CHAPTER 1: POLYMER BASED ADDITIVE MANUFACTURING: HISTORICAL DEVELOPMENTS, PROCESS TYPES AND MATERIAL CONSIDERATIONS

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Abstract

3D printing is a manufacturing technique where parts are built in a layer-by-layer fashion. The earliest embodiments were based on generating successive layers of solidified materials at the air liquid interface through exposure with actinic radiation and the lowering of the growing object into a vat of photo-active material. One of the earliest concepts was by Otto Munz in 1956 where he describes “photo-glyph recording”. However, many today consider Charles Hull the father of 3D printing as it was his patent that coined the term “stereolithography”, and was the first to commercialize a 3D printing apparatus.

Since then, there has being a multitude of technologies developed which fall into the category of 3D printing. While curing of resins remains one of the most widely techniques, other techniques based on the extrusion of polymers, cutting sheets or films and thermally or chemically binding powdered materials have all reached the commercial markets. This chapter aims to give an outline of the most common polymer based 3D printing techniques available today and describes some of the material and processing constraints which should be considered when selecting these systems for 3D printing of biomedical parts.

Keywords

3D Printing, Polymers, Stereolithography, Fused Filament Fabrication, Selective Laser Sintering, PolyJet, InkJet, Freeformer, Laminated Object Manufacturing

1.1 Introduction

Three-dimensional (3D) printing, also referred to as additive manufacturing (AM), rapid prototyping (RP), or solid freeform fabrication, is a process which involves the manufacturing of an object or structure by deposition or binding of materials layer-by-layer (Sachs, Cima and Cornie, 1990; Conner *et al.*, 2014; Gross *et al.*, 2014; Prasad and Smyth, 2016). A recent publication by (Norman *et al.*, 2016) indicates that the American Society of Mechanical Engineers (ASTM) favour the term additive manufacturing, however, these terms are routinely used interchangeably as is the case in this body of work.

The origins of 3D printing date back to 1986 when Charles Hull developed, patented and commercialised the first 3D printer. The technique was called Stereolithography Apparatus-1 (SLA-1) and was capable of manufacturing a 3D printed object without the need for moulds or other tooling (Prasad and Smyth, 2016). Further to this work, Hull also developed the .STL (Standard Tessellation Language) file format. Today the STL file format is seen as the gold standard for communication of data between the computer-aided design (CAD) software and 3D printers and it is in this that all the information corresponding to each surface of the 3D model is stored in the form of triangulated sections (Gross *et al.*, 2014)

There has been a multitude of 3D printing methods developed since the patenting of Hull's SLA-1. These methods can be separated depending on the way of layer deposition and the material feedstock. However, regardless of the 3D printing technique employed they all share similarities in the method which they create an object, as the model must be first designed and generated through the use of computer-aided design (CAD) software, e.g., SolidWorks, AutoCAD, Creo Parametric, which is then converted into a STL file and transferred to the specific additive manufacturing device for fabrication. This STL file is cut into "slices" with each of them containing the information required for each layer of the part. A platform is created to support any overhanging structures and the part is built one slice at a time.

Additive manufacturing is a simple, automated process which is fast and inexpensive. (Hiemenz, 2011). The fundamental layer-by-layer manufacturing mechanisms of additive

manufacturing provides a wide range of advantages over conventional manufacturing processes. These include: design freedom and superior levels of design complexity with fewer or single-step manufacturing required; reduced or elimination of post-production finishing; reduced or elimination of tooling and fixtures; shorter cycle times for both designs and processing; multiple material manufacturing; savings in energy and start-up cost (Gao *et al.*, 2015); and reduction or elimination of post-production assembly.

1.2 Stereolithography (SLA)

The concept of creating a three-dimensional object from a liquid precursor through photochemistry has a long history (Wohlers, 2005). The earliest embodiments were based on generating successive layers of solidified materials at the air liquid interface through exposure with actinic radiation and the lowering of the growing object into a vat of photo-active material. One of the earliest concept was by Otto Munz in 1956 where he describes "photo-glyph recording"(Munz, 1956). In 1981, Hideo Kodama of Nagoya Municipal Industrial Research Institute described the use of UV exposure controlled by a mask pattern or via a scanning fiber transmitter (Kodama, 1981) to create a 3D object. In 1984, Jean Claude André , Alain Le Mehauté and Olivier de Witte filed their patent application (Andre, Le Mehaute and De Witte, 1984) for this process (their patent was ultimately abandoned). Around the same time, Charles Hull filed his patent (Hull and Arcadia, 1986) , coining the term "stereolithography", and was the first to commercialize a 3D printing apparatus. A variety of photochemically reactive polymers have been used including free-radical, cationic and thiol-ene chemistry (Ligon *et al.*, 2017).

The original commercial SLA consisted of a photopolymer reservoir, or vat, which is underneath a movable platform. At each stage of the "build", the platform, or in latter stages, the most recently created layer is lowered just below the surface of the resin in order to create a thin layer and the laser beam passes back and forth over the liquid solidifying it onto the prior layer as it passes (Fig. 1). More recently, some manufacturers have utilized digital light processors (Hornbeck, 1997) to create an image of the layer in UV light to cure the entire layer at once. This leverages the technology for high-resolution

projectors used in the movie industry and developed by Texas Instruments[1]. Others such as UNIZ, and Photocentric have developed liquid crystal arrays which act as "shutters" create the image of the cross section (sometimes referred to as LCD-SLA).

Frequently, a wiper is drawn across the topmost layer to ensure a uniform liquid film for the next layer. Upon completion of the print, the part is pushed up out of the unreacted resin in the vat, and any sacrificial supports are removed and the parts are post-cured (a final, overall dose of UV) in order to remove any unreacted resin from the printing process. One consequence of this arrangement is that the depth of the resin vat must be at least as deep as the part being built is tall and the vat must be filled. Other companies have developed there own systems SLA including EnvisionTec and RPS. Voit (Voit *et al.*, 2016) has described a concept utilizing a dense "z-fluid" upon which the active photopolymer floats so as to minimize the amount of photopolymer used.

Another approach has been to have the resin reservoir with a UV transparent window with the UV light penetrating from underneath the platform and the build plate moving upwards after each pass (sometimes referred to as inverted-SLA)(Ligon *et al.*, 2017). This greatly reduces the quantity of photoactive resin used during the build. However, a consequence of this geometry is that the resin will cure and span the full gap between the build plate and the window at the bottom of the reservoir. This requires a physical delamination of the growing part from the window at each step. In addition to slowing down the process, there are undesirable mechanical forces on the growing part and the reservoir window. The former can cause decreased accuracy and the latter may require frequent replacement of the reservoir/window. Never the less, companies like Formlabs and EnvisionTec have been very successful in marketing their systems for a variety of applications including dental and medical device applications.

[1] http://www.ti.com/dlp-chip/overview.html retrieved Jan 22nd 2019

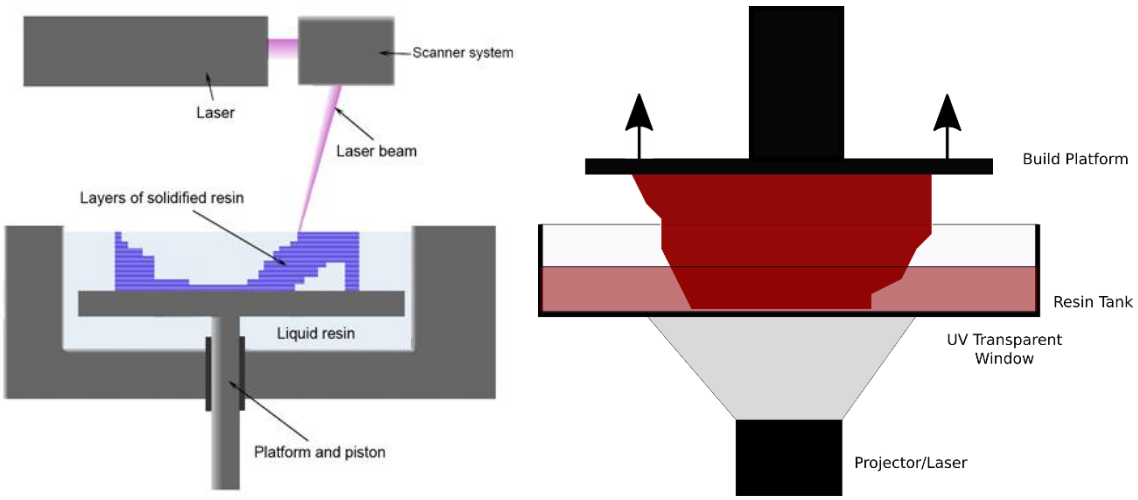

Fig. 1. Left) Conventional SLA utilizes a vat of resin which is lowered as each layer is cured. Right) Inverted SLA utilizes a UV transparent window through which the UV light penetrates from underneath, with the platform and the build plate moving upwards after each pass

In all the above-mentioned systems, there is full solidification of the growing part, either at the liquid/air interface, or at the liquid/window interface, leading to inherently layered internal structures. Recently, DeSimone and co-workers (Tumbleston *et al.*, 2015) described an inverted-SLA system wherein oxygen is introduced at the surface of the window through a transparent, permeable window. The consequence of this oxygen is to deactivate photo-generated free-radicals which initiate the solidification process. Since the oxygen concentration is greatest at the window, there is no reaction and the growing part never attaches to the window. This “dead zone” or continuous liquid interphase (CLIP) allows for the part to be repositioned immediate after an exposure and for fresh resin to flow back in for the next layer’s exposure (Fig. 2). Further, since the oxygen concentration decreases with distance from the window, the extent of solidification increase in proportion to that distance. Thus, there is a gradient in the degree of solidification moving from the growth front to the already solidified object. Each subsequent layers then interdigitates with the prior layer(s), creating a more monolithic object with substantially less mechanical anisotropy. In theory, other reactive systems could be similarly deactivated by introduction of a suitable agent at the window/resin interface (DeSimone *et al.*, 2015). The company Carbon, Inc. was formed in 2013 based on this technology and the concept of dual cure resins (Rolland, Chen and Poelma, 2016).

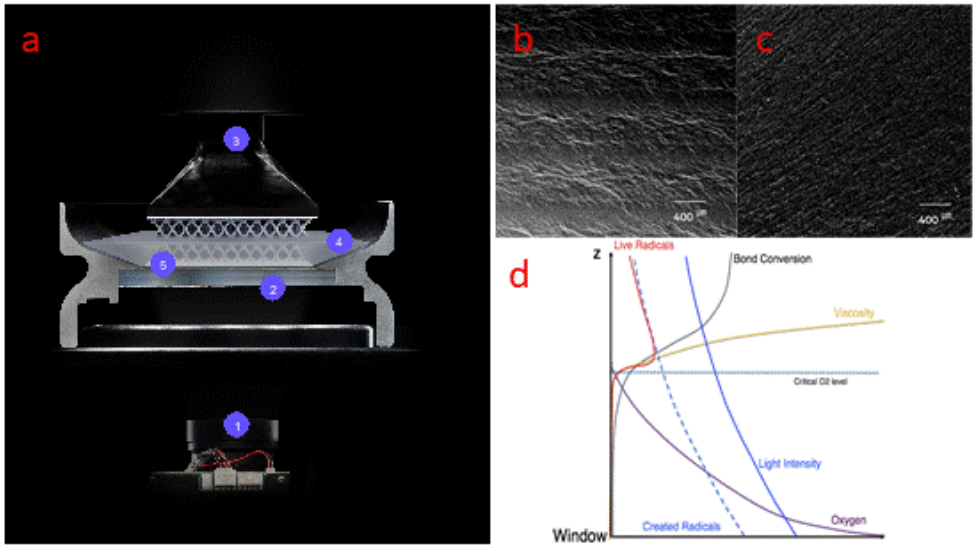

Fig. 2. a) Continuous Liquid Interphase Production (CLIP) where: 1) Light Engine; 2) Oxygen permeable window; 3) Build platform; 4) Resin; 5) Dead zone. b) Conventional SLA fracture surface. c) CLIP based print. d) Lower axis is generalized concentration; vertical axis is distance from the window. Light intensity/radical generation decreases with distance due to molar absorptivity. Oxygen concentration decreases due to diffusivity and reaction with primary radicals. Below the critical oxygen concentration (top of the "dead zone"), polymerization is possible and increases with distance from the window. Graphic courtesy of Matthew Panzer, Carbon, Inc.

As the SLA is the oldest technology it is also the most advanced and is capable of higher spatial resolutions compared to other 3D printing methods. In conventional and inverted-SLA there is a trade-off between xy resolution and build cross section. In laser-based systems, resolution is dictated by the diameter of the focused laser (beam waist) and the angular resolution of the beam steering mirrors (galvanometer). Across various manufacturers and form factors, resolution can range from a 75 to250 micron spot size. The image is "rastered" across the build plane to solidify the desired areas. Alternatively, the entire image can be projected using a large planar UV source and a digital light processors (DLP): an array of micro-mirrors which can illuminate (or suppress) each "pixel" simultaneously. For the commercially available digital light processors (DLP), these mirrors have a pitch between 8 and 14 microns. The resolution at the image plane (where the layer is solidified) is controlled by the distance of the DLP chip to the window and the imaging optics. Resolution is inversely proportional to build size. Commercial DLP-based SLA systems have resolutions ranging from 35 to 250 microns. Non-commercial systems have been

described with pixel sizes down to 10 microns, but with proportionally smaller build cross-sections.

Resolution in the “Z” or build direction is limited by the mechanical stability/reproducibility of the movement of the build platform and control of the photopolymerization process. Unfocussed light can still initiate photopolymerization and cause unwanted solidification, so light absorbing dyes and/or reactive groups in the resin serve to limit polymerization. Build direction resolution can range from 100 microns down to a few microns. Build speed decreases with increase in Z-resolution. For highly specialized applications, micro-stereolithography is now capable of building models with a layer thickness of less than 10 microns which, is limited only by the width of the concentrated ultraviolet (UV) laser or DLP resolution (Melchels, Feijen and Grijpma, 2010).

Part size limitations are related to the particular technology. For conventional SLA, the physical limitations are the volume of the build vat and the optical distortions of the focused laser as it is steered to larger angles, causing the beam waist to take on a more elliptical geometry, which can make resolution vary as a function of xy position. Prodways Technologies has overcome this by utilizing a DLP coupled to an xy stage to move the projected image across the top of the vat. The entire “layer” is projected in sections before moving to the next layer. For inverted-SLA, the mechanical properties of the window become the limiting issue. Hydrodynamic forces between the growing part and the window can cause the window to distort, necessitating slowing down the print process to allow it to mechanically recover after each print step. This problem increases as a function of window cross-section. Also, in inverted SLA, as the window size increases, the overall stiffness of the printer needs to increase to be able to handle the increasing hydrodynamic forces generated between the window and the build plate. Also, for inverted-SLA, maintaining constant resolution with increasing cross-sectional area requires either higher resolution DLPs and/or multiple “tiled” DLPs. In principle, LC shutter based systems are only limited by the technologies for fabricating larger arrays.

One of the limiting factors in the more widespread use of SLA based technologies for medical device fabrication is the limited range of materials properties and biocompatibility. Photopolymerized materials are limited in the range of physical properties they can exhibit, as they are generally non-crystalline and derived from low to moderate molecular weight building blocks. As an approach to this, Carbon has developed “dual-cure resins”(Rolland, Chen and Poelma, 2016). These use photochemistry to generate the initial 3D-dimensional object having low “green” strength. Then, a latent heat-activated thermosetting reaction is initiated by baking the part for 4-12 hours, dependent on the thermosetting chemistry and final part physical properties. Currently, polyurethane, epoxy and cyanate-ester chemistries have been incorporated in Carbon dual cure resins, leading to materials properties equivalent to those from thermoplastic elastomers to high temperature engineering resins.

In all, the polymers used must have suitable biocompatibility (Amato and Ezzell, Jr, 2015) and be able to withstand sterilization. This means at a minimum, they should be able to be tested successfully against the ISO 10993-5 (cytotoxicity) and ISO 10993-10 (irritation and sensitization)(*ISO 10993 - Biological Evaluataion of Medical Devices*, no date), to allow for extended skin contact and short-term (< 24 hours) mucosal contact. For other applications, tests such as systemic toxicity or genotoxicity of leachables will need to be assessed. While this data is not required by most regulatory agencies for the resins themselves, as they are generally interested in the behaviour of the finished device, this affords the end user a degree of security that the final device can safety utilize these materials and pass regulatory scrutiny.

These high resolutions and newer materials enable SLA to be used in biomedical applications (Chua, Leong and Lim, 2003). As such SLA printing has being used for the production of many biomedical parts. Some of the earliest applications of SLA have been in the dental space. Dentists and other oral care practitioners were some of first adopters of 3D SLA printing using the technology for the generation of dental models. While not formally medical devices, they are integral to developing solutions for dental restorations. Align Technologies uses SLA-based 3D printing to generate patient-matched templates for

the thermoforming-fabrication of their Invisalign® clear aligners(McLure, 2017). More recently, dentists and oral surgeons are using specialized software (e.g. 3Shape) and SLA-based 3D printing in the direct fabrication of drill guides to more precisely place dental implants. Lastly, Dentca developed the first FDA-approved resin for the 3D printed fabrication of denture and denture teeth. Other denture resins have since been cleared by the FDA and other regulatory bodies and a number of manufacturers are now using this approach.

Another early adopter of 3D SLA is the hearing aid industry. Most major hearing aid manufactures now fabricate the "in-the-ear" components using 3D printing, transforming a scanned image of a model or direct scan of the outer ear and ear canal. Companies like Starkey state the 98% of their hearing aids are created using 3D printing(Sharma, 2013). Hard components can be fabricated directly using resins from several manufacturers (e.g. Dreve, Pro3Dure, Vertex) or, using sacrificial "egg-shell" or "cocoon" moulds, soft components from thermally-cured silicone resins. A related therapy is the Cerezen™ intra-aural device produced by Renew Healthcare for the treatment of Tempromandibular Disorder (TMD) which places a device in the ear to restrict excessive motion of the joint('Cerezen device provides treatment for temporomandibular joint disorders day and night', 2016).

Medical models are another important area for utilization of SLA. Having models fabricated from clear resins allow for the clinician and patient to visual the relative 3-dimensional positions of organs and lesions. Using design software like Mimics (Materialise) and simple dyes, a colourless transparent resin can have specific organs and structure coloured to mark tumours, vessels and other points of interest[2].

Further uptake by the medical device industry will be driven by greater familiarity with the materials and their acceptance by regulatory agencies. FDA's recent technology guidance for

[2] https://www.materialise.com/en/blog/how-to-3d-print-multicolored-models-formlabs-sla

the use of additive manufacture bodes well for this future [3](*FDA's Role in 3D Printing*, no date). However, SLA printing inn continually finding new applications in the biomedical field, as recent case study by students and faculty at UC Berkeley utilizing Carbon's high temperature CE 221 cyanate ester resin for creating patient-matched MRI surface coils for restriction of patient motion and enhanced signal-to-noise ratio (Corea, 2016; Zamarayeva *et al.*, 2018).

Looking forward, there are a number of academic laboratories beginning to develop bioresorbable 3D printed devices. A number of groups have demonstrated tissue scaffolds for cartilage regeneration using 3D printed poly(propylene fumarate)(Luo *et al.*, 2016; Parry *et al.*, 2017). In the cardiovascular field, Ameer and Chen (van Lith *et al.*, 2016) have constructed an inverted-SLA printer using Carbon "CLIP" technology and fabricated cardiovascular stents from a novel citrate polyester. Combining novel polymers with these new high resolution SLA print technologies will lead to new therapies and better outcomes for patients.

[3]https://www.fda.gov/MedicalDevices/ProductsandMedicalProcedures/3DPrintingofMedicalDevices/ucm500548.htm

1.3 Fused filament fabrication

Fused filament fabrication (FFF), also known under the trademarked term fused deposition modelling (FDM) is an extrusion based process which is one of the most widely utilised 3D printing technologies today (Fig.). It was developed and patented by Scott Crump of Stratasys Inc. in 1992 (Masood and Song, 2004). FFF is a widely implemented method for 3D printing of solid objects (Skowyra, Pietrzak and Alhnan, 2015). With the invention of FFF it became possible to not only print functional prototypes but also to print concept models and end-user products (McLouth *et al.*, 2017)

The FFF process fabricates 3D models by extruding materials through a heated print head that moves in X and Y directions onto a stage layer by layer (Gross *et al.*, 2014). It uses thermoplastic materials which are produced in the form of a filament and then are extruded from movable head on the FFF machine and deposited in ultra-thin layers onto a substrate, translating the dimensions of digital data into an actual printed parts (Wang *et al.*, 2017). The material is heated slightly above its melting point; this is to ensure it will quickly solidify after being deposited and welds to the former layer or printing bed. Modern domestic FFF printers consist of a heated nozzle which is fed filament by a stepper motor. A chamber before the nozzle melts the material and the filament pushed into this cavity forces out the necessary amount of molten material. Common materials used for FDM include polycarbonate (PC), acrylonitrile butadiene styrene (ABS), polyphenyl sulfone (PPSF), PC-ABS blends, medical-grade polycarbonate, wax, metals and even ceramics (Kruth, Leu and Nakagawa, 1998). It is far from a perfect process as it leaves visible seam lines between layers, overhanging parts need supports to be printed below, build times are long, the resolution is low compared to other techniques. The high relative viscosity of the thermoplastics limits the use of small diameter nozzles for FFF 3D printing with maximum resolution of 40μm (Dermanaki Farahani and Dubé, 2017). This may become a considerable challenge with using fillers/active agent with nozzle clogging occurring due to reduction in flow properties or degradation of one or more components within the filament (Ivanova, Williams and Campbell, 2013).

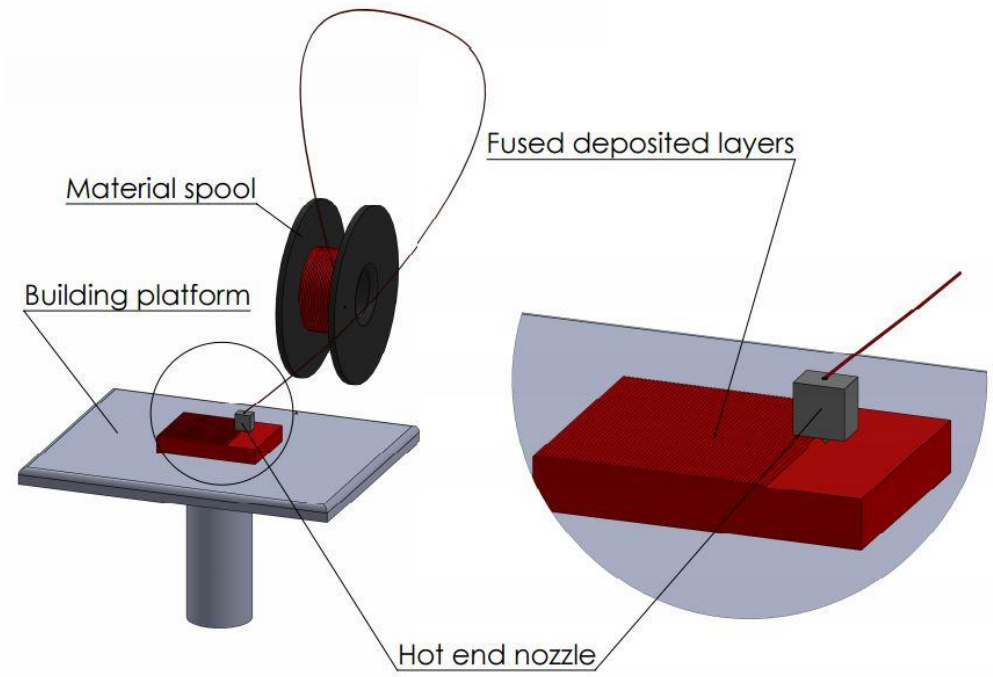

Fig. 3. Schematic of a FFF process. The filament is passed from a roll through a heated nozzle using a stepper motor where it is heated to a temperature just above its melting temperature before placement in ultra-thin layers onto a substrate

However, parts do not require chemical post-processing which is highly desirable for biomedical applications, and the material used are cost-effective and the equipment needed is considered to be simple-to-use and low-cost as compared to other 3D printing techniques (Sood, Ohdar and Mahapatra, 2010) (Bellini and Guceri, 2003).

As FFF is an extrusion based process, it can be highly versatile as in theory any thermoplastic polymer, thermoplastic composite or polymer based drug delivery platform can be used to produce parts using this process (Kokkinis, Schaffner and Studart, 2015)(Fuenmayor *et al.*, 2018). Indeed, HME is a well-established process for the production of pharmaceutical dosage forms, which ensures solvent-free production, low-cost scale-up, and enhanced solubility for poorly water-soluble drugs(Tiwari, Patil and Repka, 2016). It may also be used for the production of parts from high strength polymers such as such as Polyether ether Ketone (PEEK) and polyetherimide. The former is currently approved for use in biomedical applications such as craniomaxillafacial implants and spinal fusion cages. However, although high strength polymers are desirable for use in biomedical application, polymers such as PEEK require processing temperatures of up to 400°C which is above the capabilities of standard FFF machines thereby increasing the cost of the overall system.

In FFF some technical challenges may prevent the production of usable parts. These include low mechanical strength compared to injection moulded parts, long build time and poor surface finish (Zaharin *et al.*, 2018). Other challenges surrounding FFF include poor layer adhesion and layer delamination of the fabricated materials. In addition mechanical properties can also result from the FFF process generating void spaces between deposition lines, which adversely effects properties such as stiffness and strength (Ferreira *et al.*, 2017). These can be addressed by the post processing methods such as microwave treatment, vapour smoothing, metal plating, cold welding, gap filling, polishing, dipping, the use of resin to fill the voids, optimisation of the process parameters and structural optimisation (Dizon *et al.*, 2018)(Yao *et al.*, 2017). Li and researchers demonstrated the improvement in mechanical properties of FFF printed parts following ultrasonic treatment. These results were attributed to ultrasonic vibration causing re- entanglement and deeper interdiffusion, reducing gaps and increasing interfacial area and strength at the raster interface (Li *et al.*, 2018).

The infill density and the printing pattern significantly influence the material properties of the printed samples. The effect of these parameters were studied on the tensile, dynamic mechanical and thermoelectric properties of FFF printed conductive acrylonitrile butadiene styrene/zinc oxide (CABS/ZnO) in comparison with (ABS/ZnO) (Yun *et al.*, 2018). CABS is a mixture of acrylonitrile butadiene styrene (ABS) and carbon black residue. There was a positive impact on the electrical conductivity and thermal conductivity. However, no change was observed in tensile strength of the nanocomposite due to infill density. Samples printed in line pattern had better tensile properties with high stiffness and storage modulus while electrical conductivity also improved with line samples when compared to rectilinear samples.(Yun *et al.*, 2018). Additionally, Dul *et al.* demonstrated that the reinforcement effect of the graphene nanoplates in the ABS matrix was optimum at vertical and horizontal orientation when compared to perpendicular orientation (Dul, Fambri and Pegoretti, 2016). Mohamed and researchers developed mathematical models for FFF process parameter optimisation using I-Optimal design. Parameters such as layer thickness, air gap, build orientation show a significant effect on percentage change. This method is proposed to be used for part quality in computer generated optimal design in additive manufacturing (Mohamed, Masood and Bhowmik, 2016)

FFF may be employed in various medical applications to produce 3D parts with complex shapes because of its highly controllable channel size and porosity (Zaharin *et al.*, 2018). A common indication where this could prove advantageous is in the 3D printing of stents. Much work has being carried out in this field with PLA or variations the polymer mostly investigated (Chen *et al.*, 2016). While Coronary stents remain the holy grail of 3D printed stents, easier success may be found elsewhere where pressures are lower and failure have less catastrophic effects. An example of this was demonstrated by Mills *et al.* who successfully fabricated nasal stents by FFF in porous or mesh form made of multiple polymers in layers (Mills *et al.*, 2017).

One of the most growing area of recent research and development in 3D printing is nanotechnology. Nanotechnology can be seen in various disciplines of science and technology including the areas of polymer based biomaterials, nanoparticle drug delivery, polymer blends, nanofibers and nanocomposites (Bhatt and Anbarasu, 2017).

Nanocomposites are emerging potentially in various industries due to excellent mechanical, electrical and thermal properties. The nanomaterial can be dispersed into the host matrices by 3D printing to produce nanocomposite signifies numerous advantages due to its properties and improves the homogeneity of the product. (Ngo *et al.*, 2018). The high viscosity of the thermoplastics can be further increased by the addition of nanofillers which effects the printability of the nanocomposite filament. This can be addressed by selecting suitable mixing strategies while printing for good dispersion of the nanomaterial into the polymer matrix. Various other methods such as solution mixing by sonication and high shear mixing by extrusion can be employed to reinforce the nanomaterial into the polymer matrix before 3D printing (Dermanaki Farahani and Dubé, 2017).

3D printed nanocomposites can be created using filament which incorporate nanoparticles. Shrinking the scale size to the nano range can change the properties of the materials. A variety of nanomaterials such as carbon nanotubes, graphene, metal nanoparticles are used in 3D printing for various applications (Ivanova, Williams and Campbell, 2013). Several researches have been conducted to study the physical properties of the final printed part when they are blended with nanomaterials. Recent studies show that in FFF the mechanical properties of the filament can be increased by addition of the nanofillers with researchers

such as Healy et al. reporting that halloysite significantly increased Young's modulus 11% and 25% when the loading was two and six percent respectively (Healy et al., 2018).

Nevertheless, it has also being reported that the incorporation of nanofillers can also have adverse effects on the properties of the printed parts. Dorigato *et al.* dispersed multiwalled carbon nanotubes into an ABS matrix and conducted a comparative study of the properties of compression moulded and 3D printed materials. While the stiffness and yield properties increased by the addition nanofillers, the 3D printed samples resulted in loss of ductility and electrical conductivity due to the dependency on the printing direction (Dorigato *et al.*, 2017). Additionally, proper care is necessary during fabrication of the nanocomposite for optimised dispersion of the particles within the matrix as nanoparticles such as carbon nanotubes (CNTs) tend to agglomerate due to their large aspect ratio, chemical structure and small scale (Kim *et al.*, 2018). Functionalisation of the nanoparticles is one of the methods to overcome this issue (Chen *et al.*, 2018). However, processing through screw extrusion using high shear rates may be enough to distribute the nanomaterial without chemical treatment.

Recycling FFF parts has also shown promise. Tian et al. studies recycling of 3D printing of carbon fibre reinforced PLA composites produced by FFF. It was found that the carbon fibre reinforcement enhanced the mechanical properties of PLA (Tian *et al.*, 2016). Additionally, in a subsequent study the recycling and remanufacturing of the carbon fibre reinforced PLA composites from the previously 3D printed carbon fibre filament was assessed. Although aging of the PLA matrix was observed, the recycled composites attained comparatively higher mechanical properties with respect to originally 3D printed composite (Tian *et al.*, 2017).

1.4 Selective Laser Sintering (SLS)

SLS was discovered by Carl Deckard and Joe Beaman in 1980s (Gross et al., 2014).. It is a 3D printing technique that uses a high-power power resource such as laser to sinter powered materials (polymer, resin or metal) to build up object (Wang et al., 2017). In contrast to other Additive Manufacturing technologies, laser sintering allows the processing of almost any material that consolidates upon heating, including polymers, metals and even ceramics. High requirements of heat sources during the melting process becomes the biggest barrier to widespread use of this method. However, this challenge is lessened when using polymer

based systems as these can be sintered at temperatures which are lower than those of metals or ceramics. Nonetheless, parts produced by laser sintering can reach material properties that are close to those obtained by other manufacturing processes, such as injection moulding (Verbelen et al., 2016).

A SLS machine usually consists of a powder reserve and a CO2 to sinter the powder. As a first step, the powder bed is filled and preheated to a temperature between the melting and crystallization temperature for semi crystalline polymers and above its glass transition temperature for amorphous (Wudy, Drummer and Drexler, 2014; Shirazi et al., 2015). A layer of powder is spread across the build chamber then the high energy laser can selectively melt and fuse the thin layer of material together. The surrounding powder particles remain loose in the build chamber. As such SLS is not restricted by the need for support materials as overhanging structures can be supported by the unsinkable powder (Wudy, Drummer and Drexler, 2014; Chia and Wu, 2015). Once completed, the printing part moves down to a predefined depth usually 0.1mm and the reserve part moves up to enable a new layer of the power material spread across the build chamber by a blade or a counter rotating roller. This process repeats until the last layer has been printed (Hwa et al., 2017). After production the part is slowly cooled.

The quality of printed part is effected by a multitude of factors from powder composition and morphology, laser energy input, scan spacing and speed and processing (or powder bed) temperature (Dadbakhsh et al., 2016; Macdonald et al., 2017). In terms of powder composition much research has being conducted into the effect of powder size, shape and homogeneity as thousands of polymeric materials could theoretically be frozen below its glass transition temperature and milled either cryogenically or using standard milling processes to create powders for use in SLS. However of these materials there are only a few grades of polymers that are commercially available for use in the SLS process. This includes amorphous, semicrystalline, reinforced or filled polymers. Among these materials, semicrystalline polyamide is the dominant material used (Dadbakhsh et al., 2016). Verbelen *et al.* studied a range of polyamide (PA) grades namely: PA12, PA11 and PA6 to reveal characteristics of these materials that explain it current popularity for laser sintering in an attempt to develop guidelines that can be used for new materials. It was reported that a combination of powder availability, low initial zero-shear viscosity, and the low tendency to

warp due to a large degree of super-cooling coupled with low crystallization shrinkage were deemed to be important factors. Post-condensation behaviour also appeared to play a major role in establishing these properties. However, this behaviour was deemed detrimental for the recyclability of the powder and the consistency of part properties. Moreover, it was concluded that for SLS to become a widespread manufacturing technique, a larger variety of materials that can readily be processed is necessary (Verbelen et al., 2016). To this end the team at KU Leuven investigated cryogenic milling of thermoplastic polyurethane (TPU). The study investigated both coarse powder with rough surfaces and a fine powder which incorporated extremely fine flow modifiers. This work showed that the fine powders were easier to process and while course and fine powders were comparable in shear-punch testing the tensile properties of parts produced using the coarse powder were one third of the fine powders. As the coarse powders were 3x those of the fine powders it is clear that powder size and homogeneity are critical (Dadbakhsh et al., 2016).

Vasquez et al. also examined the characteristics of PA 12 to aid in the selection of materials suitable for SLS. In this work information on the thermal characteristics of the polymer measured by differential scanning calorimetry (DSC) and hot stage microscopy coupled with viscosity data was used to predict the viability of SLS printing of a thermoplastic elastomer (TPE) and a TPU. Thermogravimetric analysis (TGA) was utilized to determine the overall thermal stability region for the polymers. SLS printing of the selected polymer confirmed the viability of this approach for screening the suitability of materials for use in SLS(Vasquez, G.M, Majewski, C.E, Haworth, B. & Hopkinson, 2014).

1.5 Freeformer

The main drawback for additive manufacturing in the bomedical sector is that most polymers which have being approved by regularity authoritories for use in the manufacture of medical devices cannot be used without at the least the melt production of a filament. This increases cost, complexity of manufacture and lead times. Additionally, extruding of the polymer into filaments may cause a degree of thermal degradation especially in thermally unstable polymers. To overcome this challenge, the ARBURG Plastic Freeforming (APF) process was developed. This process allows the use of standard polymer granules which are commonly used in conventional injection moulding to be utilised in the production of 3D printed parts directly, without any other modification or pre-processing steps.

The APF concept of using qualified standard granulate, enables the production of parts at lower costs as there is a wide range of low-cost materials and dyes are available to choose from (Fig. 4). In principle, the APF is suitable for all melt processible resins. Indeed there are opportunities to produce bespoke polymer formulations and composites which can be used for the production of 3D printed parts through standard compounding and granulation processes. With this process there is no critical dimension as is observed with FFF where diameter variations can cause challenges in the production of parts. However, to ensure reproducible parts are produced, material qualification, and individual development work, may be necessary for any new formulation or blend. For this the most important parameters are the processing temperature and temperature resistance. This is supplemented by the layer-by-layer geometrical slicing and automatic preparation of the 3D CAD data according to quality and material-specific criteria to create a system-specific numerical control program. Aspects such as edge, filling and strength strategies as well as the build chamber temperature can also be considered. This results in pre-optimised process data for the individual material types.

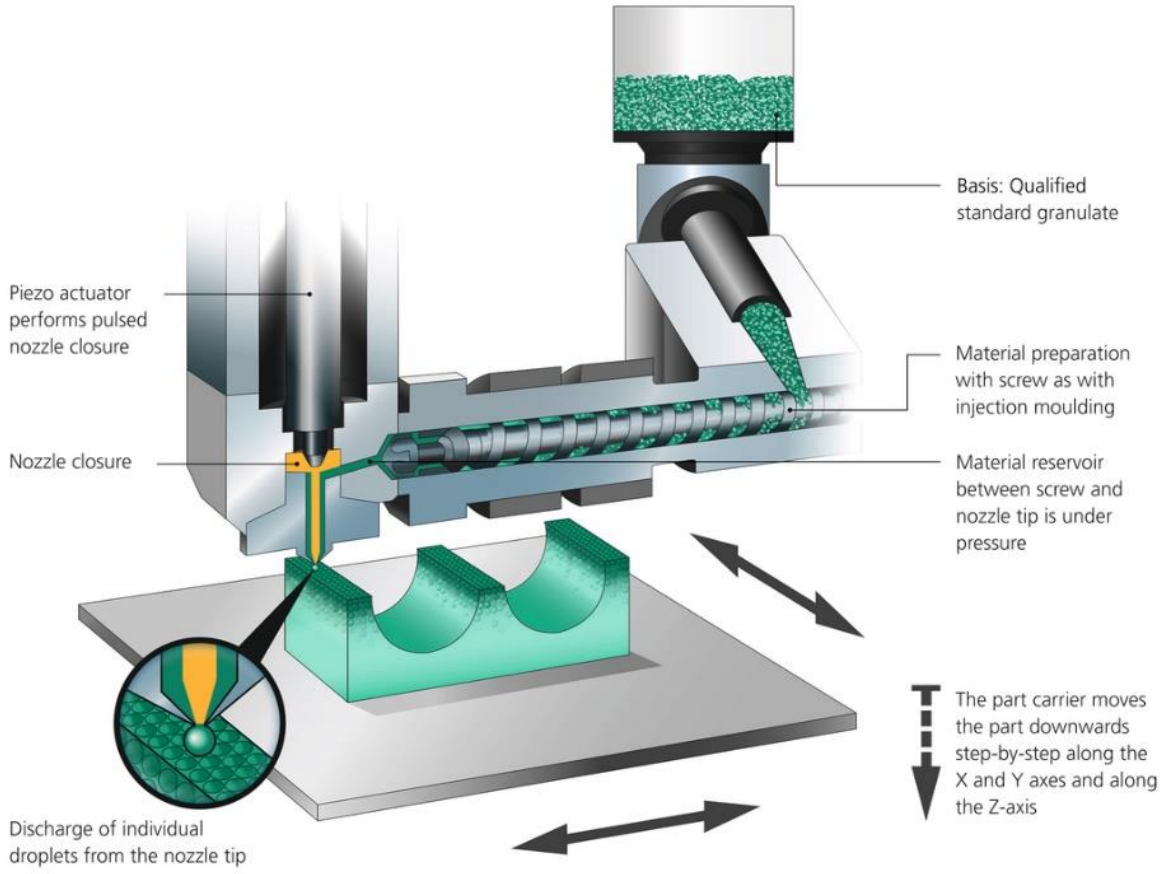

Fig. 4: The APF process principle in detail with (inset) a close-up of the surface of a part produced using the APF process: homogeneous, dense layer build-up

Developed together with the APF process, the “freeformer” is designed as an open production system. Slice and process parameters are freely programmable and can thus be individually optimised at any time. The material database for the APF process is growing continuously and includes process data for a large number of thermoplastics. These include not only the additive standard materials ABS, PC, PA12 (amorphous), but also partially crystalline PP, as well as special plastics such as the high-temperature material PEI, elastic TPU, medical PLA or biopolymers. Taking this as the starting point, modified original materials can also be used quickly and easily. In terms of biomedical implants or devices, this allows the use of polymeric materials which have previously had regularity approval for use in medical devices. The freeformer integrates material preparation with a special plasticising screw and discharge unit. Plasticising is followed by freeforming without the use of a mould where a nozzle closure controlled by high-frequency piezo technology enables extremely rapid opening and closing of the nozzle. Under a material pressure of up to 500

bar, up to 250 plastic droplets are applied per second. Three moving part carriers are positioned by means of servo motors so that each droplet is placed at the precise point. Solidification of the part is through polymer cooling where the droplets automatically fuse together as they cool in the temperature-controlled build chamber in a layer-by-layer manner.

The surface quality achievable with the APF process features a particularly even and close structure - in all directions (Fig.4). Surface quality, mechanical properties and density are determined by droplet size and process regulation (filling strategy and level). The smaller the plastic droplets and the more closely they are placed next to one another, the finer the structure and the more robust the parts. On the other hand, larger diameters and distances enable shorter build times. Depending on the available nozzle diameters (0.15 mm, 0.2 mm or 0.25 mm), the plastic droplets measure around 0.2 to 0.3 mm. The layer thickness varies between 0.14 and 0.34 mm and the minimum wall thickness is 0.6 to 1.0 mm.

The manufactured products can be used not just as reliable prototypes, but also as fully functional individual parts and small-volume batches. This opens up more efficient processes and new design freedoms when developing and producing products. Prototypes can be subjected to stress tests, for example, and the necessary product adjustments can be identified and implemented at an early stage. In the area of pre-series production, small unit volumes can be achieved using the APF method. The integration of functions by combining part production and assembly in a single process step is a further means of achieving cost efficiency. With this additive process, complete modules can be produced in a fully-assembled state. With regard to lightweight construction and weight reduction, bionically optimised parts can be designed and produced without having to factor in the technical production constraints that apply to injection moulding. In conjunction with the corresponding process regulation, the following component properties can be achieved compared to injection-moulded parts, depending on the material:

- Tensile strength is about 90-98% depending on the resin type (tensile test according to DIN EN ISO 527-02)
- Part density up to 95%

- Surface quality up to Rz = 7.84 µm / Ra = 1.69 µm

In addition the APF process can be combined with injection moulding in conjunction with Industry 4.0 technologies, this makes it economically viable to manufacture single-unit customized batches in a flexible, automated, digitally networked, cyberphysical production system. The individualisation of mass-produced products in terms of 3D geometry and functionality means that plastic parts can be enhanced in such a way as to generate added value for manufacturers. Serial production for specific jobs will commence "on demand" thanks to IT networking. An injection moulding machine and a freeformer can be linked by means of an automation component for this purpose. A digital manufacturing (DM) code applied to the part during the production process turns it into an information carrier and enables it to control its own production steps, this could also be used for part tracking for regularity purposes. The automation of additive manufacturing also reduces unit costs and improves process control. In addition to the automatic opening and closing of the hood and the loading and unloading of the build chamber with loaded parts, automated assembly with base plates or cleaning cycles can also be realised. Loading takes place with in-line measurement and automatic height correction. In addition, data is exchanged and archived at a higher level via an industrial interface. The freeformer is also equipped with several discharge units as standard. This enables functional parts to be produced using several different polymers with combinations of hard and soft polymers possible. As with injection moulding, self-dyeing is possible in master batches. In the case of complex part geometries, the second component can alternatively be used to construct support structures.

In terms of industries and areas of application, the possibilities of the APF process with its wide range of materials are virtually boundless. In the medical technology sector, for example, it can be used for the additive manufacturing of individually adapted implants and orthotics as well as models used in preparation for surgery. Another example of biomedical implants which may benefit from production using the freeformer is the manufacture of customized resorbable polylactide (PLA) based implants, conventionally used as screws or pins for securing bones and tissue. These parts are traditionally produced by injection moulding however production using the freeformer would enable these implants to be tailored precisely to a particular patient. Another opportunity would be in the production of surgical guides through the use of medical imaging to produce 3D CAD data

1.6 InkJet techniques

InkJet printing was initially described by Lord Rayleigh in 1878. It was patented by Siemens for 2D printing in 1951, however it was 2001 before InkJet printing was used for 3D printing structures (Gross *et al.*, 2014).

Inkjet technology can be dived into two separate but related 3D printing techniques. The first technology is also referred to as binder jetting, drop-on-demand or powder-liquid 3D printing. This system was developed at Massachusetts Institute of Technology in 1993 (Wang *et al.*, 2017). The system utilises photocurable polymers laid down by an inkjet head to selectively bind powders which are laid down in a similar manner to SLS 3D printing (Shirazi *et al.*, 2015). This process continues with the build bed being lowered and fresh powder spread across the surface until the final part is built. Unbound powder is removed to get the final part (Wang *et al.*, 2017). The key advantage of this technique is the flexibility of the system and processability at room temperatures. As with SLS, theoretically any polymer material in a powder state can printed using this technology. Surface porosity can be high using this technique due to unbound particles which may depending on the application be advantageous(Gross *et al.*, 2014). However, its applicability to biomedical applications may be limited as the binder may incorporate contaminates which are biologically toxic and resolution is limited (Gross *et al.*, 2014; Wang *et al.*, 2017).

Powderless Inkjet technologies such as the Stratasys, PolyJet system which can print 16 µm photopolymer layers. In this system liquid photo-polymer is heated to about 73 °C, jetted onto a surface and instantly cured with UV light. Most commercial printers contain at least two print heads similar to the ones in conventional printing, one for the support material and one for the model material. Additional print heads can be added for higher material throughput or to print multiple materials, which is one major advantage of the process (Mueller, Shea and Daraio, 2015). This system is ideally suited for the production of parts which require two or more distinct properties as combinations of resins can easily be build up within the part due to the number of heads employed. Thin layers of cured material pile up while the build tray moves down until the part is finished. The Stratasys Objet500 Connex3 is one of the most advanced commercially available PolyJet printers it is representative for the current state-of-the-art of inkjet 3D printing (Mueller, Shea and Daraio, 2015). However, as the PolyJet system is relatively new (Wang *et al.*, 2017), the number of resins available is somewhat limited and to the authors knowledge none are approved for use in implant materials.

1.7 Laminated Object Manufacturing

Laminated Object Manufacturing was developed by Helisys (now Cubic Technologies). This system generates a 3D part through stacking layers of polymer sheets. Excess material is removed with a

razor or laser which traces the desired shape. Layers are combined using an adhesive or through thermal welding (Gross *et al.*, 2014). Thermal bonding is more desirable than adhesive bonding for biomedical applications as the adhesives may be biologically toxic as was discussed in relation to InkJet printing.

This process is an important automated process used for fabrication of large composite structures in aeronautical industry (Zhang *et al.*, 2015) and in this industry is often referred to as Automated Tape Placement (ATP). Most commonly the ATP system utilises a continuous fibre thermoplastic composite tape to generate high strength composite parts. The tape is laid down in layers with pressure applied with a heated roller during bonding to ensure good contact between layers (Zhang *et al.*, 2015). Engineering materials can be utilised using this process in combination with a heated bed as if the local temperature of the bed or roller is not controlled well enough the part may delaminate due to insufficient bonding between layers or the part may suffer structural damage if the temperatures do not enable good adhesion (Gross *et al.*, 2014).

1.8 Summary

As illustrated in this chapter there are a number of additive manufacturing techniques which all have strengths the weaknesses. The type and tolerance of these machines is constantly increasing. This is due in part to the patent lapsing on the earlier techniques which has allowed new entrants into the market. This has coincided with an increase in the development of a lot of new resins for use in 3D printing as many of the new suppliers have moved to an open source resin approach.

While there are many different techniques this chapter has concentrated on the most established processes which are more likely to be used in the production of biomedical parts.

Liquid resin based systems like SLA and PolyJet are capable of the best printing resolutions. However, the resins which are approved for use in biomedical implants are limited. These systems are generally based on thermosetting polymer resins which following curing do not melt on application of heat. Nevertheless, these processes have being used for the production of a variety of products and as the material technology is developed this is set to increase.

Conversely, thermoplastic resin based systems can be used in conjunction with a vast array of regularity approved thermoplastic resins. With FFF, the challenge of delamination

between weld lines is a concern however these effects can be lessened with post production processing. The Arburg Freeformer system appears promising in this regard, however again the range of materials which can be processed using this method needs to be expanded.

SLS and Material Jetting are both based on powdered polymers they differ in how the powders are bound. With SLS thermal energy is used which Material Jetting utilises adhesives which may in themselves be toxic. However if this can be overcome both have potential for use in areas where surface roughness is desirable such as in orthopaedic implants. Similar to the previous methods Laminated Object Manufacturing uses sheets of polymers which enables the production of parts from a wide variety of polymer resins. However, these can use thermal or chemical bonding techniques similar to the previous techniques.

With this vast array of processes capable of producing complex parts with complete design freedom from a growing number of materials, it is clear that the application of 3D printing in the biomedical field will continue to grow and find new applications which will improve the lives of countless people now and well into the future.

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