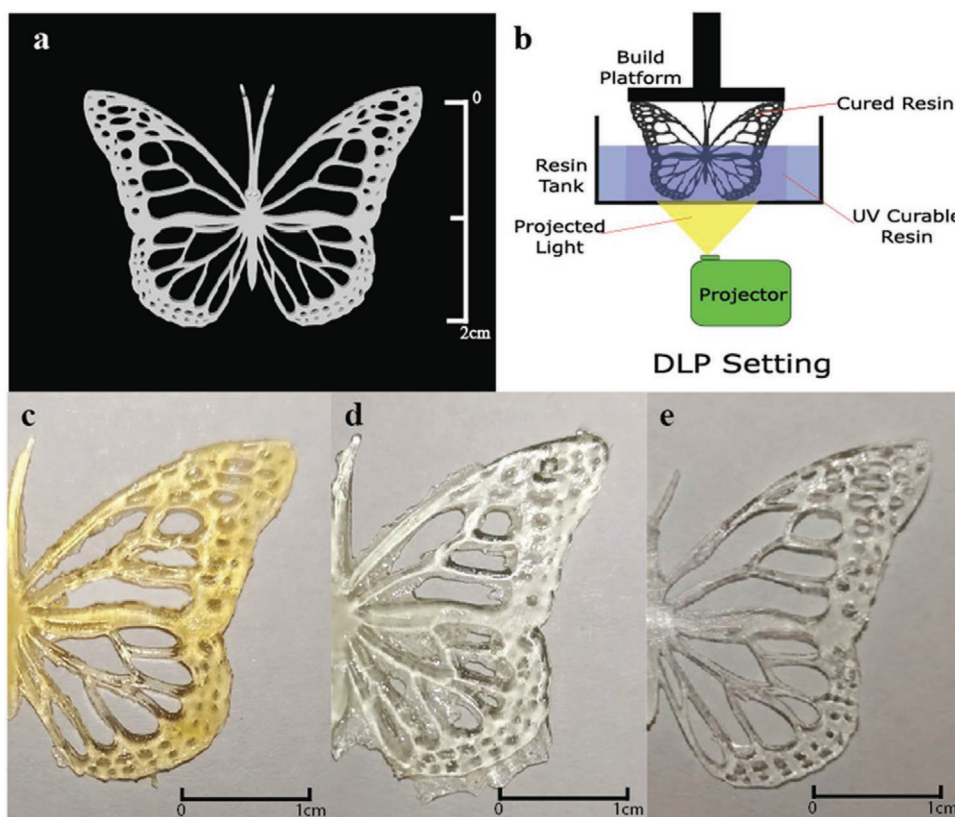
Figure 4. a) 3D butterfly digital model; b) simplified DLP printing scheme used in this study; 3D printed butterfly from c) McDonald's acrylated waste cooking oil, d) epoxidized soybean oil acrylate, and e) commercial resin MiiCraft. Reproduced with permission.[2] Copyright 2020, American Chemical Society.

Other biobased fillers applied in photopolymer resins are derivates from crustacea, such as chitin and chitosan. Incorporation of chitosan resulted in a decline in mechanical properties, however, the resulting composites demonstrated improved cell viability and proliferation.[53,54] Contrary to chitosan, chitin nanowhiskers (CNWs) improved tensile strength and tensile modulus, as demonstrated by Maalihan et al.[55] A commercial methacrylate resin was incorporated with a maximum of 1.5% w/w CNWs. Thermal properties improved with increasing CNW content.

5. (Bio)degradable Photopolymers

Resins used in stereolithography form thermoset polymer networks upon exposure to light, which generally show limited degradability. To circumvent this challenge, thermoplastic polymers which are known for their biodegradability have been used as precursors for new photopolymers. Biologically degradable polymers, such as poly(propylene) fumarate (PPF) in combination with diethyl fumarate (DEF),[56,57,58,59,60] poly(ε-caprolactone) (PCL),[61,62] poly(trimethylene carbonate)
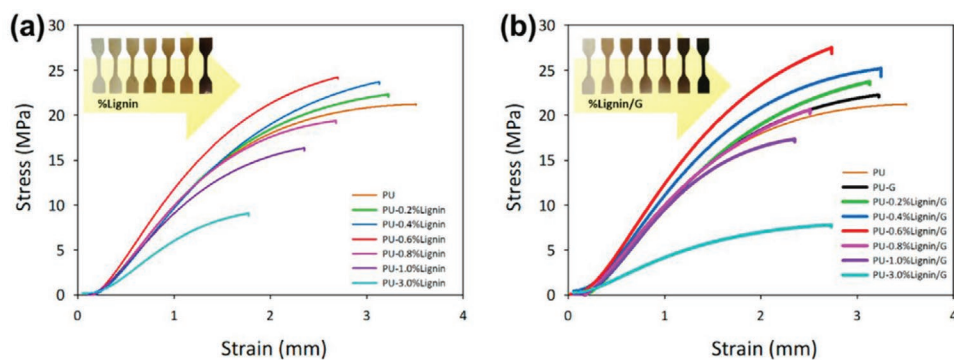

Figure 5. Stress–strain curves representing the mechanical properties of a) photocurable PU reinforced with lignin and b) photocurable PU reinforced with lignin-G. Reproduced under the terms of the Creative Commons CC BY license.[52] Copyright 2019, the Authors. published by MDPI.

(PTMC)[63,64,65,66] and poly(D,L-lactide) (PDLLA),[67,68] were functionalized and subsequently applied in vat photopolymerization to fabricate biodegradable scaffolds. Matsuda et al.[69] used a coumarin-functionalized PCL/PTMC copolymer to fabricate a well-defined microstructure. More recently, a graphene reinforced PLA-polyurethane acrylate was used to fabricate high-resolution scaffolds by SLA.[70] Noticeably, degradation of the printed objects is not studied in these reports. The polymer chains are generally modified with (meth)acrylates prior to photopolymerization, to enable fast curing which is required for lithography-based AM. The macromolecular architecture of the resulting thermoset, however, significantly differs from a thermoplastic material, even though an initial thermoplastic polymer is used to form the crosslinked network. The permanent crosslinks formed during vat photopolymerization are not susceptible to (bio)degradation, which means that degradation of the polymer network can only proceed to a certain extent.

The degradability of cured photopolymer resins, however, is reported in some studies. Matsuda et al.[71] synthesized a PCL/PTMC copolymer in an equimolar monomer ratio, using tri(methylene glycol) (TMG) or PEG as an initiator. The resulting copolymer was acrylated, subsequently applied in SLA and subjected to degradation experiments. After 3 days immersion in alkaline solution, the TMG-initiated copolymer demonstrated increased surface roughness, indicating degradation to a certain extent. The PEG-initiated copolymer completely dissolved within 1 day of immersion. In vivo degradation studies also demonstrated faster degradation for the PEG-initiated copolymer. Kuhnt et al.[72] synthesized PCL/PTMC copolymers with different monomer ratios using tri(ethylene glycol) (TEG) as an initiator. The resulting copolymers were functionalized with urethane acrylates and applied in DLP to fabricate films, which were subjected to accelerated degradation studies under alkaline conditions during 30 days. The degradation was monitored as a function of weight loss and varied from 4% to 13%, depending on the molar ratios used in copolymer synthesis.

PLA-based photocured resins have been subjected to degradation studies as well. Melchels et al.[73] monitored degradation of methacrylated PDLLA photopolymers in phosphate buffered saline by measuring tensile strength and the gel content of the samples. After 24 weeks, mechanical stability of the polymers was lost. Gel content started to decrease after 17 weeks, indicating chain cleavage. The same group of researchers used a methacrylated PEG-PDLLA copolymer to fabricate high resolution hydrogels by SLA.[74] Immersion of this polymer in sodium hydroxide (NaOH) resulted in a clear solution after ≈5 s. Contrary, the crosslinked hydrogel remained unchanged for several weeks in demineralized water. More recently, Wilts et al.[75] synthesized poly(lactide-*co*-glycolide) (PLGA) acrylates with different monomer ratios. Ductile films were fabricated and subjected to degradation in saline, which was monitored by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). It was found that the copolymer with highest lactide content degraded the slowest, in 16 weeks. The sample with the highest glycolide content, however, degraded within 4 weeks. Increasing the GA content leads to an increase in hydrophilicity, and thus a higher rate of hydrolysis/degradation.[76]
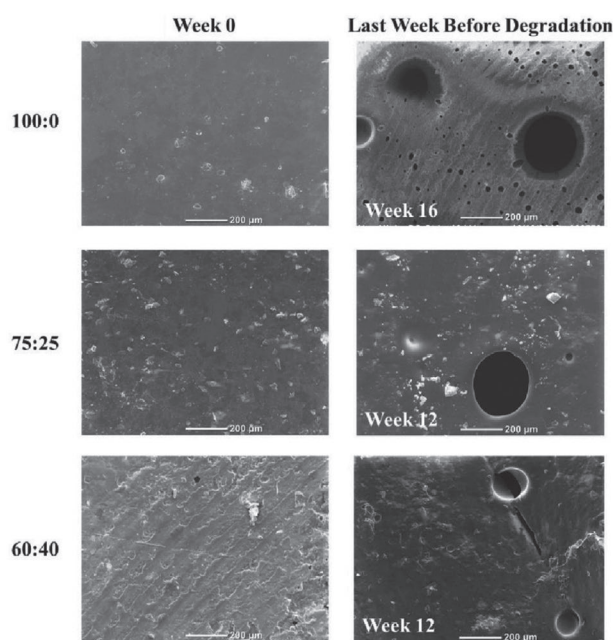

Figure 6. SEM images of fabricated PLGA films, subjected to degradation in phosphate buffered saline. The left column indicates the lactide:glycolide ratio in the acrylate-functionalized PLGA copolymer. SEM images were taken in the first week and the last week before complete degradation. Reproduced with permission.[75] Copyright 2020, Elsevier.

SEM imaging revealed cavities in the films as degradation proceeded (**Figure 6**), while T_g was found to decrease.

Farkas et al.[77] formulated a PPF/DEF based resin and tuned the laser parameters to fabricate multiple structures. A two-segment construct was build using different laser parameters. Whereas the core degraded within 7 days after soaking in Dulbecco's modified eagle medium, the rim remained intact for more than 3 weeks.

The degradability of thiol-yne networks has been studied by Oesterreicher et al.[78] Multiple alkynes were synthesized and mixed with polyfunctional thiols. The resulting resins were photopolymerized and subjected to degradation in NaOH. Whereas some thiol-ynes demonstrated ≈90% weight loss within 7 days, others showed only 5% weight loss after 40 days. The thiol-ynes with fast degradation rates revealed poor mechanical and thermal properties compared to their (meth)acrylated counterparts, contrary to thiol-ynes with slow degradation rates. Unfortunately, a fast-degrading thiol-yne was not applied in vat photopolymerization.

Recently, Smith et al. used methacrylated bovine serum albumin (BSA) in combination with PEG-diacrylate to fabricate hydrogels by SLA.[79] A dual-curing system was applied, i.e., UV-curing to polymerize the (meth)acrylates and thermal curing to denature the proteins. The fabricated hydrogels demonstrated good cell viability; however, visible deformations were observed in the structures fabricated. Degradation by the enzyme proteinase K was also tested. A weight loss of 22% was observed after 1 week of incubation. Interestingly, complete digestion was observed within 2 and 16 h, for non-thermally cured and thermally-cured BSA respectively, in case PEG-diacrylate was not incorporated.

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6. Recyclable Thermosets

In comparison to thermoplastics, thermosets demonstrate enhanced mechanical performance, thermal stability and chemical resistance due to their crosslinked nature. However, it is the same covalent network structure that restricts molecular mobility, which makes traditional thermosets infusible and insoluble. As a result, they are difficult to repair or recycle and are in general disposed by incineration or accumulation on landfills.

The incorporation of dynamic interactions offers a solution to the aforementioned dilemma. Over the past two decades, a new generation of polymeric materials has been developed, referred to as covalent adaptable networks (CANs).[80,81] CANs bridge the gap between thermoplastics and thermosets. Within the adaptable network, bonds can be exchanged under specific stimuli, e.g., heat or light. Those dynamic crosslinks enable CANs to behave as both malleable plastics and robust network polymers at the same time. Bond exchange can proceed either via dissociative or associative pathways.[82] In the latter, bond-breaking and -forming occurs in a single reaction, so crosslink density is retained during the exchange. Ludwik Leibler introduced the term vitrimers[83] for this special class of thermosets, referring to their similarity to vitreous silica. Vitrimers enable the self-healing, reprocessing and recycling of thermosetting polymers and can therefore contribute to waste reduction and lifespan extension of plastic materials.[84]

Shi et al.[85] were among the first to develop recyclable thermosets for additive manufacturing. They have reported the preparation of a viscous vitrimer ink based on fatty acids and DGEBA for extrusion-based direct ink writing (DIW). A multi-step procedure is followed (involving pre-curing, printing and post-curing steps) to obtain 3D structures, that can be recycled into a new ink suitable for the next round of 3D printing. The recycling method relies on solvent-assisted transesterification of the cured 3D architecture using ethylene glycol. Although the application of DIW circumvents the need for photocurable resins, it limits the feature resolution and geometric complexity of fabricated constructs.

An elegant two-stage method towards 3D printed reprocessable thermosets (3DPRTs) from photopolymer resins has been reported by Zhang et al.[86] First, a resin containing bisphenol A glycerolate diacrylate (BPAGA) and hydroxyphenoxypropyl acrylate was formulated and a high-resolution lattice structure was fabricated via stereolithographic printing. In the second step, transesterification between the ester and hydroxyl moieties at elevated temperature led to the formation of dynamic crosslinks within the polymeric network. The material showed good repairability, in which the repaired sample of 3DPRT recovered 100% of its stiffness and 93% of the original strength, thanks to the capability of bond exchange reactions. In contrast, the same repair approach on a conventional 3D printed thermoset was not successful. In addition, the product was grinded to powder and molded into a thermosetting sheet (**Figure 7**). The recycling process is repeatable, although some mechanical degradation was observed after each cycle.

A similar strategy was applied to fabricate recyclable light-weight architectures.[87] A photopolymer resin based on bisphenol A glycerolate dimethacrylate (BPAGMA) was developed for 3D printing on a DLP system. The printed parts were then post-cured in a UV chamber. Failed microlattices were crushed into powder via ball milling and remolded under high
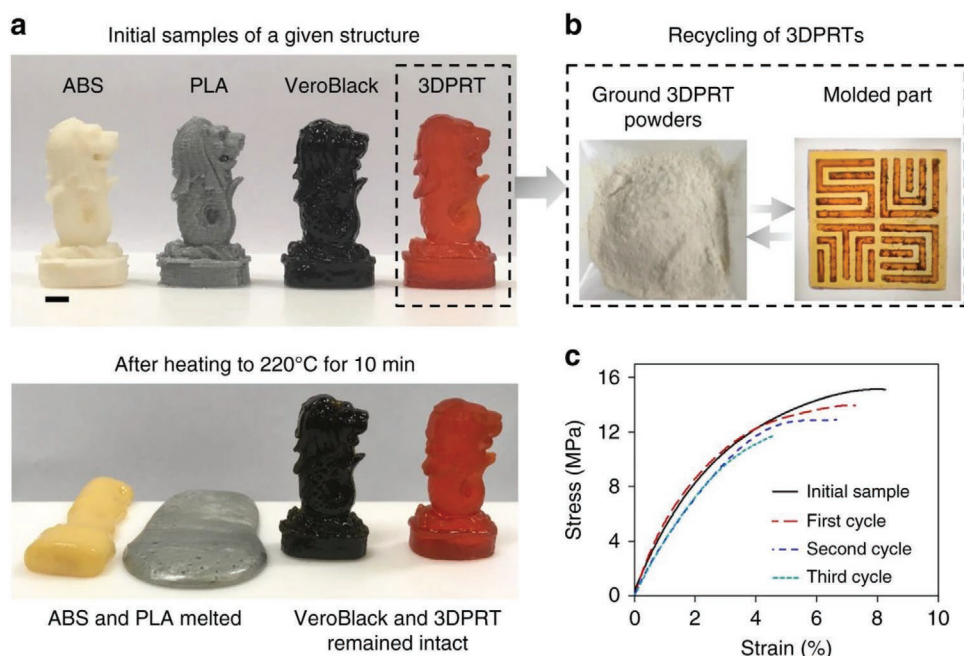

Figure 7. Recyclability of 3D printed reprocessable thermosets (3DPRT). a) Stability comparison of a printed structure with 3DPRT and structures printed with commercially available thermoplastics (PLA and ABS) and thermoset (Vero-black) at high temperature (220 °C). Scale bar = 5 mm. b) Demonstration of recycling of a structure printed with 3DPRT. c) Uniaxial tensile tests to examine the mechanical repeatability of the recycled 3DPRTs. Reproduced under the terms of the Creative Commons CC BY license.[86] Copyright 2018, the Authors. Published by Springer Nature.

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Table 1. Overview of reports on sustainable photopolymers for AM.

Category	Material Source	Authors[ref]	Year of Publication	Functionality	3D Print Technology
BIOBASED	Carboxylic acids	Gonçalves et al.[36]	2014	Unsaturated backbone	SLA
		Miao et al.[34]	2020	Methacrylate	DLP
	Vegetable oil	Miao et al.[23]	2016	Acrylate	SLA
		Voet and co-workers[25–27]	2018-2020	Acrylate, methacrylate	SLA, DLP
		Branciforti et al.[20]	2019	Epoxy	SLA
		Lebedevaite et al.[24]	2019	Acrylate	DLW
		Cui et al.[29]	2020	Epoxy + acrylate[a]	SLA
	Gelatin	Ma et al.[37]	2016	Methacrylate	DLP
		Krishnamoorthy et al.[38]	2020	Methacrylate	DLP
	Silk protein	Kim et al.[45]	2018	Methacrylate	DLP
	Lignin derivatives	Sutton et al.[31]	2018	Methacrylate	SLA
		Ding et al.[33]	2019	Methacrylate	SLA
		Bassett et al.[32]	2020	Methacrylate	SLA
	Terpenes	Weems et al.[39,40]	2019-2020	Thiol-ene	DLP
	Starch	Noè et al.[43]	2020	Methacrylate	DLP
		Cosola et al.[35]	2020	Acrylate	DLP
	Chitosan	Seo et al.[41]	2020	Methacrylate	SLA
		Shen et al.[42]	2020	Methacrylate	DLP
	Sucrose[b]	Silbert et al.[28]	2020	Acrylate, methacrylate	SLA
	Cellulose	Melilli et al.[44]	2020	Methacrylate	DLP
	Waste cooking oil	Wu et al.[21]	2020	Acrylate	DLP
DEGRADABLE	Polycaprolactone (PCL) and copolymers	Matsuda et al.[71]	2002	Acrylate	SLA
		Kuhnt et al.[72]	2019	Acrylate	DLP
	Polylactide (PLA) and copolymers	Melchels et al.[73,74]	2010	Methacrylate	SLA
		Wilts et al.[75]	2020	Acrylate	DLP
	Polypropylene fumarate (PPF)	Farkas et al.[77]	2015	Unsaturated backbone	SLA
	Alkyne carbonate derivatives	Oesterreichter et al.[78]	2016	Thiol-yne	DLP
	Cow protein	Smith et al.[79]	2020	Methacrylate	SLA
REPROCESSABLE	Bisphenol A[c]	Shi et al.[85]	2017	Epoxy	DIW
		Zhang et al.[86]	2018	Acrylate	DLP
		Li et al.[87]	2019	Methacrylate	DLP
	Cellulose/rosin	Lu et al.[88]	2020	Methacrylate	SLA

[a] Dual-curing resin to yield an interpenetrating network; [b] Reaction product of sucrose and soybean oil; [c] Bond exchange proceeds via transesterification reactions in the network.

temperature and pressure to produce a new product, thereby demonstrating the typical vitrimer behavior. The authors investigated the effect of processing conditions on the recycling efficiency (recovery of tensile strength), which relates to the reactivity of the transesterification reaction. The maximum recycling efficiency obtained, however, is 28%.

More recently, repairable 3D printed thermosets with a dual-cure network have been fabricated by a two-step strategy.[88] SLA 3D printing of photocurable resins derived from rosin and cellulose was performed to achieve a crosslinked thermoset. Next, heating triggered the reaction between hydroxyl and isocyanate groups, forming the dual-cure network. Damaged samples were repaired by coating with photoresin, followed by

UV irradiation and thermal treatment. The mechanical performance was almost fully recovered, indicating reformation of the crosslinked network across the damaged interface. Nevertheless, the actual recyclability of the 3D printed thermosets was not reported. Partial degradation of the polymeric network in an aqueous solution, attacking the glucosidic and ester bonds, yielded swollen hydrogels with an adjustable gel content.

7. In Conclusion

Vat photopolymerization provides a versatile platform for computer-aided design and precise fabrication of customized

products. However, the availability of sustainable photopolymer resins is essential for the large-scale acceptance of this AM technology. The development of environmentally friendly materials for SLA and DLP have gained considerable attention in recent years (**Table 1**). The following trends have been observed. Photopolymers based on renewable resources such as vegetable oils, terpenes, starch and lignin have been studied extensively as sustainable replacements for fossil-based acrylates and epoxides used in current 3D print resins on the market. Challenges that remain are the quality and mechanical properties of the photopolymerized products. Biobased additives have been introduced to improve the performance of printed objects. Incorporation of cellulose nanocrystals and chitin nanowhiskers in photopolymer resins have demonstrated promising results, in particular. Several studies discussed the development of (bio)degradable polymers for vat photopolymerization. The complete degradation of 3D printed products, however, is rarely reported. Very recently, the concept of covalent adaptable networks has been applied to print thermosetting polymers that can be repaired and recycled successfully. Clearly, the field of sustainable photopolymers for 3D printing is rapidly evolving. It is expected to generate new and advanced materials to accommodate the ever-increasing demand for AM materials in the latest industrial revolution and to facilitate the unstoppable transition towards a circular economy.

Conflict of Interest

The authors declare no conflict of interest.

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