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# Functional 3D Printed Polymeric Materials

*Denisse Ortiz-Acosta and Tanya Moore*

## Abstract

Additive manufacturing (AM) is an emerging 3D printing technology that enables the design and rapid manufacturing of materials with complex microstructures. Advances in 3D printing have allowed manufacturing companies to expand from design and 3D printing of prototypes to the rapid manufacturing of end products. Additive manufacturing enables the manufacturing of components in a layer-by-layer fashion, opposite to common manufacturing methods that rely on machining, molding and subtractive methods to obtain the final product. AM employs a computer-aided design software that allows for the design of virtual objects and the control of the nozzle and/or stage of the 3D printer. Due to their versatility and wide range of mechanical and chemical properties, polymers are the most utilized materials for AM. Polymers used for AM covers thermoplastics, thermosets, elastomers, polymers with incorporated fillers, biopolymers, and polymers blended with biological materials. The architectural design and choice of polymers can lead to materials with enhanced functionalities, mechanical properties, porosity, and stability. This chapter focuses on the development of polymer-based 3D printing materials with multifunctionalities used specifically for the production of biomedical devices, electronic devices, and aerospace-relevant products.

**Keywords:** 3D printing, additive manufacturing, polymers, biomedical devices, aerospace, electronics

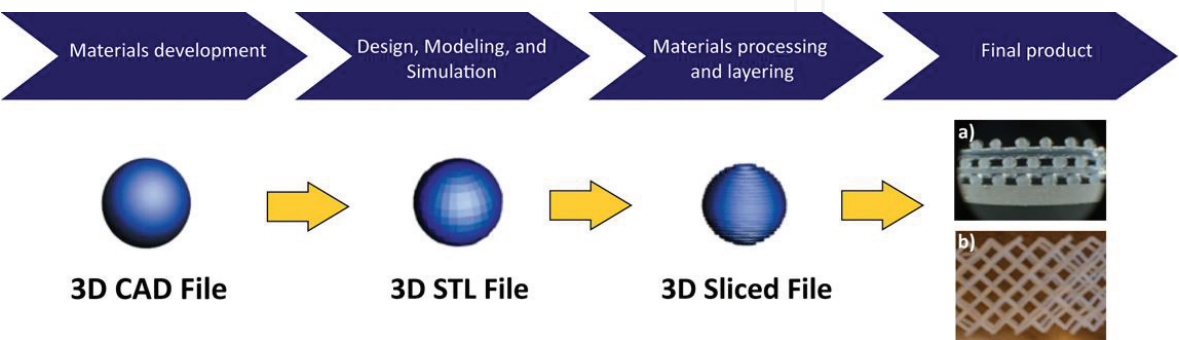
## 1. Introduction

3D printing is an additive manufacturing (AM) process that enables the manufacturing of components with complex geometries in a layer-by-layer fashion. 3D printing became popular after the first machine was introduced to the market in 1986 by Hull [1]. Charles Hull created the first stereolithography (SLA) manufacturing method which he used for the rapid design and manufacturing of small prototype plastic parts. Stereolithography uses light to activate polymers within a resin (photopolymerization) to create 3D, complex shapes [2, 3]. This SLA system was commercialized in 1987 by the company 3D Systems. Since this breakthrough invention, there has been great effort in producing machines that can process a variety of plastics. Some of the machines currently in the market are fused deposition modeling (FDM) [4, 5] and direct ink write (DIW) for extrusion-based processes [6, 7]. Powder bed fusion (PBF) and laser sintering (SLS) are used for processes requiring a laser to cure or fuse polymeric

materials [8]. Inkjet printers also use light to photopolymerize ink drops into complex shapes [9]. Extensive reviews on these processing and 3D printing technologies have been published elsewhere [4, 5, 10–14]. This chapter focuses on applications that use AM for the 3D printing of polymeric materials.

2. 3D printing general process

Since the 1980s, 3D printing has become very popular as a result of the rapid manufacturing of components with architectures designed to meet specific applications. AM allows for the manufacturing of a variety of shapes in a layer-by-layer fashion, often without the need of post-processing such as machining. As a general scheme, AM starts with the design of a virtual object using CAD (computer-aided design) software that generates a STL (stereolithography, named after Charles Hull’s SLA process) file format [15]. A slicer program interprets the STL file and converts it into g-code (e.g. Slic3r, 3DPrinterOS, MakerBot Print, and others). The computer controls the stage and dispenser of the 3D printer allowing prototypes to be manufactured. Rapid prototyping allows one to refine product ideas while saving significant time and money because it allows for iterations prior to creating a final product. Optimization via an iterative process involves touching and feeling the prototype, in real time, in order to finalize the shape and geometry, leading to a final product. Characterization methods during iterations and on the final design include optical microscopy, SEM, and mechanical tests. Others methods, such as bio-compatibility (cell-adhesion and proliferation) and electrical performance are performed depending on the application. **Figure 1** demonstrates a general scheme for the AM process. Despite the many advances in AM, the technology still has many challenges that need to be addressed. These challenges are related to the speed of the processes (which in many cases is slower than injection molding processes and machining), cost of the machines, and limited feedstock. However, advantages outweigh the challenges due to the fact that AM allows for compositional flexibility, complex macro and microstructures, and easy modeling and optimization. As a result, industries including biomedical engineering, transportation, and the military have adopted AM as the main manufacturing method for the printing of prototypes and final parts [16, 17].

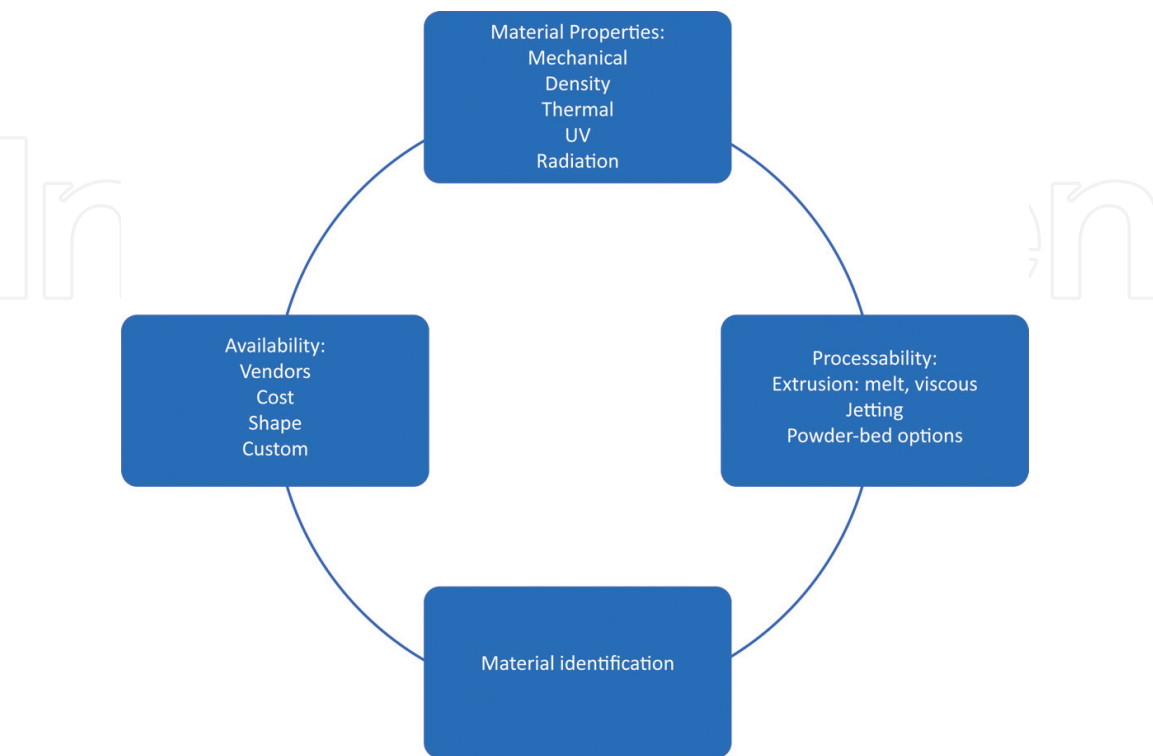


**Figure 1.** General scheme for the use of additive manufacturing processes, from the choice of material to the final product. The 3D printing of parts involves the use of a computer-assisted design software that generates a STL file format that is then sliced and formatted into gcode. The computer controls the stage and dispenser to generate materials with specific architectures, e.g. faced-centered tetragonal cushion using direct ink writing (a) and diamond structure using FDM (b).

### 3. Polymers in 3D printing industry

Careful attention is imperative when choosing a material to print a given part. While there are a variety of commercially available polymers, not one polymer is inclusive and will give one the properties needed for a specific application. Furthermore, a single AM technique is not capable of printing any one individual polymer available in the market. The selection of material depends on the application and the customers' needs. **Figure 2** lists the decision criteria for the selection of a material. One must take into consideration the environment at which the part will be exposed and the properties required (e.g. temperature, mechanical load, humidity, chemical exposure, radiation, UV light), the processability, 3D printing method, and availability.

Polymers have become consumer goods, for they are used to manufacture bottles, toys, tools, bags, phones, computers, tools, cushions, electronics and transportation components [18]. Thus, it makes sense that efforts have focused on developing materials that can be 3D printed, which allows for rapid manufacturing [2–4, 17]. **Table 1** lists commercially available polymers used in some of the AM processes. Polycarbonate (PC), acrylonitrile butadiene styrene (ABS), poly ether ester ketone (PEEK), polyetherimide (ULTEM) and Nylon are common polymers used in processes requiring thermoplastics, or plastics that are processed by heating to a semi-liquid state and close to the melting point. Upon extrusion, the printed layers fuse and solidify. AM techniques that use thermoplastics are Fused-Deposition Modeling (FDM), Jetting (InkJet), and Selective Laser Sintering (SLS). SLA and Direct Ink Writing (DIW) use thermosetting polymers in their liquid state, or polymers that become solids after curing. A chemical reaction occurs prior to the melting point, resulting in a solid-state material. In SLA and DIW, polymers are formulated to meet specific properties, most importantly rheological. For example, each layer should be self-supporting and should allow for the printing of multiple layers while retaining the designed geometry [14, 19–21]. Rheologically, this corresponds to a resin that has a yield stress at high oscillatory stresses, such that the



**Figure 2.**  
*Material selection chart for product design and manufacturing.*

AM technology	Process	Physical state of starting material	Feedstock
FDM	Melting-solidifying	Solid	PC, ABS, PLA, ULTEM, Nylon, Carbon-filled Nylon, ASA
SLA	Photocuring	Liquid	Thermosetting- acrylates and epoxy
SLS	Melting-solidifying	Solid	PCL, PLA
Jetting	Photocuring	Solid	ABS, ASA, PCL, PLA, Vero
Direct Writing	Extrusion-heat/UV curing	liquid	Thermosetting- any material with adequate viscosity

**Table 1.**  
*List of polymers used for 3D printing applications.*

resin is solid-like at rest (low stress) and liquid like during flow (high stress) [7]. One of the main challenges in the polymer 3D printing industry is the limited feedstock available for purchase. Polymers listed in **Table 1** cannot be used in all applications. Particularly, polymers in the pure state lack mechanical strength for load-bearing applications. The addition of fillers, such as silica [22, 23] and carbon fibers [24, 25], is often used to generate materials with high mechanical strength. Furthermore, the incorporation of additives enhances materials properties by adding functionality to the parts that include getter [20], UV and radiation resistance [26–28], and anti-fouling properties [29–31].

4. Biomedical engineering applications for 3D printing

The biomedical market represents 11% of the total AM market share today, and will be a strong driver for AM development and growth [32]. Since the early 2000s, there has been increased interest in using 3D printing to fabricate hard tissues (bones, teeth, cartilage) and soft tissues (organs, skin, and others) [2–4, 16, 33]. The manufacturing of prostheses and scaffolds with complex geometries is especially important for regenerative medicine, where a porous scaffold is implanted into the patient to serve as a template for tissue to regenerate while the implant degrades slowly in the body. Other implants need to stay in place for the lifetime of the patient. 3D printing allows for the rapid manufacturing of customized prosthetics and implants with controlled architectures. The structure can be designed through the translation of x-ray, MRI, and CT images into STL file formats. The STL file can be processed by software and a design can be generated based on the patient’s specific needs. Metals are commonly used to generate prosthetics for bone reconstruction. ABS and PLA are the most suitable non-biodegradable polymers used for the manufacturing of scaffolds. However, materials used in medicine must enable cell adhesion, growth, and differentiation. Current feedstock for biomaterials is limited to collagen, gelatin, fibrin, and chitosan, which are similar to natural tissue, have high affinity to cells and are highly hydrated. The main challenge with these soft natural polymers is their low mechanical strength [33]. In biomedical engineering, the main focus has been on the development of biopolymeric materials for tissue and scaffold generations with improved flexibility, strength, and patient compatibility in order to prevent implant rejection and toxicity. Some polymeric mixtures include living cells isolated from the patient and grown in the laboratory. These types of polymers are often hydrogels suitable for ink jet 3D printing technologies. **Table 2** shows various polymers used for biomedical applications.



Material	3D printing techniques	Comments
PLA, PCL, PLGA	FDM	Scaffolds. Biodegradable. Can add fillers, e.g. HA, for improved cell adhesion and mechanical properties
Collagen, alginate, PEG, fibrin, chitosan	Inkjet, extrusion	Biodegradable scaffolds. Can add fillers and cells for improved cell adhesion and mechanical properties
PCL, methacrylate copolymers	SLS	Biodegradable scaffolds. Improved mechanical properties

**Table 2.**  
*Polymers and processes used for the additive manufacturing of biomedical devices.*

Some examples of biomedical devices developed using 3D printing are implants, prosthetics, dental, orthodontics, hearing aids, and drug release tissues.

Polymers used for tissue and organ fabrication need to have various functions in order to (1) allow for cell attachment and migration, (2) transfer growth factors and waste products, (3) maintain its shape while cells are growing and (4) maintain adequate mechanical properties. Wu et al. [34] reported the generation of a biopolymeric material based on chitosan dissolved in an acid mixture of acetic acid, lactic acid, and citric acid. This biomaterial was 3D printed using an ink-writing technique, then dried under vacuum and neutralized to remove any acid residue. The structure of the scaffold was characterized using confocal laser scanning microscopy and the images showed wrinkles attributed to the volume change. Tensile mechanical tests show that the printed material exhibits a strain to failure of 400% under tensile load and a 7.5 MPa ultimate strength when in its neutralized form. Furthermore, the 3D printed material allows for excellent cell adhesion, growth, and proliferation, as demonstrated using the Live-Dead staining method, fluorescence microscopy, and SEM.

Luo et al. [35] reported the 3D printing of a bioceramic hollow struts-packed scaffold using an extrusion typ. 3D printer and a shell/core nozzle. The ink contained  $\text{Ca}_7\text{Si}_2\text{P}_2\text{O}_{16}$ , alginate and Pluronic F-127. After printing, the ink was dried overnight and sintered for 3 hours at 1400°C to remove the alginate and F-127 materials. The morphology was analyzed using an optical microscope. The micro-pores and the microstructure of the pores were characterized using SEM. The fabricated scaffolds (16/23 shell/core size) were subjected to mechanical testing and exhibited a compressive strength of 5 MPa, comparable to cancellous bone (2–12 MPa), and a modulus of 160 MPa. The scaffold had high porosity (65–85%), adjusted with the core/shell size nozzles. The high porosity and surface area (up to 6500 mm<sup>2</sup>/g) allowed for cell adhesion and proliferation on the outer and inner surface of the scaffold, as determined by SEM. Finally, the in-vivo bone formation study in a rabbit demonstrated that the bioceramic implant allows for good cell integration and bone formation was detected with micro-CT.

Lewis' team at Harvard University 3D printed a tympanic membrane scaffold composed of PDMS, PLA, and PCL based materials using a DIW technique [36]. The team demonstrated that it is possible to design and fabricate materials with similar properties when compared to human specimens. The high frequency displacement and acoustics were organized by concentric rings for each 3D printed graft, and it was very dependent on the patterns and mechanical properties, characterized via digital opto-electronic holography, laser Doppler vibrometry, and dynamic mechanical analysis. In a different study, the team 3D printed cellular materials with vascular networks for flow [37]. The 3D printed structure was fabricated using an ink composed of Pluronic F-127, GelMA (gelatin methacrylate to allow for UV curing) and fibroblast cell culture. After curing, the Pluronic F-127

was removed by cooling to 4°C, yielding open channels that represent the vascular networks. Lewis' team demonstrated that blood and other cellular liquids can flow through the channels with minimal death of cells.

Patients with skin burns and thick wound injuries often suffer from long term recovery and extensive and expensive treatments. The autologous split-thickness skin graft (ASSG) is the technique most often used to treat large wounds [38]. A skin tissue is placed in the injured area and assists with the wound closure and healing. This technique relies on the removal of a piece of skin from a different part of the patient's body and reapplying it on the place of injury. The drawback with ASSG is that it is limited by the size of donor sites and also creates another place of injury [38]. 3D printing of biomaterials would alleviate the problems related to ASSG. Skin cells are cultured in a laboratory and mixed with biocompatible polymers for bioprinting. In 2012, Koch Singh et al. [39] reported the 3D printing of skin using a laser-based inkjet printing method. The inks were composed of blood plasma/alginate solution and fibroblast/keratinocytes/collagen biomaterials. Collagen is the main component of the extracellular matrix (ECM) in skin. The team proved that the laser-based printing method does not harm the cells by performing proliferation of the cells in histologic sections 10 days after printing. Ki-67 staining, which includes the protein present in cells during their active cell cycle phases, shows that proliferating cells can be found in all regions, verifying vitality. In addition, a build-up of basal lamina, cell adhesion and proliferation- sign of tissue generation was observed.

The dental industry is taking advantage of 3D printing technologies for restoratives, implants, and orthodontics purposes. Currently, professionals in the dental field have access to 3D printers and it is possible to print designs in a clinical environment. A CT scan is used to generate a defined shape based on the patient's morphology and quickly fabricate and replace a missing tooth [40]. 3D printing is used for the manufacturing of aligners, braces, dental implants, and crowns [40]. Biocompatible materials are used for the fabrication of dental parts using 3D printing, e.g. polylactic acid, polycaprolactone and polyglycolide, and acrylates [3]. It is possible to fabricate dental implants with antibacterial properties by the incorporation of additives, such as quaternary ammonium salts [41–43]. At the age of 23, Amos Dudley fabricated his own orthodontic aligners while he was a student at New Jersey Institute of Technology [44]. He used equipment available at the institute to scan and print models of his teeth. A non-toxic plastic was used to mold and eventually generate 12 clear aligners. Amos had access to a Stratasys Dimension 1200 3D printer and used a mixture of alginate powder and PermaStone as the resin to print the aligners, which were tested by fitting them on his teeth. While it was not a trivial problem to solve, Amos proved the ability of 3D printing orthodontic materials for teeth alignment.

AM has been widely used in the biomedical industry and will continue to impact work in the future. Some challenges will persist, such as regulatory issues, limited materials, and inconsistent quality [45]. AM biomedical products require FDA approval, which can be time consuming and difficult to obtain [46]. Biocompatibility will require the development of new techniques and materials to produce high quality, high performing AM materials [47]. Furthermore, mechanical properties of AM materials need to be well assessed such that final properties can have reliable and reproducible behaviors. Further development for on-demand and patient-specific applications will be exciting work in this field. For example, designing patient-specific implants following a CT-scan will result in quick results [48]. Complex parts with specific mechanical properties and biocompatibility can be constructed on demand and with multifunctional components if needed. AM Research and development may help to improve

bio-printed scaffolds and tissues for clinical applications to reduce cost for tissue engineering [49]. Manufacturing AM artificial organs, which includes multifunctionality (i.e. bionic ear [50]), will revolutionize the field of 3D printing for biomedical applications.

## **5. Additive manufacturing in the aerospace industry**

One of the most promising fields in the future of AM is the aerospace industry. According to Wohlers' report, this industry account for almost 20% of the total AM market today [32]. Aerospace applications typically require light weight and high strength materials. The importance of AM relies on the reduced cost, increased flexibility of design, and increase in a variety of products to meet customer needs. Additive manufacturing is an important technology that enables the design and manufacturing of complex structured products with improved mechanical strength and lower weight, at a lower cost and reduced lead-time. The aerospace industry has replaced the conventional manufacturing methods of molding and machining with 3D printing technology for small scale production. At a small production scale, AM offers effectively low-cost design and assembly [17].

The aerospace industry implemented the use of AM approximately 20 years ago [51]. The main use for 3D printing has been focused on prototyping, modeling and producing jigs, fixtures and tools [17]. Furthermore, AM is used to build replacement parts on-demand when required. The ability to build on-demand spare components reduces costs for the production of parts that may never be used due to them becoming obsolete to new technology, which also saves warehouse storage space. For example, BAE Systems is currently 3D printing window breather pipes used in jetliners [52]. These pipes cost 40% less than pipes manufactured using injection molding processes and are manufactured on an as-needed basis.

Recently, NASA designed a rover, named Desert RATS, that can support humans in a pressurized cabin in space [53]. The rover is intended to transport humans to Mars. It contains 70 3D printed parts that include flame-retardant vents and housings, camera mounts, large pod doors, front bumpers, complex electronics, and others. The materials used for the 3D printing of the part used in the rover were ABS, PCABS and PC, and were printed using a FDM Stratasys 3D printer. Piper Aircraft manufactures tools using PC that can withstand hydroforming pressures of 3000 to 6000 psi. Aurora Flight Science additively manufactured wings that weigh one third of the fully dense metal components [54]. Some wings have integrated electronics. Lepron generated 200 different designs for use in piloted helicopters [17]. It is foreseen that aerospace companies will replace small components with 3D printed parts, thus reducing the weight of the machines. Some examples are arm rests, seat belts, food trays, and many others [17].

Companies have adopted AM for fast production without making substantial changes to their products [17]. This modification is mostly due to the fast-changing market and low cost of generating such small builds. Several challenges would have to be overcome to facilitate the growth of AM. Some of these challenges include: (1) current speed of AM machines is slow for bulk production; (2) few polymeric material options; and (3) current machines do not allow for the manufacturing of large components [17, 55]. In the future, it is expected that companies will pursue a completely different business model by performing product customization for end-product while maintaining the on-demand part supply. Future work will focus on the development of multifunctional structures with complex geometries, which allows for novel solutions for complicated problems. AM techniques, such as using functionally graded materials, can be used in order to tailor the mechanical and/or



thermal response of components [56]. Furthermore, on-demand manufacturing will reduce costs and eliminates potential damage caused by storage [45].

## 6. 3D printed electronics

Electronic devices require suitable mechanical, geometrical, and optical functionalities to allow for miniaturization, low energy consumption, and smart capabilities [57]. The production of prototypes and end-products has to rapidly change due to the fast-changing technology. The conventional method for manufacturing electronic devices is using subtractive methods that involve masking and etching of sacrificial materials [58]. AM allows for the reduction of material waste, energy consumption and processing time and steps. 3D printing is being used to substitute steps for mounting and assembling electronic devices [59]. The additive process deposits material in a controlled layer-by-layer process allowing the manufacturing of complex geometries and dimensions. In addition, it enables 3D orientation of important components to improve performance. With miniaturization, AM allows for the manufacturing of small parts that would otherwise be difficult to obtain. AM has found application for thin films [60], inductors [61], solar cells [62], and others. The most common 3D printing techniques for electronics are inkjet and direct writing of conductive inks.

Jennifer Lewis and colleagues fully 3D printed a quantum-dot (QD) light-emitting diode (LED) system, including green and orange-red light emitters embedded in a silicone matrix [63]. The printed device exhibits a performance of 10–100-fold below the best processed QD-LEP but could potentially be optimized with the addition of an electron-transport layer. A copper nanoparticle stabilized with polyvinyl pyrrolidone was mixed with 2-(2-butoxyethoxy)ethanol to prepare ink for inkjet printing [64]. The ink was printed onto a polyimide substrate and sintered at 200°C. The prepared electronic device resulted in low electrical resistivity ( $\geq 3.6 \mu\Omega\text{cm}$ , or  $\geq 2.2$  times the resistivity of bulk copper). Bionic ears were printed using an inkjet printer [50]. The inks were composed of cell-cultured alginate and chondrocytes hydrogel matrix and a conductive polymer consisting of silicone and silver nanoparticles. The 3D printed ears exhibit enhanced auditory sensing for radio-frequency reception allowing the ear to listen to stereo music. This result demonstrates that bioengineering and electronics can be merged, resulting in advanced technologies. Students from Northwest Nazarene University and Caldwell High School designed the 3D printed CubeSat [65]. The CubeSat was launched aboard Delta II rocket as part of a NASA mission in 2013. It carries miniaturized electronics and sensors and is intended to collect real-time data on the effects of the harsh environments of space (oxygen, UV, radiation, temperature and collisions) on the polymeric materials- ABS, PLA, Nylon, and PEI/PC ULTEM.

Future research and development in the electronics field will take advantage of low cost methods, flexibility in design, and fast speed of 3D printers for designing and prototyping new products. For example, printing circuit boards will offer superior accuracy and flexibility, with potential cost savings, environmental impacts, faster production times, and increased design versatility. Furthermore, adaptive 3D printing, which takes advantage of a closed-loop method that combines real-time feedback control and DIW of functional materials to construct devices on dynamic surfaces, is an exciting field of research [66]. This method of 3D printing may lead to new forms of smart manufacturing technologies for directly printed wearable devices. New possibilities will emerge in the wearable device industry, in biological and biomedical research, and in the study and treatment of advanced medical treatments.

## 7. Recycled plastics for 3D printing

Unsurprisingly, the amount of plastic pollution on the planet is alarming [67]. Plastics have dominated our marketplace due to their utility and versatility and make up at least 10% by mass of our waste streams. Plastics are designed to be durable and to withstand harsh environmental conditions. Therefore, the amount of plastic waste is only expected to increase in the future. Currently, 91% of plastic is not being recycled. The negative impact plastics have on our ecosystem is well recognized and researchers are using this as a business model and opportunity [68, 69]. Considerable efforts are being placed on recycling and reusing plastic waste. Prof. Sahajwalla at the University of New South Wales Sydney and her team work on turning plastic waste into usable polymers, including 3D printing polymers [70]. The company Reflow is collecting polyethylene terephthalate (PET) waste bottles and turning them into filaments suitable for 3D FDM printers [71]. A company in Belgium, Yuma, is using recycled plastics for the 3D printing of sunglasses [72]. The U.S. Army Research Laboratory and the U.S. Marine Corps are working together to repurpose plastic waste by printing items from recycled plastic useful for soldiers [73]. This process allows for a decrease in transportation costs and manufacturing of parts on demand. This large effort is expected to have a positive impact on both the environment and communities by turning polymer 3D printing into income for waste collectors and removing waste from the streams.

## 8. Conclusions

Industries are moving toward the implementation of 3D printing as a manufacturing process because it facilitates the design of complex structures and rapid production of prototypes. AM utilizes a computer-aided design software that allows for the design of architectures with defined porosity and structures at a microscopic level. Because of the easy production of 3D printed prototypes, modeling based on a specific application can be performed to further improve the design of the end product and potentially reduce failure risks. The 3D printing of polymers and polymer composites has significantly progressed over the last 40 years and is expected to increase in the near future. Thermoplastic materials are readily commercially available for use in FDM, SLS, and inkjet processes. Materials like PC, ABS, PLA, ULTEM, and PCLA are commonly used for the manufacturing of tools, prototypes, and items used in the aerospace industry. However, these polymers are not one-size-fits-all types of polymers and are not necessarily a good choice for all applications. Thus, research efforts are focused on developing materials that are capable of meeting specific applications. For examples, polymers blended with cultured cells can be used for scaffolds and implants on biological systems. Cells can be obtained from the patient and cultivated in the laboratory, thus producing a material that is less likely to be rejected by the patient. Fillers and additives can be used to generate multifunctional materials with improved mechanical properties. Fillers, such as CNTs and graphene, can be incorporated into the polymer to produce a material that is electrically conductive.

Despite all of the advances in the design and development of new polymeric materials for AM applications, challenges still remain. The availability of polymeric inks suitable for extreme applications, such as low temperature environments, high load pressures, and radiation resistance, is very limited. The development of new materials is necessary to increase the usefulness of polymer 3D printing

technologies. Ideally, some of these composites are recyclable and/or biodegradable to reduce the negative impact plastics have on our environment.

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## Conflict of interest


The authors declare no conflict of interest.

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