Sustainable Materials and Chemical Processes for Additive Manufacturing

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ABSTRACT: Additive manufacturing (AM) is energizing the fields of chemistry and materials science to develop new inks for new applications within fields such as aerospace, robotics, and healthcare. AM enables the fabrication of innumerable 3D geometries that cannot be easily produced by other means. In spite of the great promise of AM as an advanced form of future manufacturing, there are still fundamental challenges with respect to sustainability that need to be addressed. Some of the material needs for AM include sustainable sources of printing inks, resins, and filaments, as well as pathways for polymer recycling, upcycling, and chemical circularity. Furthermore, the combination of bio-sourced and biodegradable polymers with additive manufacturing could enable the fabrication of objects that can be recycled back into feedstock or degraded into non-toxic products after they have served their function. Herein, we review the recent literature on the design and chemistry of the polymers to that enable sustainability within the field of AM, with a particular focus on biodegradable and bio-sourced polymers. We also discuss some of the sustainability-related applications that have emerged as a result of AM technologies.

1. INTRODUCTION

Additive manufacturing (AM) is an advanced form of manufacturing that holds great promise for the customized, distributed, and on-demand production of parts. Three-dimensional (3D) models are produced in the virtual world, and then a 3D printer deposits a material (via layer-by-layer or continuous deposition) according to the 3D model provided. AM, also known as 3D printing or rapid prototyping, emerged several decades ago as a method to generate previously unattainable geometric structures and functions.[1, 2] This manufacturing process is also useful across many industries, such as aerospace, where it is used to produce a small number of highly complex aircraft components that can reduce the fuel consumption, or in the medical sector where highly personalized products are required.[3]

AM is a multi-faceted technology that requires the convergence of hardware, software/modeling, and materials for its success. While the re-emergence of the field over the last decade has largely been driven by advances in the hardware and software/modeling, there is a growing interest among polymer chemists and materials scientists to design materials specifically for AM processes.[4, 5] Polymeric materials, including thermoplastics, thermosets, elastomers, and composites represent a growing body of suitable materials for AM. However, with increasing concerns of sustainability and the growing volume of plastic waste worldwide, it is imperative to understand how AM can affect global visions of sustainability.[6-9]

In order for AM to reach its full potential, sustainability within the AM ecosystem (hardware, software/modeling, and materials) must be addressed. Some of the material needs for AM include sustainable sources of printing inks, resins, and filaments, as well as pathways for polymer recycling, upcycling, and chemical circularity. **Figure 1** shows a representative life cycle of AM products, which draws its parallels from the new plastics economy as proposed by the
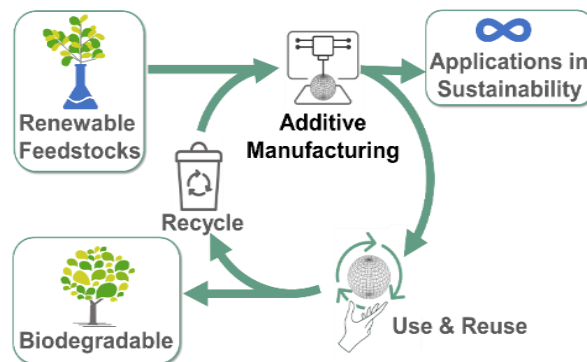

Figure 1. Additive manufacturing in a sustainable plastics economy.

MacArthur Foundation.[10] Substitution of petrochemical feedstocks by renewable ones for AM would reduce the global reliance on fossil fuels that can only be regenerated on geologic

timescales. AM could then be utilized as a production technology whose products potentially undergo multiple cycles of use and re-use. At the end of its useful lifetime, the product could either biodegrade or be recycled back into the material feedstock for a closed AM loop. Another benefit of AM is its ability to afford materials and object geometries that could not be previously achieved, which can open opportunities for new applications that promote sustainability.

With this in mind, there are four contexts by which sustainability in AM can be addressed: (i) AM hardware and processes that can minimize the production of waste or unwanted byproducts, (ii) renewable material feedstocks for AM, (iii) end-of-use options for 3D printed products that include the next generation of materials to re-use and recycle, and (iv) applications in sustainability that emerge as a result of new AM capabilities. This review will address each of these points, with a particular emphasis on the chemical processes and polymeric materials that have been developed recently in the field.

2. ADDITIVE MANUFACTURING TECHNIQUES

2.1. Material Extrusion.
Material extrusion technologies extrude a material in a layer-by-layer manner from a nozzle that follows a predetermined path over a build plate (**Figure 2a**). This is an attractive technology in AM due to the simplicity of operation, as well as the availability of low-cost printers that offer relatively good resolution. This platform accommodates many different printable materials through manipulation of printing temperatures or via shear-thinning behavior of the material. It also offers the possibility of producing a multi-material product with different inks, including cell-containing inks for bioprinting. Many biologically sourced monomers and polymers either already offer advantageous behaviors for extrusion printing, or such behaviors can be introduced through simple synthetic schemes to change the viscoelastic character of the ink.[11] Material extrusion methods require careful control over the viscosity of the material during and after printing to successfully extrude the material through a nozzle and maintain the patterned 3D form after deposition.[5]

Fused Deposition Modeling (FDM) (also referred to as Fused Filament Fabrication or FFF) is the most widely available 3D printing technology. FDM builds parts using a thermoplastic material in a filament form. The filament is pushed through a heated nozzle where it is melted. The printer continuously moves the nozzle to deposit melted material at precise locations following a pre-determined path. In this case, the waste plastic filament from misprints and undesired outputs can be minimal and can be reclaimed and reused. The plastic waste is first ground into granules and then fed into a filament extruder. Polymers, such as poly(lactide) (PLA) can be recycled in this manner with minimal loss in quality.[12]

2.2 Vat Photopolymerization.
Vat photopolymerization utilizes patterned light to initiate the chemical cross-linking of a resin. Typically, UV light is used to activate a catalyst or reactive species for the radical polymerization of acrylates and methacrylates, or cationic ring opening polymerization of epoxides.[13] Vat photopolymerization is particularly attractive for its resolution and the speed at which objects can be printed.

There are different types of vat photopolymerization AM that have been developed.[14] Laser-scanning stereolithographic apparatus (SLA) printing uses a build platform submerged in a resin tank filled with liquid photopolymer resin. A focused laser irradiates the resin above through a transparent surface in a patternwise manner (**Figure 2b**). Even though each layer is patterned individually, the printed resin also forms covalent bonds between layers resulting in highly isotropic and smooth parts. The two key parameters for a successful SLA printing are the viscosity of the resin and the curing speed upon light exposure. Thus, each layer of an object must cure rapidly (on the order of seconds) for good mechanical integrity while printing, and the resin viscosity should be minimized to allow resin flow around the build platform and form new layers. While the viscosity requirement seems to vary with the resin composition, values between 0.2 and 10 Pa·s have been reported in the literature.[14-16]

Similarly, digital light processing (DLP) uses light to initiate cross-linking of a photopolymerizable resin. In this approach, patterned light is projected onto the resin, polymerizing an entire layer at a time (**Figure 2c**). Continuous liquid interface production (CLIP) uses an oxygen permeable window to create a persistent liquid interface between the polymerizing part and the transparent window, and the result is a much faster method of 3D printing (~10^2 mm/h). Consequently, light projection methods can achieve faster print times compared to SLA, which can reduce the overall energy consumption and environmental impact of the AM process.[17]

3. RENEWABLE MATERIAL FEEDSTOCKS FOR ADDITIVE MANUFACTURING

The feedstock used in an AM process has an important role in the sustainability of the process itself. Bio-based small molecules and polymers derived from plants and/or microorganisms, offer a viable source of precursors that can be modified and formulated into resins and inks for sustainable AM. [18, 19] These alternative materials will offer AM users environmentally friendly manufacturing options.

A central challenge when developing resins and inks for 3D printing is the spatially controlled cross-linking of the material during the AM process. The speed of printing (and rate of parts production) is dependent upon the rate at which physical cross-links (non-covalent interactions such as van der Waals
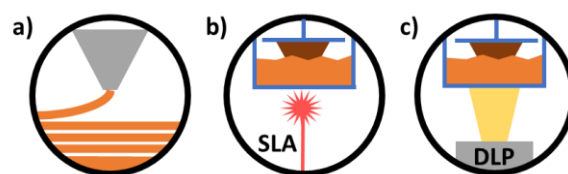

Figure 2. AM techniques considered in this review: (a) material extrusion printing, (b) stereolithography (SLA), and (c) digital light processing (DLP).

interactions, hydrogen bonding, ionic interactions, and polymer entanglement) or chemical cross-links (typically photo-initiated radical polymerization) can be formed. These cross-links also determine the mechanical properties of the printed object, which is of great concern when used in load-bearing applications.

In general, naturally occurring biopolymers (DNA, proteins, and polysaccharides) possess a high molecular weight, which translates into inherently viscous polymer solutions. As a result, the processing and printing of these biopolymers in AM processes can be a challenge. Some of these biopolymers also require chemical modification to undergo light-initiated cross-linking. Alternatively, synthetic polymers can offer greater control over polymer composition, molecular weight, and the polymer architecture to accommodate the requirements of the printing technique.[20] Examples of biopolymers and synthetic polymers for AM are summarized in **Figure 3**.

These biopolymers are typically biodegradable, biocompatible, and have a life cycle that is the model form of sustainability. In their native roles, these biopolymers serve as signaling elements, infrastructure for energy storage and consumption, information storage, and structural frameworks that provide living systems with their 3D form. The latter example has attracted significant interest in AM as these biopolymers meet the mechanical requirements to afford 3D objects that can maintain their shape fidelity. Thus, as nature has employed its structural biopolymers, such as cellulose, to create the stiff cell walls found in plants and trees, chemists and materials scientists
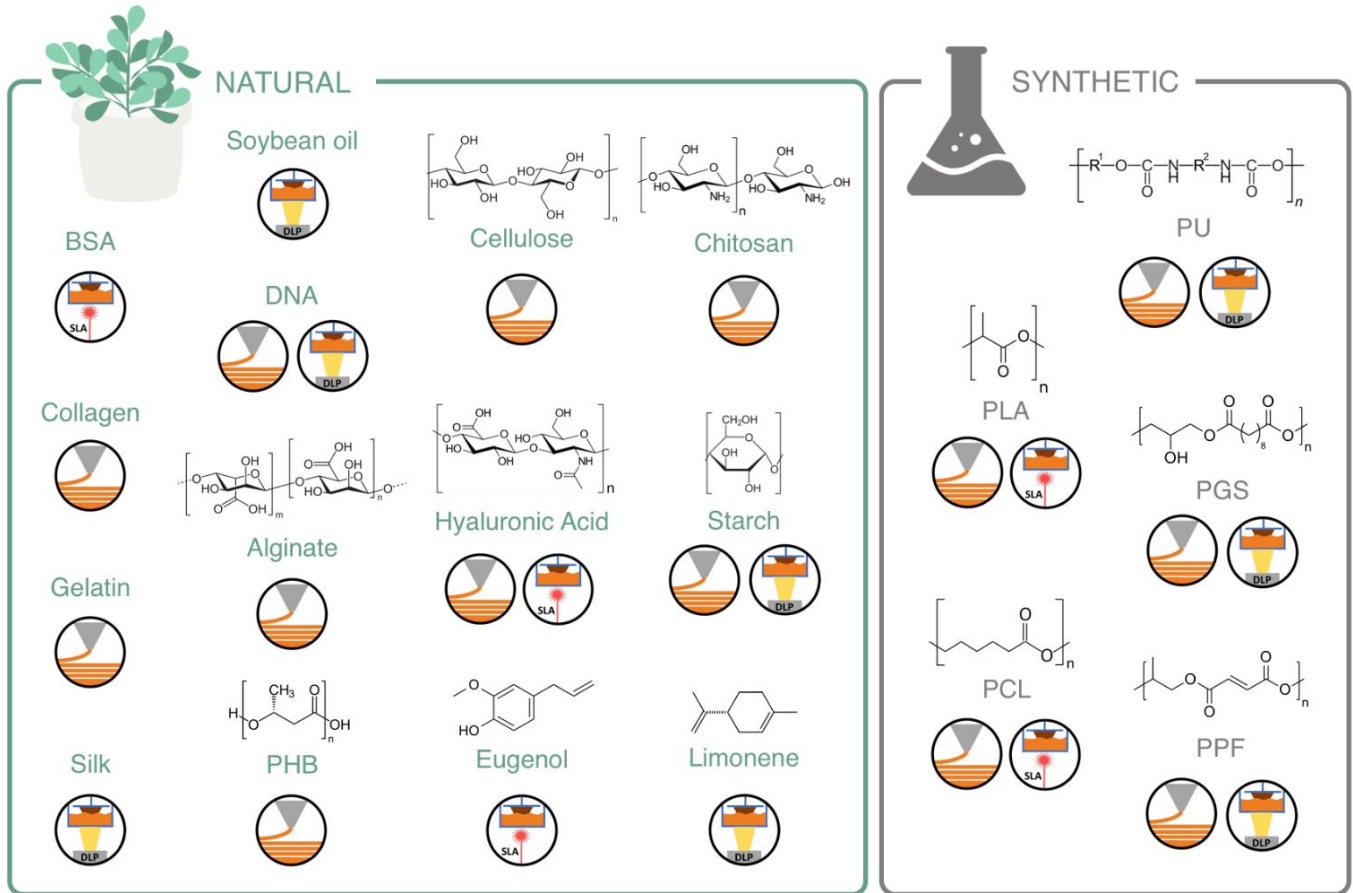

Figure 3. Some renewable feedstocks developed for sustainable AM. Natural: Bovine Serum Albumin (BSA),[15] collagen,[21] gelatin,[22] silk,[23] soybean oil,[24] DNA,[25, 26] alginate,[27] PHB,[28] cellulose,[29] hyaluronic acid,[30, 31] eugenol,[32] chitosan,[33] starch,[34, 35] and limonene.[36] Synthetic: polyurethane (PU),[37, 38] polylactic acid (PLA),[39, 40] poly(glycerol sebacate) (PGS),[41, 42] polycaprolactone (PCL),[43, 44] and poly(propylene fumarate) (PPF).[16, 45]

3.1. Renewable and Degradable Feedstocks for AM.

3.1.1. Polysaccharides, Proteins, and DNA. Naturally occurring biopolymers (polysaccharides, proteins, and DNA) are a source of renewable feedstock materials for AM that can be obtained on large scales from microbes, plants, and other organisms.

have sought to co-opt these biopolymers for use with AM tools to pattern 3D objects.

Cellulose is the most abundant organic polymer on the planet, and is an important structural polysaccharide found in the primary cell wall of plants. Due to their outstanding mechanical properties, cellulose fibers have been used to strengthen the matrices of biomaterials used in material extrusion 3D printing.[46] Likewise, nanocellulose (in the form of cellulose nanocrystals (CNC) or cellulose nanofibrils (CNF) has also been used as a reinforcing agent in inks designed for AM.[47, 48] The high orientation capacity of the nanocellulose, allows tailored responses to the applied mechanical load, inspired by the design principles found in wood.[49] In addition, nanocellulose can exhibit the shear-thinning and thixotropic behaviors required for an extrudable material: as the piston of the extruder applies stress, the ink flows out from the nozzle but recovers its gel state once deposited, thus preventing its flow once it is deposited on the building platform. Siqueira et al.[47] created viscoelastic CNC-based inks for direct writing by just dispersing CNCs extracted from wood pulp in water. Correspondingly, Magdassi et al.[29] 3D printed objects composed of 100% wood-based materials, using a low value byproduct of the wood industry known as wood flour from grinded eucalyptus, pine or maple, in combination with a binder composed of CNCs that gives the ink shear-thinning properties, and xyloglucan hemicellulose. Both materials can be obtained from industrial side streams, and the modulus and strength of the printed woods were within the range of natural woods. Additionally, Wallace et al.[50] printed scaffolds made of CNFs with good fidelity by adding a very low concentration of the UV cross-linkable gelatin methacrylate (Gel-MA). In this study, CNFs were produced by the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation to successfully disintegrate cellulose fibers, and avoid needle clogging during material extrusion.

Crustacean shells can be used to harvest chitin, which can be deacetylated to form chitosan. While cellulose is comprised entirely of β-1→4 linked glucopyranosides, chitosan is comprised of structurally similar β-1→4 linked 2-amino-glucopyranosides. Chitosan hydrogels have been successfully 3D printed using extrusion-based processes for engineering bone tissue.[51] Inorganic molecules have also been mixed with chitosan for the purpose of improving its bioactivity to resemble bone. Muller et al.[52] integrated the natural polymer polyphosphate into a N,O-carboxymethyl chitosan matrix using calcium (Ca^{2+}) bridges.

Starch is a polysaccharide blend produced by plants for energy storage. The mixture is comprised of amylose (D-glucopyranose units joined by the α-1→4 glycosidic linkages) and the branched amylopectin (D-glucopyranose units joined by the α-1→4 and occasional α-1→6 glycosidic linkages). Similar to cellulose, the structure of starch also has abundant hydroxyl groups, offering the possibility of chemical modification to produce starch-based polymers for 3D printing. Maniglia et al.[53] used ozone oxidation to modify cassava starch for extrusion printing. Ozonation was used to cleave the glycosidic bonds of both amylose and amylopectin molecules, and also to replace hydroxyl groups by carbonyl and carboxyl groups. The high inherent viscosity of this natural polymer was reduced due to the depolymerization of both amylose and amylopectin, yet the additional interactions between the oxidized molecules improved the printability of the starch-based inks.

Burdick and co-workers have reported an alternative strategy for physically cross-linking polysaccharides using the host-guest interactions that occur between cyclodextrin (CD) and adamantane (Ad). Hyaluronic acid (HA) was functionalized with either CD or Ad and the two polysaccharides were blended to afford a physically cross-linked hydrogel (**Figure 4**).[30] These shear-thinning hydrogels served as excellent inks for material extrusion printing. The Cd-Ad pairs disassociated during the extrusion process, and then self-healed after deposition onto a substrate when shear was removed. Alternatively, these modified biopolymers were also developed as jammed microgels that also demonstrated shear-thinning behaviors.[54]

Alginate is a polysaccharide isolated from the cell walls of brown marine algae (seaweed). The viscosity of alginate is tunable with the changes to concentration and degree of oxidation.[55] The rapid ionic cross-linking of sodium alginate in the presence of calcium ions has been utilized for material extrusion printing. Its ease of use without additional modification has led to the widespread use of calcium alginate gels in bio-printing applications.[27, 56-59]
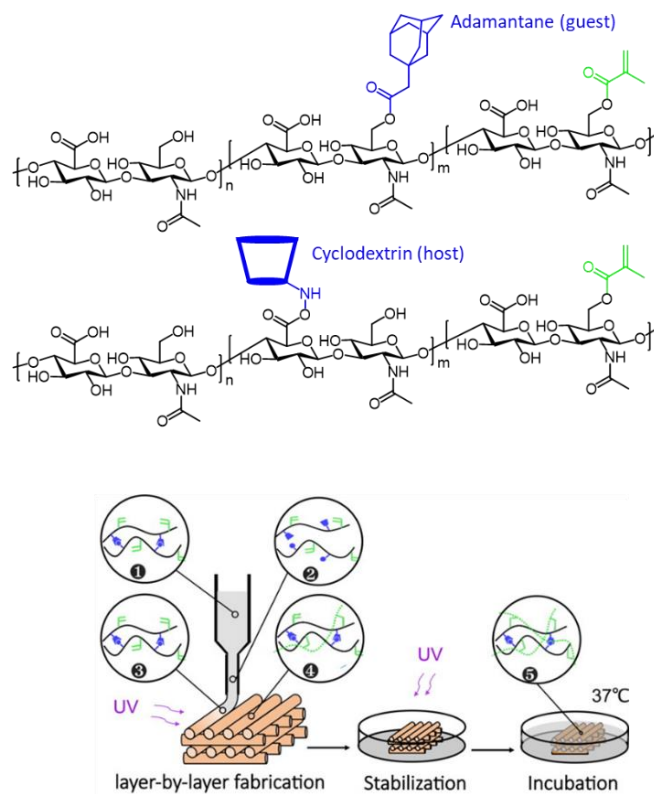

Figure 4. General printing scheme for extrusion printing layer-by layer of a chemically modified hyaluronic acid.[30] Reprinted with permission from ref. 30. Copyright 2016 American Chemical Society.

Aside from polysaccharides, proteins represent another versatile class of biopolymers that have been adopted for AM. Collagen is a structural protein that is the primary component of connective tissue. This protein is well suited for bio-printing

applications due to its ability to promote cell adhesion.[60, 61] Collagen is comprised of elongated fibrils of a triple helix of polypeptide chains, which makes it difficult to process in AM. Alternatively, gelatin is derived from hydrolyzed collagen and has improved processability as a consequence of its lower molecular weight. Gelatin methacrylate (Gel-MA) has seen growing interest in AM for tissue engineering and regenerative medicine.[20, 22, 62-64]

All of the biopolymer examples discussed to this point have been printed via material extrusion, which is the predominant AM technique for 3D printing biopolymers. There are relatively fewer examples of vat photopolymerization approaches for printing biopolymers because the viscosity requirement for resins (up to 10 Pa·s maximum has been suggested) is difficult to achieve with polymers that intrinsically have a high viscosity.[14] One strategy has been to create composites with cellulose nanocrystals, but the biopolymer component is relatively small compared to the matrix material.[65, 66] This is particularly true when structural proteins are employed in these types of processes, as these proteins are designed to associate into larger aggregates or to form fibrous assemblies. However, there are a few recent examples of structural proteins in a vat photopolymerization processes. Silk fibroin is a material that can be harvested from silkworms and chemically processed to afford a water-soluble (and processable) form of the protein.[67] This amorphous form has random coil conformations that facilitate its solubility in water, and has been utilized in resins for vat photopolymerization.[68] Methacrylated silk fibroin was developed as a primary resin component, producing printed parts with excellent structural stability and biocompatibility.[23]

Globular proteins have also been shown to be suitable for vat photopolymerization. Methacrylated bovine serum albumin (MABSA) was shown to be highly soluble in water (up to 40 wt% w/v) due to its compact globular shape. The protein was formulated into low viscosity resins for vat photopolymerization using a commercial SLA printer. The 3D printed objects were subjected to a post-print thermal cure, which denatured the proteins and afforded bioplastic with mechanical properties comparable to poly(lactic acid) (PLA).[15] This demonstration opens opportunities for implementing recombinant proteins as sustainable sources of resins for vat photopolymerization.

3.1.2. Synthetic (Bio)degradable Polymers for AM. Aliphatic polyesters are a leading alternative to polymers from petrochemical sources because of their range of mechanical properties (as thermoplastics and elastomers) and their chemical and enzymatic degradability.[69] For example, different forms of poly(lactic acid) (PLA) have been synthesized, such as semicrystalline poly-L-lactide (PLLA), or amorphous poly(D,L-lactide) (PDLLA), which can affect their mechanical properties and rates of degradation. The copolymer of PLA and PGA (polyglycolic acid), i.e. PLGA, is commonly used in AM processes to increase the degradation rate of PLA.[70] The rate of degradation of this biodegradable polymer is proportional to the strength of the acidity or alkalinity of the surrounding media. Gassensmith et al.[39] benefited from this degradation behavior to overcome the resolution limitation of FDM. They constructed PLA microneedles with tip sizes as small as 1 μm, via chemical etching of 3D printed needles in an alkaline solution. Poly(L-lactide-co-ε-caprolactone) (PLC) copolymer was also examined for FDM printing which is softer and more elastic than PLA, but degrades faster than poly(ε-caprolactone)

(PCL).[43] PLA can also be combined with other dynamic covalent processes, such as thermally reversible Diels-Alder reactions, to obtain tougher 3D printed objects due to the creation of new covalent bonds between filament layers.[71]

Polyhydroxyalkanoates (PHAs) are a class of polyesters that can be naturally produced by bacteria with tunable mechanical properties.[72, 73] Among them poly(3-hydroxybutyrate) (PHB) is a natural thermoplastic polyester produced by microorganisms. While PHB possesses many great properties, it is a very brittle substance on its own. However, many studies have investigated various methods to improve its mechanical strength for bone tissue engineering applications. One example involves the formation of composite scaffolds consisting of PHB and hydroxyapatite nanoparticles.[74] Interestingly, it was observed that in the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) microbial polymer, the increase of 3HV content increased the crystallinity and hydrophobicity of the PHBV.[75, 76] A PHB composite containing biorefinery lignin demonstrated a shear thinning profile which enhanced layer adhesion for extrusion 3D printing. Although not discussed in detail here, lignin has promise as a feedstock for AM.[28, 77, 78]

PCL is a well-studied, biocompatible crystalline polymer with a low melting temperature. While PCL in the past was mainly produced from non-natural sources, in the last decades intensive research has been devoted to its production from biomass. Due to its compatibility with many drugs and slow degradation kinetics, PCL is especially suitable for long-term drug-delivery systems.[79] The hydrolysis rate and the mechanical and viscosity properties can be tailored by copolymerizing with other polymers or by incorporating more labile bonds into the PCL backbone. PCL has been widely used as a feedstock material for extrusion-based AM, owing to its excellent processing ability. In fact, high molecular weight PCL lacks printability by methods other than extrusion AM. Hart et al.[80] discussed the modification of PCL diols with a multitude of hydrogen bonding and π-stacking moieties through 2,4-toluene diisocyanate end-capping reactions. The inclusion of these groups at relatively low concentrations led to the formation of supramolecular networks that exhibited shear thinning behavior and successful inkjet printing (**Figure 5a**). To create PCL amenable to other AM techniques, chemical modification is necessary. Elomaa et al.[44] produced three-armed PCL oligomers of various molecular weights, which were end-functionalized with methacrylic anhydride and photocrosslinked to obtain a porous scaffold with a high resolution by SLA (**Figure 5b**). Since macromers were heated above the melting temperature (60 °C) to obtain the suitable viscosity, no solvent was needed. Due this solvent-free SLA approach, no material shrinkage was observed after extraction and drying of the printed scaffolds.

Highly biocompatible hydrogels that degrade in the body for vat photopolymerization can be prepared by tuning the hydrophilicity of PLA with polyethylene glycol (PEG). Seck et al.[40] synthesized PDLLA-PEG-PDLLA-based resins for SLA that allows the generation of designed three-dimensional cross-linked structures. The hydroxyl end groups of the synthesized PDLLA-PEG-PDLLA oligomers were reacted with methacrylic anhydride to obtain MA-DLLA-PEG-DLLA-MA photo-cross-linkable macromers (**Figure 5d**).

Polypropylene fumarates (PPF) are another promising class of biocompatible and biodegradable polymeric biomaterials. PPF degrades to propylene glycol and fumaric acid which are biocompatible subunits. PPF is normally processed by vat polymerization method, since it possesses unsaturated sites in its backbone desirable for photopolymerization, and it is usually combined with diethyl fumarate (DEF) to reduce the viscosity of the ink.[70] Even when it is printed by FDM a UV curing head is incorporated to the printing systems, and a photosensitive cross-linker is added to the formulation.[45] The materials made of PPF are generally post-cured to obtain a higher cross-linking ratio, and improve the mechanical integrity. Melchiorri et al.[81] printed PPF tubes to address challenges caused by a congenital heart disease by using 3D CAD models made from medical imaging technologies such as MRI or CT, and Lee et al.[82] used micro-stereolithography to print tridimensional microstructures
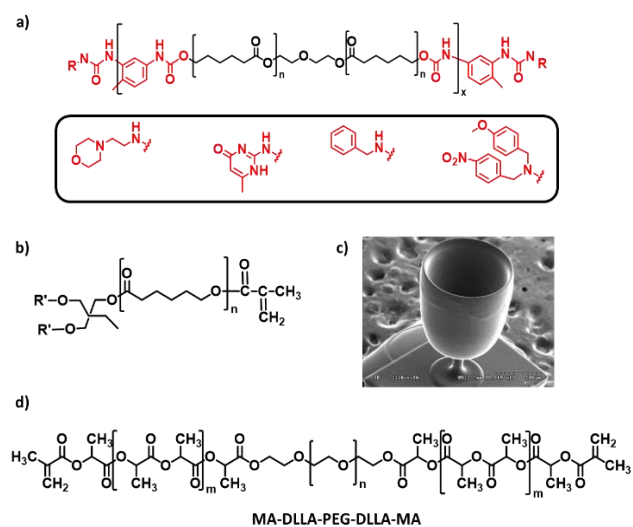
Figures 5. Biodegradable polyesters: (a) Addition of hydrogen bonding moieties to a biodegradable poly(caprolactone)-diol to obtain a tunable ink.[80] Reprinted with permission from ref. 80. Copyright 2016 American Chemical Society. (b) Synthesis of PCL macromer by methacrylation of hydroxyl-terminated PCL oligomer.[44] Reprinted with permission from ref. 44. Copyright 2011 Elsevier. (c) Printed microstructures using microstereolithography comprised of PPF.[82] (d) Synthesis of PDLLA-PEG-PDLLA oligomers and subsequent functionalization with methacrylic anhydride (MAAH) to give MA-PDLLA-PEG-PDLLA-MA macromers.[40] Reprinted with permission from ref. 40. Copyright 2010 Elsevier.

(**Figure 5c**).[83] Becker et al.[16] 3D printed scaffolds with shape recovery following compression, based on PPF star polymers. It should be noted that they used magnesium ethoxide catalyst to avoid the toxicity of cobalt,[84] for the synthesis of star-shaped poly(propylene maleate) (PPM) subsequently converted to PPF upon isomerization by using the sugar-based alcohol meso-erythritol as an initiator.[85]

Poly(glycerol sebacate) (PGS) is a widely used biodegradable elastomer synthesized via the thermal condensation of glycerol and sebacic acid. Curing of PGS usually requires high temperature and high vacuum. Lei et al.[41] 3D printed a PGS/salt composite in an extrusion-based printer, and then thermally cured it under vacuum to obtain a stable cross-linked 3D structure. The salt particles were subsequently removed by dissolution in water to form interconnected micropores throughout the construct. In addition to its excellent biocompatibility and biodegradability, one of the most important advantages of cured PGS is its robust elasticity due to its chemically stable cross-linked structure. Langer et al.[86] 3D printed poly(glycerol sebacate) acrylate (PGSA), a photocurable degradable elastomer compatible with light-based 3D printing. By tailoring the PGS elastomer to the viscoelastic properties of native soft tissues, porous PGS patches were printed to treat myocardial infarction.[41]

Apart from polyesters, polyurethanes have also been investigated as biodegradable polymers for sustainable AM. One of the key features of most polyurethanes is their ability to phase-separate into soft and hard segments. This phase separation, which is driven by hydrogen bonded physical cross-links that make up the hard segment, could potentially facilitate the printing process.[87] Unfortunately, polyurethane synthesis usually necessitates the use of isocyanate monomers and organic solvents, all of which have toxicity issues and are environmental pollutants.[88] As an alternative to the traditional solvent-borne PU in response to the environmental concerns, waterborne or water-based polyurethane (PU) have been developed. Waterborne biodegradable PUs can have a range of tunable mechanical and degradation properties, and can even undergo gelation by varying the composition of soft segments in polymer chains.[89] The biodegradable and biocompatible elastomeric PU is used in many biomedical applications, such as scaffolding material for repairing neural and venous defects.[90] Hsie et al.[91] combined a water-based biodegradable PU nanoparticle dispersion with a gelatin solution to prepare a PU-gelatin bioink that could be loaded with cells to print tridimensional constructs with a 3D bioprinter. Additionally, Hsu et al.[37] developed a water dispersion of PU biodegradable nanoparticles by incorporating ionic hydrophilic groups onto the hydrophobic backbones to form an emulsion without the use of toxic organic solvents. The soft segment was based on PCL diol and polyethylene butylene adipate (PEBA) diol. They designed the soft-segment compositions with the intention of generating mechanical properties and degradation rates appropriate for cartilage tissue engineering. The resulting

extrusion printed scaffolds can be seen in **Figure 6a**. In turn, Huang and coworkers[38] synthesized a type of polyurethane acrylate containing disulfide bonds which mixed with the reactive diluent hydroxyethyl acrylate and photo-initiators resulted in a photopolymer resin for DLP with self-healing properties (**Figure 6b**). In spite of the undeniable benefits of polyurethanes in comparison to other polymer families, the starting common isocyanates are synthesized using phosgene, and taking into account the need to guarantee the users' safety, it is important to find alternative and greener routes to PUs, involving non-toxic reagents. In the last decade, alternative and environmentally friendly approaches have been developed to synthesize non-isocyanate biobased polyurethanes (NIPUs) but their use in AM processes is still rare.[93, 94]

As an example of the advantageous combination natural and synthetic sustainable polymers for AM, an L-alanine-derived depsipeptide was used to synthesize a biodegradable, photocrosslinkable poly(ethylene glycol-co-depsipeptide) (PEG-co-PDP) macromer for the SLA-based fabrication of hydrogels. The photocrosslinkable macromer combined both naturally derived and synthetic building blocks. The depsipeptide units introduced biodegradable bonds to the PEG backbone, and by adjusting the light exposure time in the SLA, they could be controlled the swelling capacity, degradation rate, and mechanical stiffness of the resulting hydrogels without the need for changing the intrinsic composition of hydrogel solution (**Figure 7**).[95]

3.1.3. Small Molecules as Renewable Resins. While
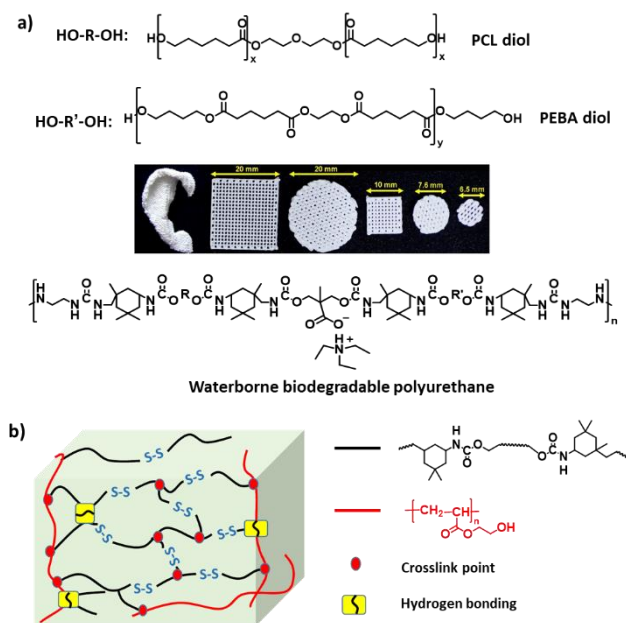

Figure 6. (a) Synthesis of the biodegradable PU nanoparticles and 3D printed scaffolds with various shapes and dimensions.[92] Reprinted with permission from ref. 92. Copyright 2016 Elsevier. (b) Synthesis of a self-healing polyurethane elastomer for DLP 3D printing.[38] Reprinted with permission from ref. 38. Copyright 2019 American Chemical Society.

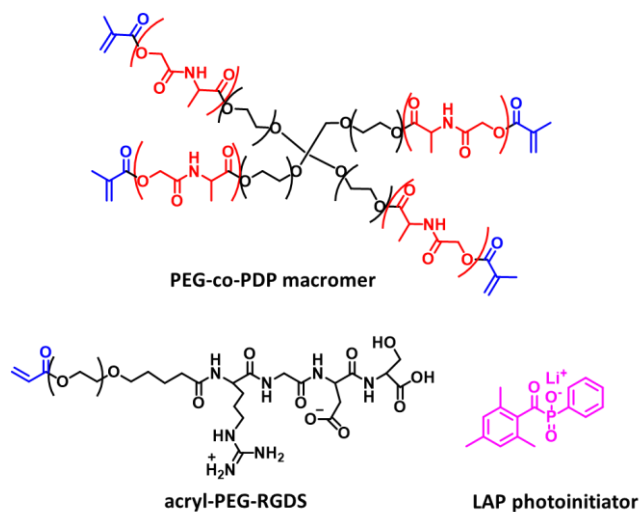biologically derived molecules for vat photopolymerization

Figure 7. Photocrosslinkable poly(ethylene glycol-co-depsipeptide) (PEG-co-PDP) macromer for the SLA-based fabrication hydrogels.[95] Reprinted with permission from ref. 95. Copyright 2015 Royal Society of Chemistry.

have not been quite as widely explored as their extrusion counterparts to date, it is an expanding field with promising resin candidates emerging. Voet et al.[24] formulated a number of bioderived resins including isobornyl acrylate, 1,10-decanediol diacrylate, pentaerythritol tetraacrylate, and multifunctional acrylate oligomer. They also developed biobased photopolymer resins based on modified soybean oil methacrylates from commercial epoxidized soybean oil with different stiffness and toughness values depending on the number of functional groups per oligomer (**Figure 8a**).[96]

One such class of resins are based on terpenes, molecules that can be harvested from many plants and even some insects. Weems et al.[36] showed that through the use of various terpene materials and a four-armed thiol linker, 3D mesh structures could be printed through the use of thiol-ene click chemistry. By using these materials in the presence of a radical initiator, the photo-cross-linked materials exhibited mechanical properties that ranged from brittle elastomers to engineering grade thermosets. These properties could be easily tailored through simply altering the terpene monomer or prepolymer content of the resin.

Ding et al.[32] utilized natural phenols and thiol-ene click chemistry to develop a resin suitable for SLA printing, aiding in the shift away from dependence on petroleum-derived polymers. They created photoreactive resins from renewable biomass to substitute acrylates combining a structural diacrylate synthesized by a facile dimerization of eugenol (4-allyl-2-methoxyphenol) with a dithiol through the radical thiol–ene click reaction, guaiacol (2-methoxyphenol) methacrylate as diluent, and the photocrosslinker vanillyl alcohol (4-(hydroxymethyl)-2-methoxyphenol) dimethacrylate with a radical photoinitiator (**Figure 8b**). More recently, Basset et al.[97] created a resin suitable for SLA by combining methacrylated vanillin and glycerol dimethacrylate as a cross-linking agent in a solvent-free manner. These interesting inks based on naturally occurring biomolecules are promising alternatives that can
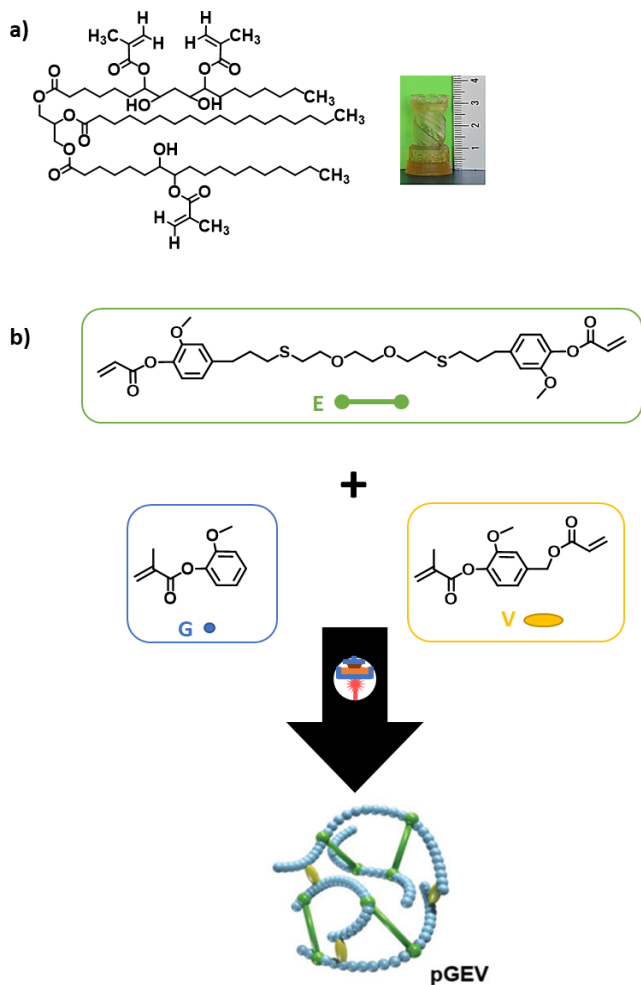
Figure 8. Additively manufactured constructs created through vat-photopolymerization of naturally derived polymeric resins: (a) Soybean oil acrylate.[24] Reprinted with permission from ref. 24. Copyright 2020 American Chemical Society. (b) Acrylates based on natural phenolics for SLA: E = 3,6-Dioxa-1,8-octanedithiol eugenol, G = guaiacol methacrylate, V = vanillyl alcohol methacrylate.[32] Reprinted with permission from ref. 32. Copyright 2019 Royal Society of Chemistry.

circumvent many of the drawbacks of traditional petroleum-derived polymers for 3D printing.

4. NEXT GENERATION OF MATERIALS THAT RESHAPE, REPROCESS, AND CHEMICALLY RECYCLE

The increase in the volume of plastic waste and its contamination to the environment are global challenges which require innovative solutions. Plastic re-use and recycling are crucial components for a future plastics economy. As 3D printing grows as a viable manufacturing option, it is essential to develop approaches for 3D printed polymeric materials that do not exacerbate the already serious plastic waste issue.

4.1. Resins From Plastic Wastes. One approach to reduce the impact of 3D printing on plastic waste involves the recovery of consumer-grade plastics and their recycling into a material which could be then 3D printed. Because of the broad commercial use of polymers such as polyolefins, polystyrene or poly(ethylene terephthalate), their associated plastic wastes have been explored for incorporation as feedstock materials for AM.

Investigations of polyolefin waste streams have evaluated the possibility of employing such materials as a feedstock for material extrusion printing. Attempts to recycle both high- and low-density polyethylene (PE) have demonstrated that, while high thermal stability and good barrier properties are advantageous, the adhesion and warping issues of the obtained material make it difficult to handle.[98, 99] Similar studies on polypropylene (PP) emphasized the need for obtaining a material that meets the required properties for 3D printing by mixing such PP wastes with natural fibers or different polymers and compatibilizers.[100, 101] Recycled PET (rPET), obtained by grinding and pelleting PET waste, was also employed as raw material for material extrusion processes. The resulting bulk material demonstrated similar tensile strength to commercial filaments.[102] It was also determined that polycarbonate (PC) coming from e-waste could be re-used as filaments for 3D printing up to three times before the properties of the material degraded to a non-printable state.[103, 104] Finally, polylactic acid (PLA) and acetonitrile butadiene styrene (ABS), two polymers regularly employed in 3D printing, have been very recently investigated in their respective recycled forms. Both polymers cannot be re-printed more than twice because of the significant increase in viscosity for PLA,[12] and the decrease in both tensile and compressive strengths for ABS.[105]

Although these studies revealed the systematic depletion in the material quality after several cycles of mechanical recycling, some life-cycle assessments suggested that it can be a cost-effective method to reduce plastic waste and increase re-use of these materials – even if for only one additional time of use.[106, 107] While these results are encouraging, more sustainable and durable alternatives are still required.

4.2. Circular-by-Design Materials. A circular-by-design material by definition has been designed and synthesized with consideration to its end-of-life management.[108] By instituting a "switch" into the life cycle of the material (irradiation, temperature, change of catalysts, solvent conditions, etc.), these polymers are synthesized with the intention of post-use recycling and its re-implementation as a material feedstock. This cycle provides the material with a theoretically infinite closed-loop lifecycle, which in turn, drastically reduces waste. The three different methods to recycle a 3D printed polymeric object are categorized as reshape, reprocess, and chemically recycle (**Figure 9**).

A polymeric material that can be reshaped is one that can be reformed into a new shape upon heating or irradiation with
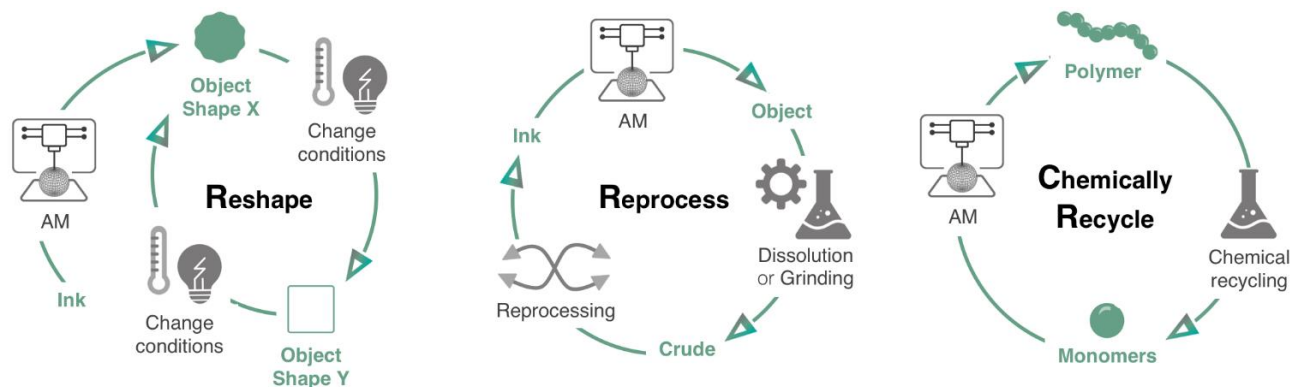
Figure 9. The classifications of options for managing the end-of-life of 3D printed objects: reshape, reprocess, and chemically recycle.

light. This strategy increases the lifetime of the printed object, as it enables repair if damaged or scratched,. A polymeric material can be reprocessed if a 3D printed object can either be grinded or dissolved to obtain pellets or a powder, which can be remolded into resin, ink, or filament for 3D printing. Finally, to be depolymerized, a polymer should undergo a chemical reaction to recover monomers that can be re-polymerized into a fresh resin, ink, or filament which can be 3D printed to obtain a new object with the exact same properties than the initial one. In all three cases, the 3D printed objects must retain the same physical properties. The ideal resin, ink, or filament should comply with these three requirements, but obtaining such a material is a significant challenge. With that being said, the recent literature offers some interesting advances in this pursuit.

In a recent publication, Wei et al.[109] synthesized a polyurethane/carbon foam composite with encouraging reprocessability performance. A commercial thermoplastic polyurethane (TPU) was mixed with carbon black and nanoclay in DMF before its application as a thixotropic fluid for direct ink writing (DIW). After removal of the solvent and freeze drying, a compressible porous and conductive material was obtained for use as a strain and gas sensor. While the ease of reprocessing this material by dissolution in DMF, the notable reduction in mechanical properties after the fourth reprocessing cycle left some room for improvement when considering a truly circular lifecycle.

In addition, Hu et al.[110] developed a fully renewable and 3D-printable material by mixing the biobased elastomer PLBSI with PLA via an in situ dynamic vulcanization process. Morphological studies of the material demonstrated that agglomerates of PLBSI nanoparticles are dispersed in a PLA phase, resulting in good rheological properties. By increasing the PLBSI content to 60-70 wt%, the resulting material exhibited excellent elastic recovery, comparable to that of similar commercial materials. Cytotoxicity tests also suggested that PLBSI/PLA blends could be used as biocompatible materials. Finally, the material can be reprocessed once with a minimal loss in both tensile strength and elongation at break. However, after 5 reprocessing of the same sample, significant mechanical loss can be observed, from 15.8 MPa for fresh sample to 10.3 MPa in tensile strength and from 255 to 135% in the elongation at break.

4.3   The peculiar Case of Thermosets: Reprocessable and Recyclable? In contrast to thermoplastics, thermosets are

inherently non-recyclable because the polymer chains are permanently cross-linked by covalent bonds. As a result, this family of polymers are more resistant to solvent and possess superior thermomechanical properties. Thermosets are typically better candidates for applications such as high-temperature electronic devices or automotive components, which account for 15-20% of current plastic production.[111] Thermosetting polymers actually represent almost 50% of the 3D printing materials market, but they exhibit deficiencies in reshaping. However, the reprocessing and even the chemical recycling of such materials has been recently explored in a very limited number of reports.

Covalent adaptive networks (CANs) are polymer networks that contain exchangeable covalent bonds.[112-116] A sub-category of CANs, known as vitrimers, are particularly attractive as reprocessable and recyclable materials for AM.[117] Vitrimers undergo associative bond exchange reactions upon thermal activation, thus preserving the number of cross-links in the matrix and maintaining the mechanical properties of the thermoset.[118] For example, Shi et al.[119] first presented a fully recyclable thermosetting epoxy ink for 3D printing. This printing method uses solvent-assisted transesterification type bond-exchange reactions of vitrimer epoxy to achieve 3D printing and recycling. The printed epoxy materials were recycled by being dissolved in ethylene glycol in a sealed container at 180 °C for 6 h to obtain the depolymerized vitrimers. Then, the ethlylene glycol was evaporated after 8 h at the same conditions, resulting in a partially cured ink with sufficient viscosity for a next round of 3D printing. After four dissolution-3D printing loops, the obtained ink demonstrates equivalent properties than the initial material. However, the fastidious polymerization reaction reduces this material to direct-ink-writing 3D printing techniques, which limits both the geometric complexity and resolution.

Zhang et al.[120] used an innovative method for the preparation of a reprocessable thermoset for UV curing-based high-resolution 3D printing. Employing a photoinitiator and a cross-linker together with hydroxy-3-phenoxypropylacrylate as
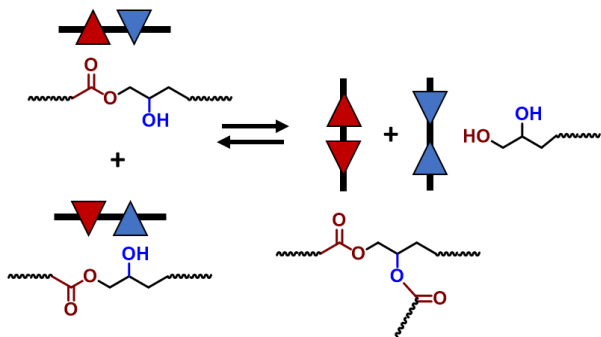
Figure 10. Formation of dynamic covalent bonds for the creation of a reprocessable thermoset.

monomer, a polymer was produced containing both permanent and dynamic covalent bonds. This allowed the material to be reshaped at elevated temperature, due to the bond-exchange reactions that occurred at temperatures higher than 180 ℃ (**Figure 10**). The same material also demonstrated self-healing properties. After being damaged, a structure was polished and additional material was added to re-build the exact same structure with no mechanical performance losses observed in the previously damaged region. Finally, the material was mechanically reprocessed by grinding the printed structure. The resultant powder was subjected to high temperatures to obtain a new ink as a result of the bond-exchange reactions. The uniaxial tensile tests performed on the reprocessed structures demonstrated minimal stiffness lost through the second cycle, but exhibited decreasing performance in subsequent cycles, from a maximum tensile strength of 15 MPa dropping to less than 12 MPa after the third cycle.

Finally, a recent publication on 4D printing lightweight microlattices reported a UV-curable resin prepared from a molecule otherwise only employed as cross-linker for such applications: bisphenol A glycerolate dimethacrylate (BPAGMA). The shape-memory, self-healing polymer can be reprocessed by means of heating and compressing (9 to 12 MPa) for 2 h at 150 to 200 ℃. The mechanical tests performed

poor mechanical properties, likely due to the thermal conditions increasing the prevalence of transesterification reactions. The authors propose that a balanced ratio between hydroxyl and ester groups on the BPAGMA polymer is a key parameter for a optimally recyclable material.[121]

5. ADDITIVE MANUFACTURING FOR APPLICATIONS IN SUSTAINABILITY

When compared with traditional manufacturing methods, AM possesses potential benefits with respect to sustainability: efficient material utilization, reduced waste from the manufacturing process, freedom in the design of printed parts, and AM also allows the instant fabrication of customized parts in the place of need, reducing the transportation costs and environmental impact. In this section, we highlight examples that show how AM can contribute to a more sustainable fabrication.

5.1 Mass Reduction. While we have discussed the implementation of sustainable materials in the future of manufacturing, there are also additional ways in which the implementation of AM can have a significant impact on existing manufacturing practices and procedures with commonly employed materials. One such example is through the use of 4D printing.[122, 123] This practice consists of the production of simple 3D printed parts that undergo further shape change as a response to an additional external stimulus, such as osmotic pressure, temperature change, or light exposure.[124, 125] One area in which this can be particularly influential is through the reduction of shipping costs. Through the manufacturing of 2D parts that can be assembled to form furniture,[126] or through shape morphing foods that transform from flat shapes to their final 3D form during cooking,[127] making shipped goods more
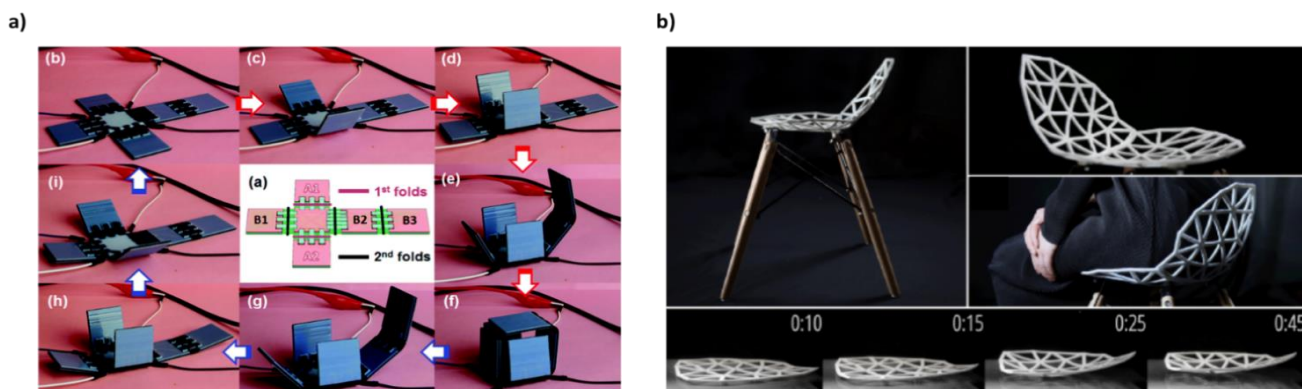

Figure 11. 4-dimensionally active additively manufactured parts. (a) Sequential folding cubic box by printing multiple groups of conductive wires in different layers to heat the liquid crystal elastomer strips with addressability.[131] Reprinted with permission from ref. 131. Copyright 2017 Royal Society of Chemistry. (b) Combination of the shrinking and bending properties of thermoplastic (PLA) actuators with customized geometric algorithms to 4D print functional non-developable surfaces.[126]

on the reprocessed rectangular samples show slight depletion in the quality of the material. The increase in temperature leads to

compact can make shipping volumetrically efficient, reducing environmental impact (**Figure 11**).

On the other hand, AM techniques allow for a reduction of infill density of a printed part. This is a process that involves software analysis of a CAD design prior to printing, allowing for a reduction in material used during fabrication of the final part, while maintaining structural integrity of the part. Through the use of lower infill percentages and commercially available printers and design software, significant energy savings can be made when compared to traditional processing and shipping of plastic products.[106]

Lastly, AM could have a significant effect on energy consumption in commercial construction, by moving the entire assembly process to the designated site, reducing the need for transport of pre-assembled goods and parts. Large industrial-scale printers can be deployed on site for the customized manufacturing of individual pieces, or the entirety of buildings of various sizes. By reducing the complexity of shipped goods from pre-assembled and manufactured components down to the raw construction materials of low embodied energy, shipping costs, construction site waste, and their associated environmental impacts could be greatly reduced. Many examples of entirely additively manufactured buildings already exist today, and are being more common, such as seen in Dubai,[128] and Italy.[129] In addition, by introducing more automation and ground-up manufacturing in construction processes, it is even believed that on-site worker injuries and fatalities could be reduced.[130]

5.2 3D Printed Catalysts and Reactors.
AM has also enabled the production of intelligently designed devices for the fermentation or production of high-value product compounds from a feedstock of less-valuable starting materials. While the idea of reactor technology is not new, the practice of AM of solid-state reactors allows for the precise deposition of catalysts or introduction of reactants at a specific point in space or time during reaction. Cronin has been particularly influential in this space in the production of "Reactionware",[132-135] in which low cost appliances are additively manufactured from inexpensive starting materials. By printing these reactors, researchers are able to introduce reagents or catalysts in pre-programmed positions in the Reactionware, allowing for reduced manufacturing times and costs, while simplifying operational procedures. Many different types of compounds have already been successfully produced using this technology, including heterocycles, Diels-Alder products, imines, amines, and coordination polymers.[132-135] In one such example, various reaction chambers were printed with connecting channels, allowing for the sealed device to be operated through 90 degree rotations (**Figure 12**).[133] By using this methodology, a multi-step synthesis was possible without the need for any pumps or handling of the liquid reagents during operation. Another strategy for developing fluidic reactors includes the immobilization of enzymes within a printed construct.[136, 137] Precursor material can be flowed into the reactor and exposed to the active enzymes to undergo the designed transformation. Many aspects of the device, such as flow rate and feature sizes, can then be tailored to optimize efficiency of the fermenter for a particular reaction type.

Other materials have also been explored to create reactors via the encapsulation of metabolically active cells (**Figure 13**).[138-141] By entrapping microbes into a porous matrix, the metabolic activity of the cells can be harnessed to act as whole-cell

catalysts in designed reactor processes. Many biologically-derived and synthetic materials alike have successfully been 3D
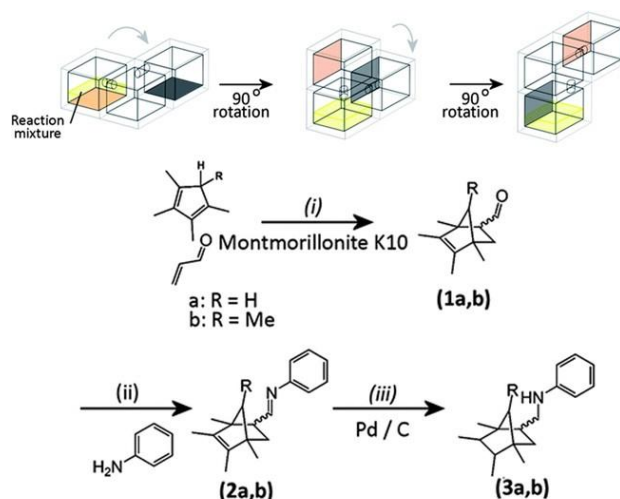

Figure 12. Schematic diagram of the multi-step reaction using Cronin's Reactionware. The reaction mixture is transferred from chamber to chamber upon the completion of each reaction step by rotating the device. Three-step organic reaction sequence is performed: (i) Diels–Alder cyclization, (ii) the formation of an imine, and (iii) hydrogenation of the imine to the corresponding secondary amine.[133] Reprinted with permission from ref. 133 published by The Royal Society of Chemistry (https://creativecommons.org/licenses/by/3.0/).

printed to produce these technologies. Naturally occurring polymers such as carrageenan and hyaluronic acid have been combined in blends to produce a printable material that can encapsulate microbes for degrading chemical pollutants, or to produce medically relevant bacterial cellulose.[142] Similarly, synthetic polymers such as functionalized pluronics, or other novel triblock copolymers have been used to create soft hydrogel materials for the 3D printing of encapsulated yeast cells.[143, 144] The 3D printed lattice constructs have shown to be mechanically robust post-printing curing step, allowing for reusability in many rounds of fermentation, producing small molecules and polypeptides. With so many industries already relying on cellular fermentation for the production of pharmaceuticals and other molecules of interest, these materials offer immense promise in the future of sustainable and reusable batch reactor processes.

6. CONCLUSIONS AND OUTLOOK

AM presents many exciting opportunities in on-demand and distributed manufacturing of parts and equipment worldwide for medical, aerospace, and other consumer products. Thus, it is imperative to develop sustainability into all aspects of the AM ecosystem (hardware, software/modeling, and materials), but in particular, AM must fit into the future plastics economy. Inks, resins, and filaments for AM will need to rely on renewable sources of chemical feedstocks. Natural biopolymers, (bio)degradable synthetic polymers, and small molecules can be produced using plants, microbes, and other organisms. Chemical modification to alter viscoelastic properties, physical cross-linking, and/or chemical cross-linking of these renewable
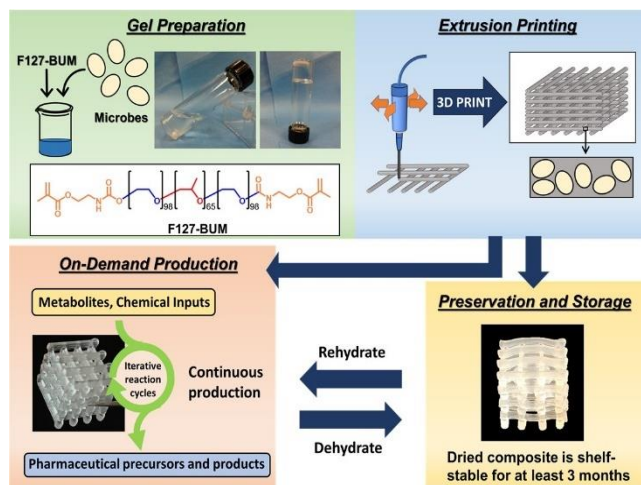
Figure 13. F127-based hydrogels used to immobilize yeast and bacteria consortia for the development of a 3D-printable class of living materials. The materials can either be directly employed in iterative bioprocessing cycles or preserved for on-demand production at a later time. Multiple rounds of reuse are possible without a reduction in efficiency.

feedstocks may be required in order to be compatible with AM processes. Currently, materials are largely modified to incorporate functional groups for photo-initiated radical polymerization as it is widely applied in AM. Future research should explore methods to introduce chemical and physical cross-links into a material in a spatially defined manner. For example, new photo-acid and photo-base catalysts can be developed for vat photopolymerization, as well as to provide an expanded set of renewable monomers and polymers for AM.[145]

Plastics have become ubiquitous in our society, and the volume of plastic use and production is expected to increase. The future plastics economy will undoubtedly require methodologies to re-use and recycle (mechanically and chemically) plastics. Recent trends include the use of discarded plastic as a feedstock for the preparation of resins for AM or the implementation of new resins that are circular by design in AM processes. Recycling the excess and unwanted material primarily into new feedstock, or finding new methods for the material to be easily recyclable is imperative for the evolution of AM. Indeed, when the environmental impact of a product is evaluated, both the sustainability of the source and its life-cycle assessment must be performed.

While the ideal scenario is to create circular-by-design materials, few polymers can actually be depolymerized to efficiently close the loop. Thus, the quality of the polymers obtained from chemical recycling (*i.e.* the properties of the material) to date is limited. Future research should extend the range of materials which exhibit quantitative polymer reversal and isolation of pure monomers, especially the ones derived from renewable resources. And while plastic recycling has been implemented for reducing the tremendous volume of plastic waste generated, the use of plastic waste as a sustainable and low-cost source for the production of new 3D printable resins could ultimately be hampered by the cost. Therefore, future chemical recycling processes should not only be focused on

minimizing the plastic waste but also on designing new materials that can be produced more cost effectively.

Finally, AM will provide the capability to develop new solutions to applications that previously could not be solved. Some examples have already been reported, such as 4D objects that can be shipped globally as sheets that can fold into a 3D object upon the application of a stimulus, or immobilized catalysts and reactor systems that provide more efficient chemical production. AM is a highly interdisciplinary field that involves chemistry and materials science, in addition to a diverse set of engineering disciplines that include mechanical engineering, chemical engineering, and computer science. Broader collaboration across all of these disciplines is required to provide 21st century solutions to sustainability.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing interests.

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