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Review of high-performance sustainable polymers in additive manufacturing

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Additive manufacturing (AM), commonly referred to as 3D printing, is viewed as a method of rapid prototyping and an alternative to traditional manufacturing. Recently, there has been increasing interest on sustainability of AM approaches and the materials that can be used. Advances in both AM technologies and polymer chemistry present multiple pathways for AM to become more sustainable, such as raw material sourcing, green synthesis, and end-of-life processing. This review provides a brief overview of AM techniques for polymers, sustainable sourcing of polymers in AM, and the advances of degradable/recyclable polymers in AM. It also provides a perspective of the potential role of AM in economic and chemical circularity, as well as opportunities for digital manufacturing for the future. Biodegradable materials for medical or other biological applications are beyond the scope of this review.

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Introduction

Our world today is full of incredible advancements in science and technology, but the unintended consequences of these advances threaten our future. Synthetic polymers, which have only been manufactured widely since the 1950s, offer one of the most explicit and severe examples. Although synthetic polymers have many benefits, their durability has led to a global plastic pollution problem that now presents one of the most pervasive and extensive challenges to the health and future of our planet and its inhabitants.

Polymeric products constitute about 9% of the \$12T manufacturing market sector, and 30% of that is comprised of injection molded products.¹ Recent advances demonstrate that 3D printing is poised to make the jump from a “prototyping only” \$8B industry to replace injection molding techniques—a \$330B industry—in many areas.² This transition in technology represents a unique moment in time to pre-emptively put polymer additive manufacturing (AM) on a sustainable trajectory. A “benign by design” strategy represents a critical step in this exciting trajectory, focusing a sustainability lens on next-generation materials for next-generation advanced manufacturing platforms.

AM is an increasingly attractive option for both rapid prototyping and manufacturing objects with complex geometries, and it's often viewed as an environmentally sustainable manufacturing option because of its intrinsic potential to leverage on-site pro-

duction that minimizes both production waste and emissions from transporting manufactured goods from factory to facility. AM integrates polymer synthesis and part fabrication into a single process step, leading to chemical process intensification. This potential to go from basic feedstock resins to a final product without intermediate isolation, reprocessing, or large-scale capital allocation for reactors reduces risk for product development and drives innovation. In addition, some have predicted that AM can reduce CO₂ emissions by 130.5–525.5 million tons and energy demands by up to 9.30×10^{18} J by 2025.³ Nevertheless, there are additional motivations to design for minimal environmental impacts as AM scales.

AM has spawned the demand for highly customizable, uniquely functional, and high-performance objects, which results in a rapid increase in products created by AM. However, many of these products are not designed to be recycled. There is a need to develop high-performance materials and a way to recycle the materials. Alongside material properties, high-performance products can be further enhanced with geometrical structures. Lattice geometries enabled by AM have gained special interest because of the unique strength-to-weight ratio, as well as the ability to obtain excellent mechanical properties while reducing the amount of material wasted in production (buy-to-fly ratio⁴) and used in the final part. Indeed, AM is driving the “de-materialization” of products in ways not possible with injection molding using latticed geometries not achievable via injection molding. Architected structures allow objects created from a single material to have a range of mechanical properties. When looking at high-performance use-cases such as an automobile, many different materials—nearly 40 different polymers developed *ad hoc* over decades, as opposed to being designed with a sustainability-first co-design approach—are

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used in a complex assembly to achieve the range of mechanical properties needed in each part of the automobile. The sheer diversity of materials that are required in an automobile makes materials recovery and recycling very challenging. However, we believe that it may be possible to substitute the overabundance of polymer types with a much smaller subset of polymer compounds, all chemically recyclable, in which the limitations in material selection can be overcome by tailoring the geometry of a mesoscale 3D-printed structure, or lattice, to achieve similar or better diversity in functionality.

In addition to tuning the geometry for high performance products, materials selection of polymers is of particular interest because of their characteristic ability to retain desirable properties when exposed to extreme conditions such as high temperature, pressure or stress, or corrosive chemicals. Polymeric materials can be designed to withstand extreme conditions for extended periods of time, making them excellent choices for many industries such as aerospace, automotive, or construction. However, the resistance to heat, chemicals, and/or mechanical stress also means that high performance polymers are difficult to remanufacture and cannot be recycled easily. The same properties that are tailored for performance conflict with the chemical properties for depolymerization.

Over 50% of polymers in AM and almost 20% of all plastics produced in the world are *thermoset* polymers which are cross-linked to have high resistance to chemicals and heat.^{5,6} While AM has the potential to reduce waste production, energy consumption, and CO₂ emissions compared to traditional manufacturing, it does not inherently solve the issues of unsustainable production. Our evolving understanding of the adverse impacts of technological advancement on the environment makes it imperative that the design of high-performance materials must also include a vision for end-of-life treatment and re-use or re-cycling. Despite the many positive opportunities for AM to support the tenets of sustainability, there is a great need to ensure that AM materials themselves are chemically recyclable or compostable.

Herein, we will focus on sustainable, high-performance polymers for AM. Biodegradable materials for medical or other

biological applications are beyond the scope of this review. This publication reviews the current methods of additive manufacturing, current degradable polymers used in each of the following AM methods with a focus on high-performance polymers, followed by a discussion on the impact these materials will have on society.

Current methods of additive manufacturing

The earliest recording of 3D printing through an additive process was in 1981 by Japanese inventor Hideo Kodama, who developed a method of fabricating 3D models by curing photo-sensitive resins layer-by-layer with UV light.⁷ In the field of AM materials, polymers remain the most commonly used material because early 3D printers, such as the one designed by 3D Systems Inc. in 1986,⁸ used polymers for rapid prototyping.^{9–11} In more recent years, materials for AM have spanned a wide range: ceramics,^{12–15} metals,^{16–19} hydrogels,^{20,21} nanomaterials,^{22–24} pharmaceuticals,^{25–27} and even biological materials such as cells and tissue.^{28–30} However, polymers remain the most popular material for AM due to their ease of printing, well-established technology, versatile thermomechanical performance, and chemical inertness.³¹ One of the key patents for 3D printing expired in 2004, and since then, numerous research articles have been published and new patents have been filed on the expansion of the AM technology. There are now four main polymer AM process modalities: material extrusion, vat photopolymerization (VP), binder jetting, and powder bed fusion, as shown in Fig. 1.³² For each type of AM, the materials properties needed, and the challenges associated with each method are briefly summarized below.

Material extrusion

Extrusion-based AM involves the deposition of material to build an object “layer-by-layer”. Examples of extrusion-based AM include Fused Filament Fabrication (FFF)^{33,34} and Direct

Polymer Additive Manufacturing Methods

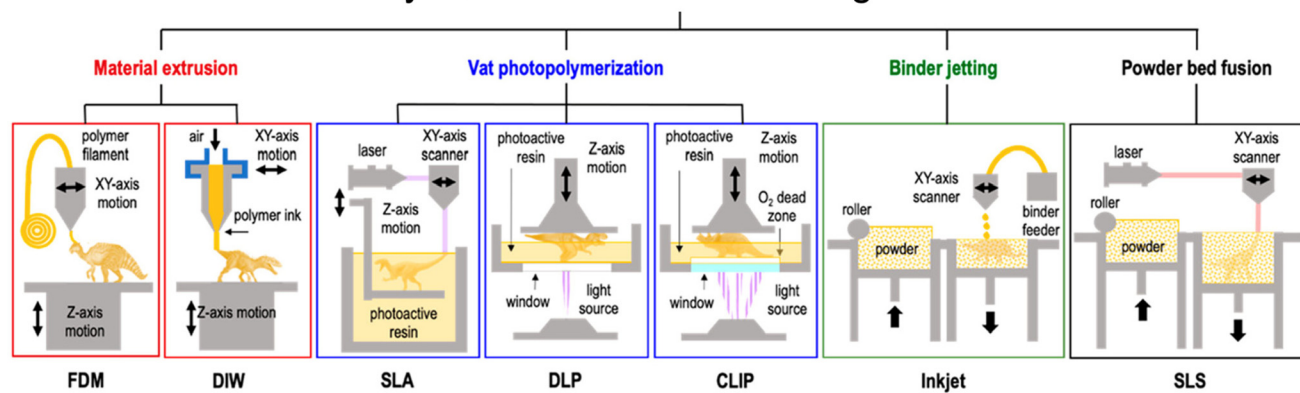


Fig. 1 Description of polymer additive manufacturing methods. Reproduced from ref. 32 with permission from American Chemical Society, 2021.



Ink Write (DIW).^{35,36} These processes construct a three-dimensional object by extruding a thermoplastic filament through a heated nozzle (FFF) or a viscous paste/gel/photopolymer (DIW) onto a build platform. In FFF and DIW, the polymer filament melt (FFF) or ink (DIW) must have a proper viscosity to be extruded through the printhead (typically a shear thinning behavior), and high zero shear viscosity, yield stress behavior, and/or rapid gel time once deposited to avoid flow and part slumping upon deposition. Due to the high melt viscosity of performance polymers, large FFF extrusion nozzles are typically required, which limits process resolution and results in a poor surface finish due to the “staircase” effect from the layered deposition. While these extrusion systems are inexpensive, they have a very low throughput due to the need to raster the extrusion nozzle to build each layer and have limited resolution, and feature capability results from the challenges in start/stop extrusion of viscous materials. FFF systems also feature significant anisotropy due to poor interlayer bonding caused by rapid cooling and solidification of the extrudate.

Binder jetting

Binder jetting is a method of AM where droplets of material are selectively jetted and photocured to build an object. In binder jetting, the starting material must have a very low viscosity (<0.1 Pa s) and tuned surface tension to enable jetting of picoliter droplets that can form well-defined primitives on the build surface. While jetting enables precise spatial control (~ 50 μm) over multiple resins in a single build, the rheological constraints imposed by jetting significantly limit the material selection to low viscosity, low molecular weight precursors. The comparison of rheological constraints for various AM methods is shown in Fig. 2.

Polymer powder bed fusion (P-PBF)

Powder bed fusion techniques involve the selective fusion of powdered polymers through the use of a scanning laser (traditionally referred to as Selective Laser Sintering (SLS)³⁷) or overhead IR heating of a selectively doped powder bed (e.g., HP's MultiJet Fusion process,³⁸ VoxelJet's High Speed Sintering.³⁹ When using powders as starting material, careful consideration must be taken to ensure that the polydispersity of the particle sizes is narrow to achieve homogenous fusion

and high resolution. Producing 30–50 μm powders from high-performance polymers has proven challenging and wasteful.⁴⁰ Furthermore, the thermal stability and hence recyclability of the powder is often limited, leading to high amounts of waste. While P-PBF has been used to make end-use components, it has (1) a limited selection of processable materials, (2) limited throughput due to long heating/cooling cycles, (3) arduous post-processing (depowdering), (4) energy intensive processing, (5) significant waste generation (due to polymer molecular weight growth and/or oxidative degradation from thermal cycling), and (6) an inability to process multiple materials simultaneously.

Vat photopolymerization (VP)

UV curable liquid resin-based AM can broadly be divided into three generations of vat photopolymerization and material jetting. In first-generation vat photopolymerization (VP), also known as stereolithography (SLA),⁴¹ a bath containing a single liquid resin is photocured spatio-selectively by a scanning laser point source. Second generation VP, referred to as digital light projection (DLP),⁴² uses a rapid sequence of projected UV images that span the entire X - Y plane of a bath containing a liquid resin in a single exposure. In third-generation VP, known as continuous liquid interface production (CLIP, Fig. 3), a layer of oxygen-rich liquid resin is continuously renewed at the build surface to provide a polymerization-inhibiting liquid interface (deadzone) between growing parts and a UV-transparent window.^{43–45} CLIP, achievable with multiple

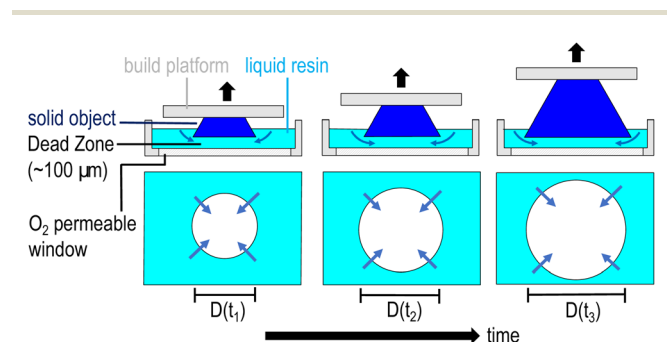


Fig. 3 The CLIP process involves the creation of a polymerization dead-zone, allowing high-speed printing.

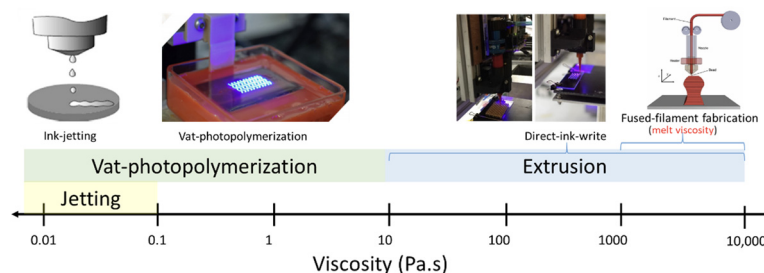


Fig. 2 Rheological considerations of polymer additive manufacturing processes. (PBF is not included here as viscosity alone is not the right framework for assessing a sintering process).



economy where all systems of production are cyclical such as that of a spaceship.⁵² Later, the term “circular economy” appeared in “The Economics of Natural Resources” by Allen Kneese.⁵³ Over 50 years later and numerous advances in manufacturing, we still have not reached a circular economy, and we are still far from it. However, as Geissdoerfer describes, we can achieve a circular economy through design. Within materials for AM, the concept of a circular economy is being used to guide design of new materials and methods for reuse and recycling. Triggered degradation, in particular, is a very useful tool for achieving a chemically circular society: any polymeric material that is produced can be collected and broken down to its components for re-production of parts. This will extend the value of raw materials far beyond initial manufacturing and aid in progress towards a circular economy.

Design for degradability and recyclability

Degradability has been demonstrated *via* multiple pathways that can be summarized in two main categories: passive degradation and triggered degradation. Passive degradation occurs when a material can degrade in a naturally occurring environment and does not require very specific chemicals to trigger its degradation. It may occur *in vivo*, such as with sutures that naturally break down when in contact with the body, or in an outside environment such as in a landfill with sufficient UV exposure from sunlight and oxygen in the atmosphere.⁵⁴ Passive degradation is an attractive field for polymer development because it has the potential to solve the plastic pollution problem while bypassing the current lack of recycling infrastructure. This suggests that a passive compostable degradation is favorable so that AM materials can degrade even when they are not properly sorted and collected to the proper waste management facility. However, even polymers that are designed to be passively degradable or compostable may not actually break down because of insufficient water or oxygen within landfills.⁵⁵ Another main challenge with passive degradation is balancing the maintenance of good mechanical properties and chemical inertness for the intended period use but still achieving a reasonable timeframe for natural and safe degradation. It is assumed that the conditions in which passive degradation occurs is different than the conditions in which the polymer is in use. Thus, passively degradable materials may lack the necessary properties of thermal, mechanical, or chemical resistance for long-term high-performance applications.

Alternatively, polymers that degrade by triggered reactions may provide the necessary properties and lifetimes required by different use-cases. Triggered degradation involves the presence of a “switch” that can initiate the degradation or decomposition of a material in conditions orthogonal to their use environment. This may involve a change of catalysts, solvent introduction, irradiation, high temperature, or another external agent. Triggered degradation is an attractive field for the development of high-performance polymers because of the potential to create materials that can rival current polymer performance and lifetime while being fully recyclable once the

The idea of a circular economy is not new: the concept dates as far back as 1966 in a famous essay by Kenneth Boulding that states society must transition to a “spaceman”

Table 1 Summary of sustainable polymers for AM with potential for use in high-performance applications

Method of AM	Source	Material	Method of degradability or reprocessability	Authors	Year of publication
Material extrusion	Synthetic	PLA	Thermoplastic, Diels–Alder network	Appuhamillage <i>et al.</i>	2017
	Consumer waste	PP, PET, PS	Thermoplastic	Zander <i>et al.</i>	2019
	Recycled powder	PC	Thermoplastic	Reich <i>et al.</i>	2019
	Wood	PLA composite	Thermoplastic	Duigou <i>et al.</i>	2016
	Wood	Wood	Biodegradable	Kam <i>et al.</i>	2019
	Cellulose, synthetic	Acrylate, composite	N/A	Siqueira <i>et al.</i>	2017
	Lignin	ABS, nylon composite	N/A	Nguyen <i>et al.</i>	2018
	Synthetic	PEEK	Thermoplastic	Hu <i>et al.</i>	2019
	Industrial waste	Geopolymer	Crush and reuse	Panda <i>et al.</i>	2017
	Synthetic	Semi-crystalline thermoplastics	Diels–Alder network	Yang <i>et al.</i>	2017
	Synthetic	Elastomer composite	Diels–Alder network	Guo <i>et al.</i>	2021
	Synthetic	Epoxy	Vitrimer	Shi <i>et al.</i>	2017
Material/binder jetting	N/A	N/A	N/A	N/A	N/A
Polymer powder bed fusion	Synthetic	Commercial polyamides, PS, PC, PEEK, <i>etc.</i>	Thermoplastic	Stansbury <i>et al.</i>	2016
Vat photo-polymerization	Synthetic	Acrylates	Thermoset – dynamic covalent bonds	Zhang <i>et al.</i>	2018
	Synthetic	Acrylates	Thermoset – dynamic covalent bonds	Rossegger <i>et al.</i>	2021
	Synthetic	DGEBA	Thermoset – dynamic covalent bonds	Zhao <i>et al.</i>	2021
	Synthetic	Epoxy	Thermoset – dynamic covalent bonds	Hao <i>et al.</i>	2020
	Synthetic	Polythiourethane	Thermoset – dynamic covalent bonds	Cui <i>et al.</i>	2022
	Synthetic	Thioester composite	Thiol-thioester exchange	Hernandez <i>et al.</i>	2022
	Synthetic	Acrylates, polyurethane	Degradable crosslinks	Poelma <i>et al.</i>	2019, 2021
	Lignin	Acrylates	Solvent-free synthesis	Ding <i>et al.</i>	2019
	Lignin	Vinyl ester	Solvent-free synthesis	Bassett <i>et al.</i>	2020
	Soybean oil	Epoxy	Natural material	Guit <i>et al.</i>	2020

material has served its purpose.⁵⁶ However, the challenge associated with this field is the lack of large-scale infrastructure that can support the chemical recycling of many different polymer types. Some processes of chemical recycling may also include mechanical comminution such as shredding or milling products into more easily reprocessable fragments.⁵⁷

The design for degradability in polymeric materials will now be reviewed as it pertains to each of the four main types of AM methods outlined above. A summary of the materials reviewed can be found in Table 1.

Material extrusion

Material extrusion typically relies on the extrusion of thermoplastic polymer melts, many of which are easily reprocessable. One of the most commonly used materials for FFF is poly(lactic acid) (PLA), an aliphatic polyester designed to be biodegradable and renewable. Compared to petroleum-based products, PLA has lower mechanical properties and is more expensive to produce,⁵⁸ but its passive degradability by self-hydrolyzation into lactic acid has made it a popular choice as a safe and sustainable material. Since the degradation rate of PLA (as with any degradable material) depends on the conditions of its environment, there have been numerous research studies on tuning its degradability and improving its mechanical properties such that it can be used in higher performance applications. This has led to the development of different forms of PLA such as poly(L-lactic acid) (PLLA) and poly(D,L-lactic acid) (PDLLA).⁵⁹ Furthermore, the combination of PLA with polyglycolic acid (PGA) formed the copolymer poly(lactic-co-glycolic acid) (PLGA) that is soluble in acetone, ethyl

acetate, tetrahydrofuran, and other common solvents, and can be used to increase degradation of PLA as an AM material, as shown in Fig. 4.^{58,60,61}

Modifications of the PLA polymer chain allows for tunability of properties beyond degradation rate, such as improving the toughness and heat resistance of the material for higher performance use-cases. For example, poly(L-lactide-co-ε-caprolactone) (PLC) is a more elastic copolymer than PLA, has a higher degradation rate than poly(ε-caprolactone) (PCL).⁶²

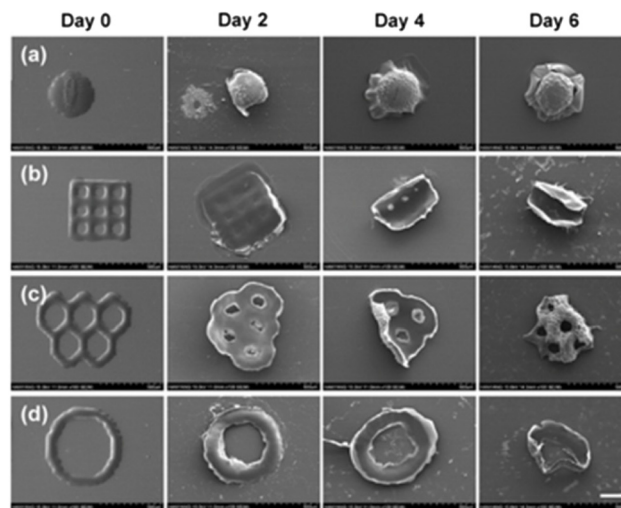


Fig. 4 PLGA as a degradable material for inkjet printing. Reproduced from ref. 61 with permission from Elsevier, 2012.



Degradation of printed polymers can also be achieved with natural materials that are sustainably sourced, such as cellulose or lignin. There have been several studies on incorporating cellulose into AM materials to reinforce current filaments, resin, and inks. Le Duigou *et al.* used wood cellulose fibers to strengthen a PLA-based extrusion filament.⁶⁹ Later, Kam *et al.* developed a method of 3D printing objects composed of 100% wood components by dispersing wood flour microparticles in a matrix of cellulose nanocrystals and xyloglucan.⁷⁰ The printed wood materials exhibited similar mechanical properties as natural wood and a higher thermal insulation. In 2017, Siqueira *et al.* developed a sustainable cellulose-based DIW ink by suspending cellulose nanocrystals (CNCs) in a photopolymerizable monomer solution.⁷¹ The amount of CNCs added to the polymer ink determined the effect on mechanical properties: a blend of 20 wt% CNC increased the elastic modulus by 80% compared to the polymer alone. Lignin, the second most abundant raw material in nature and the most abundant aromatic polymer in nature, is polymer that can also be used as a renewable alternative to synthetic materials^{72–74} for higher performance applications than cellulose. Nguyen *et al.* found that lignin could be used to form high-performance composite polymers using ABS and nylon filament, and that lignin could replace 40–60% of the synthetic

The use of covalently adaptable networks is a promising path for developing vitrimer materials in AM that can be easily processed. Instead of fully degrading a polymer and repolymerizing, it is possible to incorporate re-processability in thermoset materials using heat or catalysts.

Another recent development in sustainable high-performance materials for material extrusion is the use of degradable comonomers with thermosetting poly(dicyclopentadiene) (p(DCPD)) by Davydovich *et al.*⁸⁹ p(DCPD) is a tough and chemically resistant thermoset that is often used for automotive application such as for body panels and bumpers for trucks, buses, and construction equipment. Davydovich *et al.* demonstrated that the incorporation of dihydrofuran (DHF) in DCPD resins allowed the printed pDCPD to degrade into oligomeric products with product recovery around 80%. The printed material also had high ultimate strength around 35–40 MPa. Additionally, the use of frontal polymerization to cure the thermoset during printing reduces the amount of energy necessary for thermoset fabrication. This high-performance thermoset that is degradable into functional oligomers is a promising step towards a chemically circular economy.

Material/binder jetting

Like material extrusion, commonly used materials in material jetting are reprocessable thermoplastics, but also include thermosetting photopolymer resins and elastomers that are more suitable for high-performance applications.⁹⁰ Thermosetting resins used for material or binder jetting are typically comprised of prepolymers such as a combination of high and low molecular weight acrylates and methacrylates that can form tough materials. However, there is very little research conducted on developing specific polymers for material or binder jetting that are recyclable or sustainable. The development of degradable photopolymer chemistries beyond AM may eventually translate to material jetting, but the use of heat to lower the viscosity of materials is restricted by thermally-induced polymerization of pre-polymers.⁹¹

Polymer powder bed fusion (P-PBF)

Polymer Powder Bed Fusion (P-PBF) is a unique method of AM because it primarily uses semicrystalline thermoplastic prepolymers;⁹² the most commonly used material is nylon 12, but other polymers such as nylon 6, nylon 10, nylon 12, ABS, PS, and PC are commercially available.⁹³ Selection of high-performance polymers that can be used in P-PBF is limited because of the high powder bed temperatures required for processing.

The vast majority of sustainability research for P-PBF focuses on improving the recyclability of powders and binders, rather than the recyclability of the printed material.⁹⁴ Excess powders are typically collected, refined, and reused to minimize waste and cost of using virgin materials. However, reusing free powder poses its own set of challenges. The powder may contain defects from high temperature and sintering outside the print area⁹⁵ and the polydispersity of particle sizes usually increases after processing, which can result in

different properties from the original material.⁹⁶ Even powder from the same batch that have gone through the same number of processing cycles will demonstrate varying degrees of degradation depending on how close the powder was to the parts being manufactured.⁹⁷ Furthermore, the nature of PBF creates cross-contamination and powder separation challenges when printing with more than one material. To address these challenges, Kumar and Czekanski suggest that it is possible to salvage the excess waste from SLS and convert it into filament for FFF.⁹⁸ By doing so, it is possible to produce filaments with better mechanical strength than current commercial filaments, reduce the waste produced by SLS, and re-use the materials without the constraints of defects and polydispersity.

Vat photopolymerization (VP)

Vat photopolymerization (VP) has been a challenging AM method for novel recyclable materials because of the common usage of thermosetting resins. Traditionally, VP relied on the polymerization of simple acrylates or epoxy monomers, but has now expanded to include many polymer systems such as aromatic polyimides, polyurethanes, and PEEK.⁹⁹ Now, materials development for VP focuses on achieving end-of-life sustainability such as self-healing, reprocessability, or depolymerization for monomer recovery of thermoset materials.

For repairable thermosets, Zhang *et al.* developed a 3D printing re-processable thermoset (3DPRT) by mixing in zinc acetylacetonate hydrate as a catalyst for transesterification reactions to occur, thereby inducing dynamic covalent bonds to form and allowing the crosslinked network to rearrange and to be reprocessed at elevated temperatures as shown in Fig. 5.¹⁰⁰ Subsequently, Rossegger *et al.* applied the concept of dynamic covalent bonds in the development of an acrylate-based vitrimer for DLP that used an organic phosphate as the transesterification catalyst.¹⁰¹ The material could be repaired and reshaped by heating at 180 °C to fully recover the strength of the original defect-free material as shown in Fig. 6. Similarly, Zhao *et al.* developed an epoxy-anhydride resin using diglycidyl ether of bisphenol A (DGEBA) that can be recycled with ethyl-

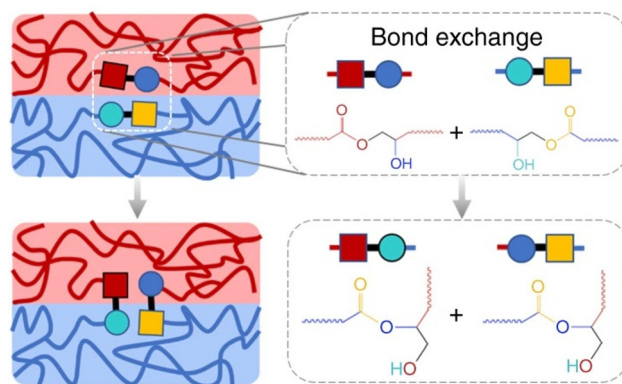


Fig. 5 Illustration of bond exchange reactions (BERs) in 3D printed re-processable thermoset. Reproduced from ref. 100 with permission from Springer Nature, 2021.



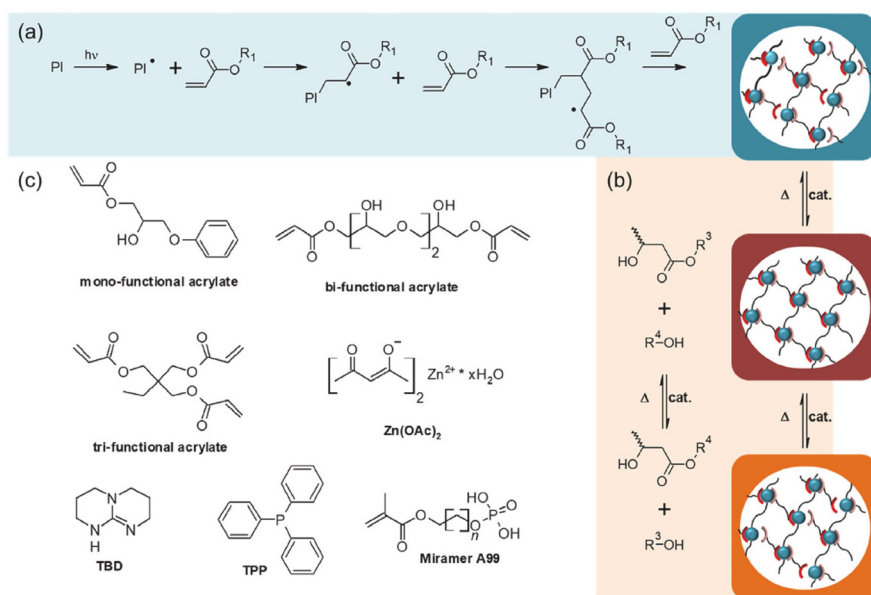


Fig. 6 Illustration of photocuring and thermally reprocessable vitrimers. (a) Photocuring process; (b) thermal reprocessing via triggered exchange reactions; (c) monomers and catalysts used for the vitrimer system. Reproduced from ref. 101 with permission from Elsevier, 2021.

ene glycol below 200 °C.¹⁰² The cured DGEBA polymers showed resistance to a range of organic solvents, including dichloromethane (DCM), dimethylformamide (DMF), 1,2,4-trichlorobenzene (TCB), xylenes, tetrahydrofuran (THF), and heptane but could be dissolved in ethylene glycol to obtain decomposed epoxy oligomers that could be reused in the preparation of a new epoxy resin with improved toughness and high chemical resistance.

Hao *et al.* developed a crosslinked epoxy vitrimer network with accelerated dynamic transesterification that exhibited a T_g of 135 °C and tensile strength of 94 MPa.¹⁰³ The epoxy vitrimer could be recycled into a fresh resin by grinding into a powder or degrading in an aqueous solution, and still maintain the same T_g and modulus as the original material. Similarly, Cui *et al.* developed a polythiourethane-based covalent adaptable network (CAN) with a T_g of 83 °C, Young's modulus of 1.2 GPa, and tensile strength of 61.9 MPa.¹⁰⁴ Damaged and rejoined pieces of this material, as well as hot-pressed powder made from the 3D printing waste, were able to regain over 80% of the original tensile strength. Additionally, the material could be fully degraded by adding excess thiol to convert the polymer network to thiol-terminated oligomers. These vitrimer and CAN materials offer paths for full chemical recyclability and repair in AM materials.

To further drive the field of recyclable polymers for high-performance applications, Hernandez *et al.* demonstrated the ability to recycle 3D printed composite polymers by using thioester-containing networks. The 3D printed thioester-based composites could be degraded to recover over 90% of the composite filler, and the mass loss experiments were in agreement with a statistical model for thiol-thioester exchange.¹⁰⁵ The capability of recycling composites makes attainable the

material properties that are necessary for very durable and high-performance applications.

A recent advancement in photopolymer research beyond vitrimers and dynamic bonds is the incorporation of degradable crosslinks and bonds such that a thermoset polymer can be depolymerized to monomer or oligomer fragments to create new resins. A method of recycling thermosets resins for VP developed by Poelma *et al.* is to use reactive pre-polymers that can be recovered after 3D printing and reused in resins for printing new objects.^{57,106,107} Poelma *et al.* developed a method of partially recycling thermoset networks by extracting regenerable reactive prepolymers into a solvent, removing the solvent, and then collecting pre-polymers for printing as renewed resin, as shown in Fig. 7a.¹⁰⁶ The collected pre-polymers could be used to form up to 90% of a new resin.

This idea was then extended to develop a resin that can form a more reversible thermoset network, consisting of polyacrylate or polymethacrylate backbones crosslinked with acrylate-blocked polyurethanes/polyureas with hindered urea bonds (HUBs) as shown in Fig. 7b.^{57,107} The 3D printed object could be comminuted and heated with a reactive blocking agent (such as *tert*-butylaminoethyl methacrylate (TBAEMA)) to achieve a homogeneous solution or suspension for resins with up to 90% recycled pre-polymer that can be used for re-printing. This very high recovery and reuse rate for a thermoset material is an enabling step forward to achieving a fully chemically circular economy for high-performance materials.

The reduction in the amounts of raw materials needed for AM reduces the environmental impact of accessing feedstocks. However, degradable thermoset photopolymers often have high viscosities that limit their use in VP methods. The vis-



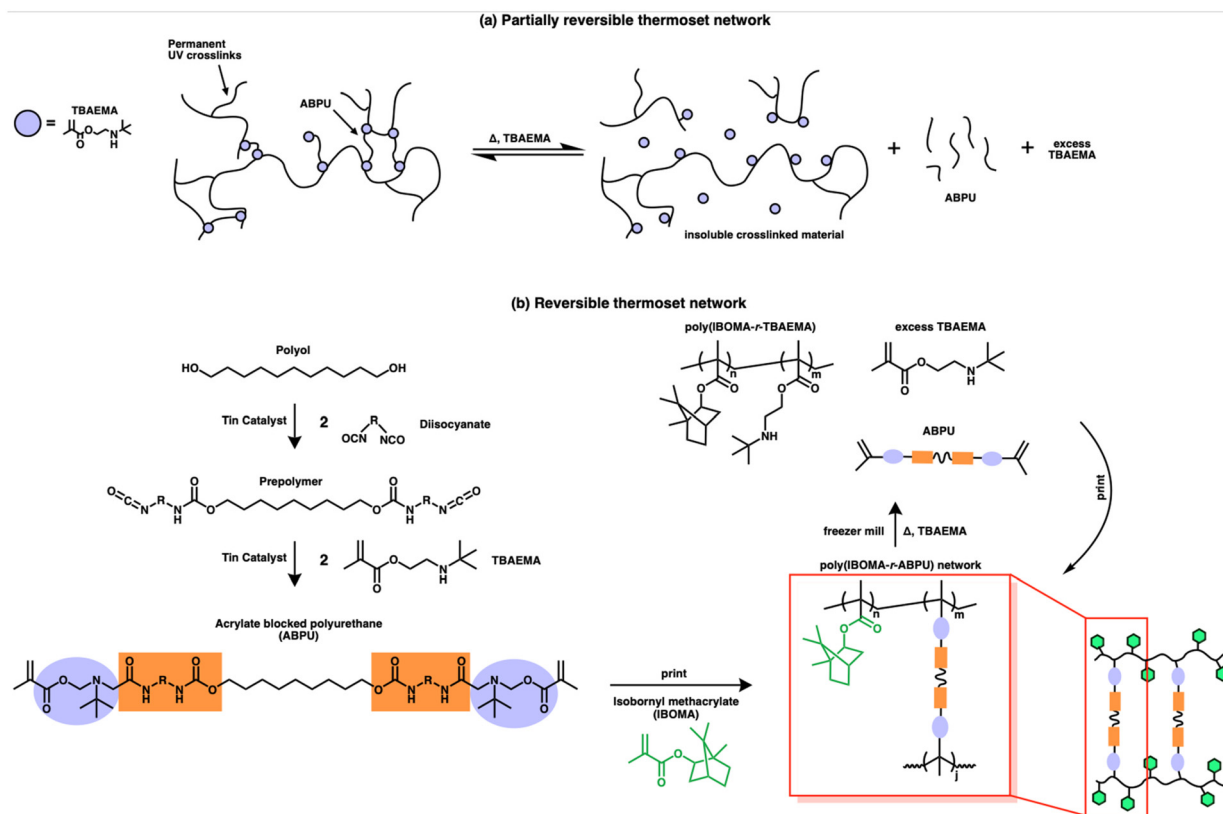


Fig. 7 Illustration of reversible thermoset acrylate networks crosslinked by HUBs. (a) Partially reversible thermoset network with insoluble cross-linked materials after pre-polymer extraction; (b) reversible thermoset network with linear chains (comprised of a monofunctional monomer such as TBAEMA) and reversible crosslinks (comprised of acrylate blocked polyurethanes). The network can be degraded and recycled by comminuting the polymer via methods such as milling, then heated with the same initial reactive blocking agent (TBAEMA) to recover linear ABPU. Reproduced from ref. 106 and 107.

cosity of the monomer resin needs to be low enough to flow during the printing process, either during the lift stage in techniques that use lift and retract mechanisms (SLA and DLP), or during continuous printing through the thin deadzone gap with CLIP. Currently, that viscosity limit is roughly 5 Pa s.¹⁰⁸ While it is possible to reduce the viscosity of the resulting resin with, *e.g.*, reactive diluents, to improve printability, these diluents can deteriorate the ultimate mechanical properties of the printed polymer part. There has been recent progress in improving the viscosity limitations of vat photopolymerizations by injecting resin to reduce the amount of time and volume of resin reflow.

In addition to diluents, solvents can help reduce viscosity of VP resins, but introduce new challenges such as post-print shrinkage and hazardous liquid wastes. To avoid solvent usage, Ding *et al.* developed a photocurable resin for AM by utilizing natural phenolic-based methacrylates and solvent-free thiol-ene click chemistry.¹⁰⁹ Likewise, Bassett *et al.* used methacrylated vanillin, a derivative easily obtained from lignin, to create a vinyl ester resin (VER) that required no solvent for synthesis and used renewable reactants.¹¹⁰ The SLA-cured VER demonstrated a high Young's modulus of 4.9 GPa and T_g of 153 °C, similar to the properties of the VER

when processed thermally. The ability to create resins with solvent-free synthesis introduces yet another pathway of sustainability upstream of physical manufacturing. This aids the field of AM to shift away from the use of petrochemical resources and hazardous solvents.

Among sustainable bio-based polymers, alginate, starches, oils, and proteins (such as silk fibroin) have been used to develop excellent biocompatible materials but lack the strength and thermomechanical stability to be used in extreme conditions.^{111–116,117} Though these bio-materials are not always suitable for high-performance applications, they do provide advancements for the challenges associated with bio-sourced AM materials such as low resolution, limited mechanical properties, and stability. For example, Shin *et al.* found that the inclusion of silk fibroin in poly(ethylene glycol)-tetraacrylate resins for DLP could enhance the resolution of printing.¹¹⁸ Additionally, Guit *et al.* synthesized a photopolymer resin for 3D printing using epoxidized soybean oil, and subsequently created a library of biobased methacrylates with tunable stiffness and toughness.¹¹⁹

Voet *et al.* has recently reviewed many other advances in biobased, sustainable photopolymers for 3D printing scopes including high performance application and beyond.¹²⁰



Opportunities for digital manufacturing

Additive manufacturing has enabled sustainable opportunities beyond materials, namely digital manufacturing. Digital manufacturing is the connection of computers and computer-aided design (CAD) models with production so that products and processes can be visualized and analyzed to improve efficiency before production begins.¹³⁰ It also allows for the quantification and tracking of products so that more in-depth life cycle analyses can be performed. This capability will allow time-stamped data collection and over-the-air software upgrades to the developing tools, which will streamline their translation to commercial partners. One could also leverage the digital fabrication approaches developed to help create a future where every part made will have a unique machine-readable QR code imprinted on it that will be tied to a unique record in the cloud. In essence, every part will be “alive”, with all of its “born-on” time-stamped data (file, resin), its “in-use” and in-field performance data (*i.e.*, an electrical connector that fails during use can be scanned by a repairman during servicing), and its death-to-recycle information to enable, perhaps for the first time, a quantitative longitudinal assessment of parts in an emerging circular economy.

For high-performance polymers that may require collection to a recycling facility to be depolymerized and recycled, a method of tracking products can give valuable insights on how much product is successfully recovered. This data can be critical for laying the foundation of new business models and practices. For example, better tracking of materials and product performances or failures can refine product recalls so that only products from the sub-section of production irregularity will need to be recalled. Additionally, this data may benefit regulatory agency confidence in additively manufactured products because it will now be possible to track adherence to product specifications and performance over the lifetime of a product.

Digital manufacturing provides the key for AM to move beyond just rapid prototyping to also provide on-demand inventory, local production of goods, flexible manufacturing plants, and access to previously impossible geometries for products. Digital manufacturing enabled by AM allows spare parts to be produced on-demand, which would eliminate the need for extra spare parts to be always held in-stock and thus also eliminate the need for their physical climate-controlled storage facilities. Additionally, the ability to access product models and manufacture a product quickly means that AM can bring more production back to local communities and avoid overseas shipping, and cut down on one of the largest air and water polluters.¹³¹ The transition to local, digital AM has contributions beyond environmental impacts: AM can bring product value back into circulation. According to UPS, over 3 percent of the world's GDP can be found in UPS delivery trucks or package cars daily.¹³² This huge economic value could be brought back into circulation simply by reducing the amounts of products that need to be transported.

Furthermore, production facilities that operate primarily on AM can switch production lines rapidly overnight as needed to

accommodate the demands of the world. For example, a local shoe manufacturer can easily maneuver from producing sneakers to producing personal protective equipment (PPE) for emergency responders simply by changing the 3D model that is uploaded to the AM equipment. This change is nearly instantaneous and does not require a complete overhaul of the manufacturing plant, paving way for flexible manufacturing plants.

Eco-efficiency in AM

"Eco-efficiency"¹³³ is a term used to describe efficient ecological and economical resource management, both of which can be achieved by improving materials sourcing, minimizing toxic material components, and enhancing recyclability. Often times, improving materials processing (and reprocessing) will allow for greater costs savings for companies (especially in high-cost applications such as high-performance products) in the form of reduced resource input, reduced liabilities and legal expenses, and improved relationships with all parties involved. Even if the sourcing and development of sustainable materials present a costly upfront investment, the amount of economic and ecological resources saved in the long-run will be beneficial for both public and private entities. Some examples of this include the elimination of toxic tin catalysts in polyurethane-based systems and the elimination of bisphenol-A (an endocrine disruptor) in epoxy systems. The change from the *status quo* to a safer, sustainable future requires a radical introduction, followed by the incremental transition to continue the step-by-step process of long-term improvement. This idea of eliminating toxic and hazardous substance usage proactively rather than cleaning up pollution reactively has been embodied in 3M's "Pollution Prevention Pays (3P)" program.¹³⁴ The amount of money, time, and health saved for both public and private entities in preventing further ecological damage is often worth more than the immediate gains of continuing to use hazardous substances.

Eco-efficiency and pollution prevention can serve as powerful driving forces for AM as a developing field for large-scale manufacturing. The overarching theme of achieving sustainable materials and processes pushes research and development to have foresight in finding creative solutions to problems before they happen. The linkage of business/research excellence and environmental excellence elevates the notion that a sustainable future does not come at the cost of developing fields, but rather is an investment in the field. For example, in 3M's 3P program, the proactive investment in re-engineering processes and approaches to materials research and development resulted in over 2.6 billion pounds of pollutants prevented and over 1 billion dollars saved over the course of 30 years.¹³⁵ The AM field can learn from 3M's success and use eco-efficiency to drive development in early stages, rather than having to reconsider and re-engineer prior standing processes. An eco-efficient mindset can provide the opportunities for massive advantages, both ecologically and economically.

Conclusions

Additive manufacturing is in a unique position to disrupt traditional methods of manufacturing. Scientists and engineers are equipped with the wisdom of foresight to prevent a decades-long amount of waste production caused by polymers from AM. While AM has the potential to reduce the amount of material waste and CO₂ emissions compared to traditional manufacturing, it does not entirely eliminate waste production. In all forms of AM (material extrusion, vat photopolymerization, powder bed fusion, *etc.*), high-performance polymers can be engineered to be more sustainable and still meet material properties demands. Polymer sustainability may come from how raw materials are sourced or how final materials are degraded and recycled. Degradability for recycling comes in two forms: passive degradation and triggered degradation. For high-performance use cases, triggered degradation shows the most promise in offering high toughness, strength, strain-at-failure, or thermal and chemical resistance for polymers that will have specific environmental demands. A high-performance polymer that is fully recyclable under very specific but attainable conditions can both promote waste collection and reduce the amount of raw material needed for production. Chemical degradation of thermoset polymers for recycling may be the most promising pathway for high-performance materials because it requires a reduced energy input as compared to thermal degradation. However, further research is required to obtain "green" solvents for chemical degradation so that all elements of the recycling process will be sustainable. The progress and future of polymer research lies in both new polymerization methods and in crucial depolymerization methods. Successful achievement of various depolymerization pathways for high-performance polymers will pave the path for a more sustainable world with both chemical and economic circularity.

Contributions

Gloria Chyr: Conceptualization, writing – original draft, writing – review & editing. Joseph M. DeSimone: Conceptualization, writing – original draft, writing – review & editing.

Conflicts of interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Joseph M. DeSimone reports financial support to our research group was provided by Wellcome Leap Fund and startup funds provided by Stanford University School of Medicine and the School of Engineering. Gloria Chyr reports financial support was provided by the Stanford University Precourt Institute of Energy. Joseph M. DeSimone reports a relationship with Carbon that includes cofounder equity.



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