FDM-based Additive Manufacturing (3D Printing): Techniques for Polymer Material Systems

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Abstract

While the developments of additive manufacturing (AM) techniques have been remarkable thus far, they are still significantly limited by the range of printable, functional material systems that meet the requirements of a broad range of industries; including the healthcare, manufacturing, packaging, aerospace and automotive industries. Furthermore, with the rising demand for sustainable developments, this review broadly gives the reader a good overview of existing AM techniques; with more focus on the extrusion-based technologies (Fused Deposition Modelling and Direct Ink Writing) due to their scalability, cost-efficiency and wider range of material processability. It then goes on to identify the innovative materials and recent research activities that may support the sustainable development of extrusion-based techniques for functional and multifunctional (4D printing) part and product fabrication.

Keywords: 3D printing; Additive manufacturing (AM); Multifunctional materials systems; Fused deposition modelling; Sustainable; Polymer-based composites.

Relevant Abbreviations:

3DP – Three-Dimensional Printing
AM – Additive Manufacturing
MFMS – Multifunctional Material Systems
VP – Vapour Deposition
DED – Direct Energy Deposition
SL – Stereo Lithography
BJ – Binder Jetting
MJ – Material Jetting
ME – Material Extrusion
ME3DP - Material Extrusion Three-Dimensional Printing
ISO – International Standards Organization
ASTM – American Society for Testing and Materials
FFF – Fused Filament Fabrication
FDM – Fused Deposition Modelling
CAM – Computer-Aided Manufacturing
CAD – Computer-Aided Design
VFR – Volumetric Flow Rate
PLA – Poly Lactic Acid
PBS – Poly Butylene Succinate
PHA – Poly Hydroxo Alkanoate
SMP – Shape Memory Polymer
CNT – Carbon Nano Tube
4DP – Four-Dimensional Printing
1 Introduction

The concept of additive manufacturing (AM) – that is most commonly referred to as rapid prototyping (RP) and free-form fabrication is governed by 3D printing (3DP), which covers a set of techniques that uses a layer by layer approach to build parts or products; usually with a small size, in low quantities, and with a complex, tailored design [1][2][3][4][5][6][7][8][9][10][11][12][13]. Such characteristics have been identified to be vastly beneficial in the biomedical industry amongst others; including the healthcare, aerospace, construction, automotive, food and dental industries [1][2][3][4][5][6][7][8][9][10][11][12][14]. 3DP requires no mould tool and offers near-net-shape manufacturing in a relatively short period of time: a feature that is most beneficial in customized part and product production while being capable of harnessing digital information for the realisation of a robust, decentralised 3D manufacturing system. Critically, there is a rising interest in the development of software for data protection and security in 3DP systems, which indicates the growing level of risks associated with their implementation; that must be tackled appropriately for the protection of intellectual property within organisations [15][16][17]. With the high demand for lightweight, more functional and cost-efficient product systems, polymer-based composites have become ‘state of the art’ in material system design and development for 3DP applications [18][19][20]. The recent levels of research and developments in nanomaterials, biomaterials, and composites, supported by improving metrological methods [21] have certainly created more opportunities for exploring potential applications for polymer-based material systems [4][18]. This is especially in the development of advanced, multifunctional material systems (MFMSs), i.e. polymer composites in the form of polymer blends, nano-based polymer composites, hydrogels, etc. which continue to be a very promising area for driving product system developments that meets the sustainability, high performance requirements of global supply chains, especially in light of toughening government regulations, and increasing demand from developing economies [22][23].

Multifunctional Material Systems in the basic sense, are material systems that have multiple functionalities that define more autonomous systems [24]. As the name implies, Multifunctional Material Systems (MFMS) usually create the possibility of using one part/product for different functions as required during application. This is achieved with the help of constituent materials that can aid the adoption of multiple mechanical, physical, or chemical, properties when desired by the user [25][24]. Material resources remain a key aspect of manufacturing systems that contributes significantly to the output of a 3DP process; just as they would in other conventional and non-conventional manufacturing processes. They are critical for manufacturing process efficiency and effectiveness, and part/product functionality, eco-friendliness, and performance [26]. Considering these, there has been an
increasing demand by industry to harness more functional and sustainable materials as candidates for future AM processes [27][28]. In general, 3DP techniques have primarily been used for applications that do not require a high level of part functionality and/or performance [29]; like in prototypes, toys, fixtures, etc., which directly implies that there are still opportunities for innovation. As a result, broadening the applicability of 3DP technologies; i.e. by developing machine-compatible, reliable and eco-friendly materials, and printing strategies that can deliver improved part functionality and performance; is understandably a goal for industrial fabrication [8][30]. Aspects related to 3DP systems and MFMSs have gained significant interest in the last two decades. The use of MFMS is a development that allows savings in the number of parts required for producing a useful product. This consequently reduces the need for joining operations that will usually have a higher time and cost-resource requirement. An effective integration/adoptation of multifunctional capabilities to a material, composite and/or structure should enable one to eliminate inefficient/ineffective product components like connectors, bulky units, etc.; thereby leading to major weight and size savings; and thus increasing system-level efficiency as desired by multiple industries. Figure 1 highlights the route to multifunctional 3D printed polymer composites, and the set of functionalities that an innovative composite, or structure can incorporate towards improving the quality and performance of products and services across multiple industries. These developments are therefore also critical for the effective realisation of the next industrial revolution (industry 4.0) [31]; characterized by increased collaboration between information and manufacturing/product systems.

Figure 1 Route to achieving multifunctionality in composite materials systems (reprinted with permission from [32]). Copyright with license number: 4700460162923.
1.1 Additive Manufacturing

Additive manufacturing is a layer by layer manufacturing paradigm, which involves using a computer-based 3D model, a 3D printer, and a post-printing step to fabricate a physical model based on the initial model design. The ISO/ASTM 52900:2015 identifies that there are 7 main categories of AM/3DP techniques available [29][33][34]. As a brief explanation of each AM technique, they include:

- **Material extrusion (ME)**, which is an AM technique in which a material heated and selectively dispensed through a nozzle to form a 3D part. Direct Ink Writing (DIW), Fused deposition modelling (FDM), and fused filament fabrication (FFF) falls into this category [6][29][35].
- **Material jetting (MJ)**, which is an AM technique (similar to stereolithography) which involves the selective deposition of a photopolymer and initiator as build material (in the form of droplets) to form thin layers that are further cured to form the 3D part. These systems use machines with an inkjet head and includes the popular polyjet machine [29][35].
- **Binder jetting (BJ)**, which is an AM technique based on bonding powder materials with the aid of a liquid bonding agent; to form the 3D part. The liquid bonding agent is selectively deposited to enable the a selective fusion process [6][29][35].
- **Sheet lamination (SL)**, which is an AM technique, which involves bonding sheets or foils of material together to form an object. Laminated Object Manufacturing (LOM), and Ultrasound Additive Manufacturing (UAM) make up the prominent technologies in this AM category [6][29][35].
- **Vat photo Polymerization (VP)**, which is an AM technique in which a liquid photopolymer is placed inside a moveable vat, and selectively cured using an ultra-violet light-activated polymerization process. Numerous lithography-based AM approaches like digital light stereolithography (SLA) as well as processing (DLP) can be classed in this AM category [6][29][35].
- **Powder Bed Fusion (VP)**, which is the AM technique, that uses thermal energy to fuse regions of the powder bed of the build material. Selective laser sintering (SLS), electron beam melting (EBM) and selective laser melting (SLM) fall into this category of AM processes [6][29][35].
- **Directed Energy Deposition (DED)**, which is an AM technique that uses a focused beam of thermal energy (e.g., in laser or plasma arc technologies) to fuse metal and metal-hybrid materials by controlled melting while being deposited. Laser deposition (LD), laser
engineered net shaping (LENS), and plasma arc melting are some of the main technologies within this category [6][29][35].

These techniques offer freedom in design (for mass product customization), waste minimisation (for lower taxes), rapid prototyping and manufacturing (for faster time to market), and ultimately a more efficient manufacturing and supply chain - as the main advantages of AM. Consequently, the development of AM and 3DP has created greater opportunities for advanced design, production, and end-user applications. In 2016, the consumption of 3DP systems, printing materials systems, software, and services amounted to approximately $13 billion, and suggested an annual growth rate of 22.3% over 4 years, amounting to ~$29 billion by 2020 [3].

Figure 2 Depicting the route in 3DP to obtain a physical model from the digital model (Reprinted with permission from [6] under the copyright creative commons attribution license)

Figure 2 shows a great representation of the basic concept of 3DP as the defining process in the AM paradigm. 3DP (the production process in AM) uses a layer-by-layer approach to build-up physical parts and products from a 3D CAD model with the help of a computer-aided manufacturing (CAM) system. Initially, (step a-b), a 3D computer model is obtained by 3D CAD design or 3D scanning, or any other available method. Next, is the slicing stage (step b-c), where a CAM software is used to obtain a model, process the model into slices, and plan the printing path (including adding support structures that aids to maintain the stability and integrity of the during 3DP). Note that the print path defined by computer numerical control codes is used by the 3DP machine to print the model. Lastly in this AM/3DP paradigm is the post-processing stage (step c-a), which occurs after the print process is finished; it usually involves removing the support structures or carrying out any other required post-processing techniques required to meet best net-shape results, in relation to the initial 3D model.
1.2 Comparing AM techniques

Table 1 helps to compare the 7 AM/3DP techniques with key information on compatible materials options, typical product feature resolution, and maximum cartesian dimensions of build volumes (found in literatures). Furthermore, it also gives a brief idea of the advantages and disadvantages surrounding their use. These points are important for understanding the capabilities of each AM/3DP technique for successful commercial applications, while also identifying their limitations. Understanding these is expected to support and drive the focus and research development of AM technologies as is required for achieving better quality processes and product fabrication.
Table 1 Comparing the typical materials, build volume, and resolution used for each AM technique (including advantages and disadvantages) [4][6][36][37]

<table>
<thead>
<tr>
<th>AM category</th>
<th>Typical materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Max. individual cartesian dimensions of existing 3DP machines (mm)</th>
<th>Typical resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vat Photo polymerisation (VP)</strong></td>
<td>Photo-polymer (acrylates and epoxides)</td>
<td>Large parts</td>
<td>Only uses photopolymers</td>
<td>x ≤ 2100</td>
<td>0.1 – 100 microns</td>
</tr>
<tr>
<td></td>
<td>Ceramics (e.g. Zirconia, alumina)</td>
<td>Very good process accuracy</td>
<td>Has a low shelf life</td>
<td>y ≤ 700</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Very good surface finish and details.</td>
<td>poor mechanical properties of photopolymers</td>
<td>z ≤ 800</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Generally high build speed</td>
<td>Expensive precursors</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Powder Bed Fusion (PBF)</strong></td>
<td>Metals</td>
<td>Relatively inexpensive</td>
<td>Relatively slow</td>
<td>x ≤ 1400</td>
<td>50 – 100 microns</td>
</tr>
<tr>
<td></td>
<td>Ceramics</td>
<td>High specific strength and stiffness of parts</td>
<td>Lack of structural integrity</td>
<td>y ≤ 1400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymers</td>
<td>(very good mechanical properties)</td>
<td>Limited scalability</td>
<td>z ≤ 500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composites</td>
<td>Powder bed acts as an integrated support structure</td>
<td>High power required</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hybrid</td>
<td>Finish depends on precursor powder particle size.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Material Jetting (MJ) | Relatively high resolution  
Large range of processing material options. | Poor reusability of unsintered powder |
|----------------------|----------------------------------------------------------|-------------------------------------|
| Polymers  
Ceramics  
Composites  
Hybrids  
Biologicals | High accuracy in droplet deposition.  
Low waste  
Multi-material and multicolor parts can be fabricated  
The good surface finish of parts | Usually requires some support material.  
Limited to photopolymers and thermoset resins can be used.  
Requires highly controllable ink viscosity.  
Limited to low-strength applications |
| x \leq 1000  
y \leq 800  
z \leq 500 | 10 – 25 microns |

| Binder Jetting (BJ) | Wide options of materials.  
Relatively high print speed.  
Relatively low cost | Produces parts with limited mechanical properties  
(inherent porosity due to limited solvent welding or chemical reaction bonding)  
Requires low viscosity ink  
Require significant post processing (e.g. infiltration process) |
|----------------------|----------------------------------------------------------|-------------------------------------|
| Polymers  
Ceramics  
Composites  
Metals  
Hybrids | | x \leq 4000  
y \leq 2000  
z \leq 1000 | ~100 microns |
<table>
<thead>
<tr>
<th><strong>Sheet Lamination (SL)</strong></th>
<th>Polymers</th>
<th>Metals</th>
<th>Ceramics</th>
<th>Hybrids</th>
<th>High speed process.</th>
<th>Low cost.</th>
<th>Ease of material handling.</th>
<th>May require -post-processing</th>
<th>Quality of part is dependent on adhesive used</th>
<th>$x \leq 250$</th>
<th>$y \leq 220$</th>
<th>$z \leq 145$</th>
<th>200 – 300 microns</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material Extrusion (ME)</strong></td>
<td>Polymers</td>
<td>Ceramics</td>
<td>Composites</td>
<td>Hybrids</td>
<td>Biological</td>
<td>Multi-material and multi-colour parts can be fabricated.</td>
<td>Inexpensive</td>
<td>Easily scalable.</td>
<td>Can build fully functional parts.</td>
<td>Parts usually exhibit vertical anisotropy.</td>
<td>Step-structured surface (poor surface finish)</td>
<td>Relatively medium-high temperature process</td>
<td>Low resolution.</td>
</tr>
<tr>
<td><strong>Direct Energy Deposition (DED)</strong></td>
<td>Metals/metal hybrids</td>
<td>The high degree of grain structure control.</td>
<td>Yields high-quality parts.</td>
<td>Very good for repairing applications.</td>
<td>Limited to metals and metal hybrids.</td>
<td>Good balance between surface quality and print speed is required.</td>
<td>$x \leq 3000$</td>
<td>$y \leq 3500$</td>
<td>$z \leq 5000$</td>
<td>100 microns – 1 cm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Very importantly, material extrusion was found to be a process category capable of using thermoplastics, hydrogels, ceramics, composites or bio-based materials to print parts. This is very unique and highlights a strong advantage over some other 3DP techniques like the DED and VP, which have more limited material options. Such a capability has been widely considered to hold significant opportunities for tissue engineering and other biomedical product developments [38][39], which identifies a possible reason for the increasing literature on bioprinting. Furthermore, considering the range of materials that are compatible with ME technologies, there is clearly a significant promise for developing advanced materials systems via AM/3DP. Other AM techniques capable of processing a similar range of materials include the BJ, PBF, and MJ techniques. However, for PBF and BJ, biological systems cannot be employed due to the harsh effects and biocompatibility issues associated with using binders. This leaves MJ and ME as the only techniques capable of processing biological systems. Between these two techniques also, MJ has a greater capability of producing parts with higher resolution and accuracy, however, it requires a low viscosity printing media, which further limits its materials to mainly photopolymer and thermoset resins. ME, on the other hand, offers more industrially desirable properties like cost-effectiveness, scalability, and a higher viscous range of processing, despite the lower resolution and higher processing temperature features of its a process. In another key aspect, BJ, PBF and ME, in that order, were highlighted to have the largest build volumes amongst those categories capable of processing a broad range of materials; thereby allowing for the fabrication of small to large-sized components. Figure 3 shows each of the 7 discussed AM process categories; identifying the state, form and suitability of material feedstock for each AM principle/category.

Figure 3. 7 AM techniques (in red), processing principles and compatible materials; with level of suitability (Reprinted with permission from [4], Copyright with license number: 4692830626888)
From Figure 3, we can identify polymers to be highly suitable with all AM process techniques, except for PBF and direct DED. More importantly, in the consideration of polymer composites; only ceramics are identified to be suitable in a polymer matrix. They were also found to be only compatible with printing with the ME and SL process techniques. Clay, glass, and cement are good examples of ceramics, which can offer semiconducting, superconducting, insulating and ferroelectric properties depending on composition. Therefore, their compatibility with the material extrusion process highlights unique advantages and motivations for material and process developments that can potentially yield better functional products in . These findings also highlight the material limitations associated with manufacturing polymer composite systems; as it offers sheet lamination as the only alternative to the versatile ME process. This is likely due to the different temperature-factors associated with processing the different material classes (i.e. metals, polymers, and ceramics). In an attempt to further assess the features of all AM/3DP techniques, Figure 4 below presents critically reviewed factors during the printing operation. Three parameters, including energy, speed, and resolution, which are very important for affecting part quality, time and cost efficiency, and process eco-friendliness, were compared. As observed, ME techniques were identified to yield next to the lowest resolution (i.e. between 10 and 100 elements/mm$^3$); only outperforming the DED technique. In another case, the ME3DP technique was found to use significantly less energy than all other techniques, except for the BJ technique, however, MJ also appeared to have similar energy than. Lastly, in the case of speed, which is greatly significant in high throughput manufacturing applications, ME critically comes up as the slowest 3DP technology; slower than both the BJ and MJ processes especially.

![Figure 4 Comparing operational and feature factors of the 7 AM/3DP techniques (Reprinted with permission from [4], Copyright with license number: 4692830626888)](image-url)
The development of AM/3DP technologies has taken several routes; involving printer technology and material system variations [8][40], which helps to deliver a wider range of possibilities for product system manufacturing. However, ME3DP has been, amongst all other AM technologies, found to be the most popular, cost-efficient, and easily accessible technique for the realisation of a decentralised, agile 3D manufacturing future. Furthermore, with the incorporation of robotic systems as a resource for manufacturing processes, a hybrid 3D manufacturing system; which is enabled by the growing capability of executing multi-machines and multi-material processes [33][34]; can have significant advantages for the production of advanced electronics and devices [33][34].

As a concept, 3DP and AM techniques have been present since the 1980s and have been the building block for developments like rapid tooling/prototyping. However, more recently there have been developments in the area of ‘bioprinting’. Figure 5 highlights the recent trends in AM-based publications ending in 2016. It also highlights the publication trend by 3DP technique for the top 4 publishing countries, amongst others.

![AM global research trend](image)

Figure 5 Recent trends in publications covering key AM areas (Reprinted with permission from [6] and [41] under the copyright creative commons attribution license).

The recent development of bioprinting has been backed by a rapid increase in research publications for at least a decade ending in 2016, since its interest surfaced [6]. This is likely supported by other recent developments in advanced material systems (composites and nano-composites), biomaterials and biomimetics. These advanced material systems give hope to greater possibilities in product design; specifically within the healthcare, dental, packaging, automotive, and aerospace industries [42][30]. In the healthcare industry, current and prospective developments in materials systems and bioprinting is suggesting that considerably high revenue is to be expected (~$1 billion) to come from the medical, dental, prototyping, and prosthetics printing sectors alone by 2020 [3].
1.3 Achieving Sustainable Developments in AM/3DP

Achieving environmentally sustainable solutions has become a very important topic for the global community; so important that investors, CEOs, managers, and other business leading professionals have AM as a key subject of focus within their businesses. Consequently, there is also a growing awareness of the public community towards issues of sustainability; a factor, which is also expected to affect the choice of products and services that attract the market. AM techniques and technologies have seen rapid growth in interest as a technology with disruptive potential. The adoption of AM has been widely accepted to introduce flexibility, reduce material waste, and deliver rapid manufacturing at a lower cost than traditional manufacturing methods (e.g. machining and injection moulding) when manufacturing complex/bespoke parts/products. In essence, AM is capable of cost-effectively improving innovation, production, and service lead times, whilst delivering a high level of flexibility to manufacturing. This enables a decentralised manufacturing system that enables more efficient, effective and agile manufacturing systems to be deployed; especially when in collaboration with other existing manufacturing paradigms. Figure 6 below gives a good reflection of the industries applying AM and 3DP (right); with the most common applications for which AM is being used within these industries (left). The medical/dental, consumer products/electronics, industrial machines, aerospace, and automotive sectors were found to be prominent industries involved with AM. Hence, as AM can be considered to deliver various forms of business solutions, partaking organisations within these industries, therefore, have a vitally responsible role to play in the development of AM technologies; using material systems and processes that are eco-friendly and sustainable.

Figure 6 Industries applying 3DP technologies (left) and some of their popular product and/or service applications in AM (right). Reprinted with permission from [6], under the copyright creative commons attribution license.
1.4 Limitations to AM/3DP

The rapid development of AM technologies has been a key limitation to its development as this is leading to the lack of specific design principles, manufacturing guidelines, and standard that guides AM. These challenges are more relevant when considering the fact that advancements, for example in materials processing and optimization, generates a positive feedback effect, which introduces new changes within a system; thereby making these guidelines, principles, and standards more difficult to define. This is a challenge that needs to be tackled strategically, maybe by meeting the requirements of AM system users within specific industries and niches.

Following a production process in AM or any other manufacturing paradigm, inspection and quality assurances are critical next steps used for ensuring high part and product quality for its users and the environment. These are the cornerstones of ancient as well as modern manufacturing; a narrative that is considerably new for AM. Following a survey by PricewaterhouseCoopers (PwC), almost half of the manufacturers that were surveyed highlighted that ‘uncertainty in the quality of the final product’ has been a barrier to their adoption of the available AM technologies [4]. This was a key finding that further suggests that the measurements (metrology) that underpin key aspects of inspection, monitoring and part/product quality assurance are not well developed. This may be linked to the effects of a rapidly developing sector, as it is with the case of limited ‘standardization of design principles’, ‘manufacturing guidelines’, and best practices.

The limited range of commercially available materials for commercial to home-friendly AM technologies [43][44][45] is also a significant setback to AM advancement. The FDM technology is the most suitable for home-friendly printing and with only specific filaments available, commercial and casual users can find it difficult to print parts that deliver the desired property or set of properties required for a function.

Another significant problem in the development of 3DP, especially for mechanically functional requirements, is the fact that printed parts are largely anisotropic [4][6][46]. Because of this, achieving isotropic AM parts, or understanding anisotropic behaviours better will enhance the potential for the adoption of 3DP for structural product fabrications.

1.5 Review Focus

Considering the points made so far, it is very important to raise the awareness of polymer-based materials as being considered the most attractive and commonly used material. In high-waste generating processes, it is however an environmentally concerning class of materials used globally; as it has low-cost and lightweight characteristics [47][48]. Furthermore, the prospect of high or increasing population demand and the reality of increasing government regulations creates concerns that would require sustainable ‘material and process developments’ for the benefit of the ecosystem, while also meeting the
sustainable and functional demands of several industries. Hence therefore, this article aims to critically review the ME3DP technique, and their use in printing functional and multi-functional polymer-based material systems; as machines and materials systems play the crucial roles in developing sustainable and robust decentralised manufacturing systems. The potential synergy that can be obtained from developments in machine and material systems are identified to be capable of leading to significant improvements in environmental sustainability; in the key areas of reusability, recyclability, recovery and disposal of products at their end-of-life, while being potentially capable of supporting a variety of standard or customized product and service quality improvements.
2 FDM: The Underlying Technique for ME3DP

Extrusion-based AM methods generally run a process where a feedstock (usually a pre-formed filament) is fed to the head of the printing system by an electrical or hydraulic motor-controlled pinch roller mechanism [49]. In the head, the filament is heated and extruded in a molten filament material form onto a platform to create a 2D layer. Repeatedly, this 2D layer, one on top of another creates a three-dimensional part that is representative of a design specification [3][49][50]. In other words, material extrusion techniques, which is based on fused filament fabrication (FFF) along with fused deposition modelling (FDM) processes [51], can be described as a 3DP manufacturing technique involving a thermoplastic material (in filament or pellet form) being extruded through one or more heated nozzles [51]. The viscous material or melt emerging from the nozzle(s) is deposited on either a moveable or immoveable build plate, before solidifying to form a part, with dimensional accuracy in the order of 100 μm [45]. Direct Ink Writing (DIW), which are considered more advanced extrusion-based processes, have been considered as relevant for delivering smarter, eco-friendlier, and more bio-compatible parts. According to [52], intimately blended colours and materials cannot be achieved in the process design of FFF or FDM processes, hence making other ME3DP (i.e. FDM technology developments, e.g. DIW) invaluable options for meeting greater product quality demands.

2.1 FDM Machines & Developments

The co-founder of Stratasys, Scott Crump, patented the name: fused deposition modelling (FDM) in 1989, and in recent times, FDM-based 3D printers have emerged as the most popular 3D printers used in printing thermoplastic polymers and composites [3][53][54]. Industrially, FDM machines (see Figure 7) are also considered to have significant advantages for cost-efficiency and simplicity [55].

![Figure 7 Typical FDM machine design with a printed part on an immovable print bed/hot plate (Reprinted with permission from [56] under the copyright creative commons attribution license)](image)
An FDM machine can be directly related to conventional, extrusion-based polymer processing machines [57]. In its basic form, the FDM technology uses only a thermoplastic filament as its material option [58]. The printer head, which holds the heating element, extruder, and nozzle, operates at a relatively high temperature (150 – 250 °C) before extruding and depositing the molten thermoplastic material to form 2D layers and consequently, 3D printed parts. As seen in Figure 8 below: each unit of polymer extruded is considered a road/bead and shows swelling effects that must be controlled partly by adequate heat distribution for the printing of dimensionally accurate parts. Also, prior to deposition, buckling or the structural failure of the filament may occur too and highlights other aspects of the FDM process that must be controlled correctly. The ability of the extruded material to maintain a predetermined diameter, shape or structure throughout the printing stage is an important point to consider.

Figure 8 Important aspects in material flow during an FDM process (Reprinted with permission from [45] under Copyright creative commons attribution license)

The simplicity of the actual process has led to rapid adaptations being made to suit developing material systems other than thermoplastics alone. Figure 9 shows the different forms in which FDM machines have been adapted for the production of multi or composite material systems and parts.

The single head design of FDM machines is the basic form of the technology, allowing only one material system to be printed at relatively high processing temperatures. When a compatible polymer-based composite material system (usually polymer blends) is obtained as a filament; composite blends
can be printed in this way, hence obtaining a composite product. Alternatively, printing can be done on a reinforcement material, which can be introduced by another external system like a human or robotic/automated system.

Figure 9 Development of FDM for advanced fabrication capabilities [5]

Dual head FDM printers make the production of polymer composites a simpler problem to solve as they can alternate the printing of two material systems. These printers offer the capability of printing with support structures. It can also be applied in the printing of layered and skeletal based composites. Additionally, in special cases, multiple parts can be printed faster by using both printer heads simultaneously, and will therefore, lead to at least a 50% improvement in time-efficiency, thereby making it a great option for small-sized, multiple component fabrication activities using FDM.

The in-nozzle impregnation technique is a recently developing type of ME3DP method similar to FDM that introduces the heated reinforcing material (usually fibres) into the nozzle head to facilitate
better mixing and incorporation of the fibres into the polymeric filament matrix [8]. These are strongly developing as a unique option for printing short and continuous fibre reinforced polymer composites (FRPs) [59], but currently, lack significant evidence for industrial adoption [60][21].

These have also further led to greater interest in the development of processes that allow advanced composites, and bio-based materials to be processed correctly. 3D bio plotting and direct ink writing are examples of other forms of ME3DP techniques that have been more recently developed via the process and material optimisation of the FDM technology; to deliver parts and products with more advanced material systems, and for bioprinting applications [61]. In DIW (also referred to as Robocasting), which is heavily utilized in mesoscale and micro-scale structures; a liquid-phase “ink” is dispensed out of small nozzles under controlled flow rates and deposited along digitally defined print paths to fabricate the desired 3D structures [21][62]. In the case of bioprinting, extrusion or FDM-based printing technologies are modified to be capable of printing biological systems like organs and tissue scaffolds and is a developing area of extrusion-based 3DP with major interest according to literature findings [38][39][61][63]. Uniquely, these methods follow the same extrusion principle as in FDM but can process materials with higher and lower temperature and physical property processing requirements.

As earlier discussed, achieving a 3D printed part involves creating a part or product from a 3D computer model; either designed in 3D software or scanned using any available scanning methods (e.g. CT and MRI scans). This is the same for all the AM methodologies. However, in the use of a specific 3DP technique (considering their post-printing processes), there is a need for the 3D manufacturing system to be tailored to that specific 3DP category. This will enable the appropriate ‘design of configuration’ and ‘control’ that affects the specific 3D printing process. In light of this, the following sections discuss, from the viewpoint of an AM process design, the configuration and control factors of CAM systems, 3D (FDM) printer and material resources in a ME3DP process. These sections cover the actual 3D printing process (including insight into the material feedstock and filament production process). These should extensively help the reader to gain a improved understanding of the process aspects and technicalities that affect the final part quality of ME3DP processes.

2.1.1 Factors Affecting the FDM process: CAM, FDM Printer and Material Resources

Below are factors that are responsible for the quality of parts produced in the ME3DP (FDM) with respect to the design and control system, printing process; as they affect process quality, surface finish, mechanical properties, and dimensional accuracy of printed parts and/or products. Highlighting these gives a good breakdown of key factors and aspects to consider during experimental review and future experimental design processes (see Table 2). They cover all the main aspects of computer design,
machine, and material design; used in most manufacturing processes to define the part or product output.

Table 2 Important resources factors and key aspects of the ME3DP process [3] [7][49][64]

<table>
<thead>
<tr>
<th>Factors</th>
<th>Aspects</th>
<th>Affecting</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAM: Design &amp; information system (i.e. Control system)</td>
<td>• path planning,</td>
<td>• Part surface finish</td>
</tr>
<tr>
<td></td>
<td>• part orientation,</td>
<td>• Part mechanical properties</td>
</tr>
<tr>
<td>Machine (FDM or FFF machine)</td>
<td>• speed of 3D dispensing or filament feed,</td>
<td>• Part dimensional accuracy</td>
</tr>
<tr>
<td></td>
<td>• pressure and temperature gradient,</td>
<td>• Process efficiency and effectiveness</td>
</tr>
<tr>
<td></td>
<td>• nozzle design,</td>
<td></td>
</tr>
<tr>
<td>Materials</td>
<td>• die swelling,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• long-chain branching,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• melt viscosity,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• crystallization rate of melt material,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• shear-thinning induced by tailored molar mass distributions,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• addition of stabilizers and other additives,</td>
<td></td>
</tr>
</tbody>
</table>

2.1.1.1 Computer Aided Manufacturing: for part and process design & control

A CAM system is an embodiment of part and process design system software and/or functionalities, which typically enables a streamlined part production process - from part design to production. CAM systems allow the user to importantly control the part/model design, and process parameters, which ultimately determines the quality of the ME process, and especially the printed part quality. Prior to printing, the CAM system uses a CAD or 3D model (in tessellated file format, e.g. .stl) to define a tool-path (in G-code) [49][50]; which is to be followed by the nozzles’ tip during the extrusion and deposition stage of the 3DP process. The G-code is a computer language that can be understood by CNC-based machines; such as those used for extrusion-based processes [49][50]. Other processing information regarding the individual fibres’ width and height can be set before or after printing starts, assuming in the latter case, that a preferred value is realised to be more beneficial for the printing process. Various deposition strategies can be exploited and developed during the slicing stage with several parameters available to the user. Once a strategy has been developed and set in the slicing
software (e.g. Cura, Quickslice, etc.), slices (i.e. cross-sections of the part model) is developed in the CAM system, and a tool path is defined as a G-code; before being communicated to the extrusion-based 3D printer [49][50]. If support structures are desired, they can also be included prior to slicing the model. Essentially, as the varying process factors are updated, the tool path and G-code are updated accordingly; to reflect on orientation, size, or any other process factor change that causes a change in point location. The tool path and G-code should, therefore, be well considered, as they have a significant effect on the thermal stress accumulation in the deposited fibres. This signifies that when various CAM programs using the same inputs may produce parts with different responses to the environmental stresses experienced by the extruded fibres. In a study by [64], an open-sourced G-code program, Slic3r 1.2 was used to fabricate specimens. Another G-code program, Voxelizer 1.4, with a differing G-code generating algorithm, was used with the same input values for tool path and process parameters as the Slic3r 1.2; to check the effect that different CAM programs have on the properties of the final printed part [49]. It was found that specimens created with the different CAM programs exhibited different fracture morphologies [49]. Therefore, in choosing a successful printing and deposition strategy, the tool path and G-code must be optimized for a specific set of CAM and 3DP machines so that more reliable sets of results can be obtained for improved part quality. Usually, a good deposition strategy is to deposit continuous contours of the 2D-layers boundary for a given cross-section of the 3D model, before filling the spaces in between them with a choice of infill patterns [50]. This could enable the design of deposition strategies that suites a desired mechanical property.

### 2.1.1.1.1 Part orientation & path planning

The part orientation of a part; in relation to the infill orientation and to the printing system’s main axes of movement for Cartesian 3D printers plays an important role in the mechanical behaviour, dimensional accuracy and surface finish of printed parts” [49]. Also importantly, part orientation can further define the need or extent to which support structures are needed, which is important for managing the cost efficiency of the process.

An important aspect of path planning is the choice of infill patterns. When using a rectilinear pattern, each individual layer is filled with a raster (see Figure 10) of parallel roads with the next adjacent raster layers at a fixed alternating angle of 90° (see Figure 10) between them. Adjusting the infill density, affects the level of occupied space in the hollow sections of the part, and can therefore create a scantier or denser part with bigger or smaller distances between the extruded fibres/roads. [49]. A slightly negative raster to raster distance; corresponding to fibre overlapping, has been found to limit void density and increase the contact area among fibres, hence leading to stronger fibre-to-fibre bonds. However, on the other hand, the excessive build-up of polymer material at the layer’s perimeters can
significantly affect the dimensional accuracy of the part in the XY plane. This, therefore, highlights the sort of considerations to make when deciding on the many factors in FDM or ME3DP processes.

![Raster Angle](image)

Figure 10 shows a raster of parallel roads deposited to form a layer. Also shows the raster angle of relative roads in a rectilinear road pattern Reprinted with permission from [45] under the Copyright creative commons attribution license)

2.2 The FDM Production Process
The FDM printing process was considered to generally involve three main stages; highlighted below: i.e. pre-deposition, deposition and post-deposition, as a means of gaining a better understanding of the processing factors involved throughout the FDM part production process.

![Pre-deposition, Deposition, Post-deposition stages](image)

ME3DP techniques are similar to conventional extrusion processes, using the same mechanism as in other extrusion-based manufacturing processes like injection moulding. However, in the case of ME3DP, moulds are unnecessary, and the extrusion nozzle is vertically mounted. They are however both significantly temperature-dependent processes; requiring relatively higher energy input at the pre-deposition stages of the process - to achieve better control of the feed material’s rheology.

The pre-deposition and deposition stages, respectively involving ‘filament in-feed’ and ‘molten material flow through the melting reservoir and nozzle’ of the print head is a pressure-driven flow of material mass (non-Newtonian polymer melt). This controlled flow is mainly related to:

- nozzle geometry [34][45][49].
• pressure gradient [34][45][49], and the
• melt’s apparent viscosity, and can, at the point of extrusion, be described to be a fully-developed laminar flow of polymer through a capillary die with a generally circular cross-section [34][45][49].

The desired pressure for polymer fibre extrusion is applied by the pre-heated parts of the 3D printing filament, acting as a piston as it is being pushed by a pinch-roller feeding mechanism into the melting reservoir of the printer head [49]. This helps in a successfully controlled extrusion and deposition process of semi-molten thermoplastic fibres on a fixed or spatially translatable platform. Some important process parameters, using example values for PLA include: filament feed velocity (e.g. 15-30mm/s), extrusion temperature (e.g. 160-210 °C), cooling rate (e.g. 20% cooling fan speed), print bed temperature (e.g. 0-60 °C), print area/chamber temperature (e.g. 0-60 °C), and volumetric flow rate (VFR in m³/s or mm³/s). As printing initiates, the rate at which the filament is fed to the liquefier/melting reservoir (i.e. feed velocity) is dynamically controlled and connected to velocity changes of the print head, thereby allowing the printing system to maintain a constant material VFR. The amount of melt material that is present in the reservoir chamber, the melt temperature, and consequently, the viscosity and surface energy of the melt are inherent material factors that controls with feed rate/feed velocity of the extruded molten polymer. On extrusion, the print head generally exhibits a constant linear movement; where the extruder motor within the print head is set at a speed that is proportionate to the printing speed, therefore enabling an indirect control of feed and extrusion velocity of the thermoplastic polymer material.

Consequently, the extrusion temperature and feed/deposition rate represent the most important process parameters influencing the inter-layer and intra-layer bonding of deposited roads as each fibre layer is deposited on a previously deposited layer/road of material [45][49]. Once an extruded fibre makes contact with other previously deposited roads, heat exchange by conduction occurs; and by convection and radiation with their surroundings to facilitate or hinder the bonding process. This consequently creates new physical-chemical interactions that lead to the formation of bonds among individual fibres via a complicated heat and mass transfer phenomena, which also causes phase changes, and thermal and mechanical stress within the printed structure and material fibres. During the heat transfer and bond formation process, air traps can also be developed between contiguous filaments depending on the level of bonding achieved. The degree of bonding depends on the neck growth between adjacent fibres, and the random molecular diffusion at each interface [34][45]. When heat transfer and bonding processes are limited, partial bonds are created, which consequently leads to a printed part with inherent pores - hence producing a part with lower integrity. This phenomenon, which
occurs after the deposition (i.e. post-deposition stage) is a critical stage of the process where the printed fibres or roads can be further controlled by thermal, chemical and/or atmospheric conditions surrounding the print bed are and highlights the extent of control that can be achieved during the FDM process. This post-deposition control feature can be used during the ME3DP process to address issues like air traps, non-uniform cooling and poor inter or intra-layer bonding.

According to [56], the extrusion process particularly affects the maximum strain, because during material extrusion through the nozzle; the polymer chains are subjected to stress-induced orientation, that reduces the elongation characteristics of the extruded material, hence leading to the development of anisotropic properties. In a typical case of FDM-printed parts showing anisotropic properties, fully dense PLA blocks were fabricated [65]. In another case where printed parts were obtained using a RepRap printer that used the same FDM-based technology, can match and even outperform commercial 3D printers in terms of the tensile strength (for the same polymers); [66]. However, the tensile strength test results obtained for these parts fluctuated when a large sample set was observed, thereby suggesting the ease with which slight changes in fabrication method and resources specifications can affect the reliability of printed part quality. Although composites like polymer blends use similar polymeric materials, the nature of polymer composites and nanocomposites are different.

In summary, an AM part is created by superimposing a predefined number of 2D layers in a pattern defined by a G-code. The printer head uses the G-code for each 2D layer to generate a specific pattern of fibres (with predefined widths and heights). Achieving a functional, robust part involves optimum control of filament production, 3DP extrusion temperature, deposition rate, and print-bed area conditions (pressure, temperature, etc.), amongst several other factors that favour the best inter and intralayer bonding of a given material system. These factors will also have implications on the total print time, which is an important factor when considering the cost of production, and other resources available for the job.

### 2.2.1 Potential Part Limitations with FDM

The most common challenges or drawbacks associated with printing parts with the FDM technology include:

- **Stepped layers** [5][54]: these are visible trails of the material deposited because of a certain distance among subsequent layer’s edges. Through reduction of the diameter of the extruder, this effect can be minimised by and/or printing lower layers and. However, it will also lead to longer print times and more material usage, which increases the cost of the process.
• **Overhang and bridging** [5]: this is an overhang effect, which occurs when elements of a part set at an angle comparative to the vertical axis; the filament may not have support, thereby leading to a collapse. In these cases, support should be generated at the model preparation stage to prevent the part from breakdown and damage during and after printing. A bridge is highly similar to an overhang but has support at both ends. Therefore, a bridge characterised by a long overhanging part is a big problem, which usually requires auxiliary supports added during the design stage and subsequently removed through the final machining of the print.

• **Stringing** [5]: this is an issue that occurs when the extruder is moving between two discontinues points and leaks some of the plasticised filament from the nozzle due to gravitational forces or loading from the filament. Improving this effect usually involves an appropriate retraction of the filament back into the nozzle; to limit any acting forces.

• **Warping** [5]: this takes place when the edges/ corners of the model deflects because of shrinkage of material and uneven temperature distribution across the model. This is a popular issue with polymer-based fabrication processes like injection and compression moulding, We can partly counteract the warping effect by controlling the cooling rate, and other temperature settings, An alternative method has involved putting a Kapton tape on the print bed surface, as this was thought to likely limit the transfer of heat.

• **Hygroscopicity** [5][54]: this is a term, commonly used to refer to occluded or precipitated porosity is a property of polymer materials that makes them more prone to absorbing moisture from the air, thereby leading to parts with more inherent pores.

• **Structural inhomogeneity** [5]: this is referring to the heterogeneity of structure particle size and/or insufficient density of a printed part. It is connected with the filament’s selective deposition on the bed surface, with differing temperature and road-bonding effects (i.e. inter-layer and intra-layer bonding). Reduction of the length among the spits of the filament could minimize this [5]. However, faulty or inaccurate nozzle performance may also hinder improvement.

### 2.2.2 Material Feedstock for FDM

The most frequently used materials for FDM or FFF machine processing are acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) [67][68], having typical bulk strengths between 30 - 100 MPa, and elastic moduli in the range of 1.3 - 3.6 GPa [45][69]. Other polymeric material option used includes polycarbonate, polyamide, high-impact polystyrene, poly-oxymethylene and others. In achieving the material extrusion process, a form of material feedstock; either in the form of pellets or
filaments is required. However, filaments are very common for the FFF and FDM processes. Table 3 shows the majority of commercially available filament stocks, which also further highlights, the material limitations to ME3DP. It is important to note that these values can differ depending on the supplier, and their specific filament fabrication methods. This is important because mechanical properties can diverge meaningfully from the bulk material properties because of the specifics of the process and part design (Blok et al. [45]), hence also highlighting the need for more standardized research and experimentation in the development of ME3DP operating procedures that yield reliable parts.

Table 3 Commercially available filaments [53][69]

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ASA</td>
<td>33</td>
<td>2010</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>ABS-ESD7</td>
<td>36</td>
<td>2400</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>ABSi</td>
<td>37</td>
<td>1920</td>
<td>4.4</td>
</tr>
<tr>
<td>4</td>
<td>PC-ABS</td>
<td>34</td>
<td>1720</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>ABSplus-P430</td>
<td>33</td>
<td>2200</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>FDM Nylon 12</td>
<td>48</td>
<td>1310</td>
<td>6.5</td>
</tr>
<tr>
<td>7</td>
<td>PC</td>
<td>68</td>
<td>2300</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>PPSF</td>
<td>55</td>
<td>2100</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>PLA-3052D</td>
<td>62</td>
<td>2050</td>
<td>3.5</td>
</tr>
</tbody>
</table>

ABS, ABS blends, and other petro-based thermoplastic blends have generally been the most frequently encountered materials in FDM before PLA emerged and joined the group as a more recent and promising material for filament fabrication. PLA is very promising because of its biodegradable characteristics [49][70]. PLA was identified as the most-used renewable polymer in tissue engineering because of a variety of benefits such as biocompatibility, low cost, nontoxicity, excellent mechanics, biodegradability, ease of processing, and the green feature of its synthesis routes (from renewable resources) [38][71]. PLA is gradually making up more of the FDM 3D printing feedstock, and although the just-mentioned benefits of PLA render them suitable for broad applications in biomedical and pharmaceutical areas, it also has some disadvantageous properties. These include its lack of cell motif sites, hydrophobic nature, small particle size, low ultimate elongation strain, and the generation of acidic by-product during degradation; some of which could induce foreign bodies or cause clinical
complications [70]. As these may lead to the limited use of PLA in biomedicine, there are increasing efforts to enhance the hydrophilic properties; increase the cell motif properties and introduce less acidic bioactivities; aspects that should be strongly considered in future research and development activities.

2.2.3 Filament Production

A filament production process uses a single or twin-screw extruder to extrude a filament with specified diameter tolerance; based on the screw extruder’s nozzle design, and the FDM 3D printing machine used. Considering this, the adjustable screw speed, pressure, and temperature were found to be the key parameters during filament production; that must be well controlled to achieve the target diameter of the required pre-formed polymer-based filament [49][72]. These offer the route to achieving optimum extrusion values for the filament production process. More specifically, the 3D printing filament should have the capability to provide as well as sustain the pressure needed to achieve a successful extrusion process. However, failure to do this results in filament buckling that occurs at the stage when the extrusion pressure is higher or lower in comparison to the critical buckling load that the filament supports. In such cases also, load carrying ability of the filament determines elastic modulus, while the resistance to extrusion (or extrusion pressure) is determined by the melt viscosity.

Choosing the right filament material for achieving process efficiency and effectiveness would involve using material systems with favourable and controllable physical-chemical, rheological, structural and mechanical properties [7]; considering their effects on printability, applicability, and post-processing [7]. These key material factors are highlighted below:

![Figure 12 Material factors to consider in ME3DP (reprinted with permission from [7], Copyright with license number: 4692831280732)]
In highlighting some of the critical physical-chemical and rheological properties identified above, wettability is the ability of a polymer to wet another solid surface that it comes in contact with. This is defined by the wetting angle, of which angles greater than 150° indicate superhydrophobicity, while angles less than 5° indicate super hydrophilicity [73]. Essentially, the ability of a polymer to wet another surface improves its bonding capability, which is important in the interlayer bonding of polymer roads during ME3DP. Viscosity, which is another critical factor in ME3DP, is defined as the ‘resistance to flow’ of a given material, or polymeric material in this case [74][75]. It is the governing characteristics of polymers in ME-based manufacturing, which defines the ability of the polymer to maintain a desired flow property while in transit from the heating chamber, through the nozzle, and onto the print bed; The strength of the intermolecular bonds between individual polymer chains in a polymer significantly defines this property; with stronger bonds leading to higher viscosities, and vice versa. In another case of polymeric properties, the isoelectric point (pI) of a polymer is defined as the pH at which the polymer has a net charge of 0 (i.e. a neutral charge) [76]. Acidic polymers have a higher pI, while basic polymers have a lower pI. This factor will also define the electrostatic behaviour of the polymer during a ME3DP process and may affect the adhesion and separation properties with the materials and surfaces it comes in close proximity with during processing. Flowability, as earlier highlighted, is a resulting property that is strongly related to the viscosity of the polymeric material [77]. More viscous materials have a limited level of flowability and vice versa and will affect the polymer's ability to flow from the heated nozzle head through to the print bed. Lastly, the glass transition temperature (T_g) of a polymer is the temperature at which the random molecular structure of amorphous polymers begins to flow due to thermal energy input [75]. Similarly, the melting temperature (T_m) follows the same principle but applies to the flow-initiation of the ordered (crystalline) molecular structure of a polymers.

The ability of the polymer to maintain an appropriate viscosity value throughout the various stages of printing dictates the quality of the polymer deposition control and sintering, which in turn, has a direct impact on the mechanical properties of the printed components. With the demand for greater sustainable developments within financial, economic, and environmental areas amongst others, there is a significant opportunity for ME3DP and materials development projects to support ‘blue ocean’ strategies for businesses, while creating more efficient and sustainable supply chains.
3 Innovative Polymers/Nano-based Materials, with Research Developments in ME3DP

Despite the dominance of commodity plastics (i.e. PET, PP, PS, PE, etc.), natural and synthetic, bio-based and biodegradable polymer materials like polybutylene succinate (PBS), and polyhydroxyalkanoates (PHA), cellulose, and lignin have recently emerged as a subject of important focus for the development of polymer-based material systems with functionalities that are significantly in demand by economies and the ecosystem [78]. Although these materials might not completely replace petroleum-based plastics, there appears to be a lot they can do to minimize the carbon footprint of AM products and process life cycles. Depending on the target industry for the polymer-based material, there are some key properties (highlighted in Figure 13) that must be innovated for to enable their successful adoption. For example, the biomedical industry will require innovative polymers that are printable, and more importantly biocompatible; with acceptable degradation kinetics and degradation by-products. Meanwhile, in the automotive industry, more emphasis may be on the printability and tailored mechanical properties of the in-use polymer as is required for optimum applicability. Having highlighted these needs, the earlier-mentioned innovative polymers will now be discussed; followed by a review of developments in the use of polymer-based systems for ME3DP.

Figure 13 Desirable properties of innovative materials for ME3DP [7], Copyright with license number: 4692831280732
3.1 Poly Butylene Succinate (PBS)

PBS is one of the most imperative biodegradable aliphatic polyester known commercially as Bionnelle. It is a biopolymer obtained via polycondensation of succinic acid and 1-4 butanediol; offering plastic producers an exciting building block for biopolymer compounds and polymers [79][80]. It has properties similar to polypropylene, polyethylene, etc. that are popularly used in extrusion, injection, compression or blow moulding processes [48][81][82]. Importantly, Bionelle has a similar processing ability to conventional resins like the commodity plastics. Bionolle has been utilized for some applications; like in shopping bags, and agricultural products [48]. It is an emerging substitute for polypropylene (PP), polyethylene terephthalate, polyolefin, and polystyrene in some applications; therefore it is possible to understand why other grades of this polymer have now been made to include PLA and starch [48][81][83]; used to develop eco-friendlier polymer composites with tailored capabilities. Chemically, Bionolle™ is stable under ordinary conditions but will become biodegradable in the presence of microorganisms that exist in composts, wet soil, freshwater, seawater, and activated sludge [48][84]. It will decompose completely into water and carbon dioxide, thereby making it an eco-friendly material. Polybutylene succinate adipate (PBSA), a copolymer of PBS, has been found to show more degradability due to its lower level of crystallinity [48]. PBS is a promising biomaterial that significantly lacks research and holds promising features that could significantly impact the development of high performing and eco-sustainable material systems and products. Their most useful characteristics include [80][47]:

- Relatively high service temperature, which can be used for hot beverage cups, boxes, and utensils.
- High-performance heat-sealing ability; having at least the same level of seal strength as conventional petrol-plastic at a lower temperature.
- Lower environmental cost than most other polymeric materials available.
- Good printability without significant pre-treatment
- Compatibility with natural fibres and biopolymers
- Excellent processing characteristics

3.2 Poly Hydroxo Alkanoates (PHA)

PHAs consists a class of natural-based polyesters synthesised using microbial fermentation of carbon-based feedstock; which are biodegradable and readily compostable thermoplastics, [85][86]. PHAs are both bio-based and biodegradable, with physical and chemical properties similar to polypropylene, thereby making it a good alternative to PLA and PBS in biopolymer system developments. PHA is generally known to be:
• Insoluble in water, and relatively resistant to hydrolytic degradation.
• Resistant to ultraviolet light, but with poor resistance to acids and bases.
• Biocompatible and non-toxic, thereby making it suitable for biomedical and food packaging applications [85][86][87].

3.3 Lignin
Lignin is a biopolymer that is highly aromatic and is found naturally in the fibrous part of plants, and extracted as a by-product of wood pulping industries during a delignification process [88]. Lignin properties such as its high abundance in nature, antimicrobial, lightweight, environmentally friendly, antioxidant, and biodegradable nature, along with a neutral CO$_2$ footprint makes it a potential candidate for next generation materials. However, low-purity, heterogeneity, smell, and issues with colour remain the existing problems with commercially available lignin products [88].

3.4 Cellulose and Nano-cellulose
Cellulose is an inexhaustible sustainable polymer. This highly innovative polymeric material is synthesized by numerous living organisms and used extensively in the pharmaceutical and food industries [89][90]. Its abundance is a consequence of the constant photosynthetic cycles occurring within the cells of plants, which can synthesize several tons a year [91][89]. They can be obtained from plants or agricultural waste; from husk fibre, bamboo, wood, and sugar cane bagasse [89]. The main characteristics of cellulose include its biodegradability, hydrophilicity, chirality, broad chemical modifying capacity, and capability of forming versatile semi-crystalline fibre morphologies [90]. Most importantly, in the context of this review, it has the potential to encounter the cumulative demand for environmentally friendly, lightweight products but, similar to lignin, it can be limited by its poor mechanical properties [33][42].

3.5 Graphene
Graphene is a 2-dimensional (one atom thick sheet) carbon-based nano-material that has been considered to be a revolutionary and sustainable. It was first synthesised in 2004, for which a noble prize in physics was received in 2010 by Dr. Andre Geim and Dr. Konstantin Novoselov. Graphene is obtained from graphite or from carbon-containing gases like methane in a top-down (mechanical exfoliation) or bottom-up (chemical vapor deposition) processes. Due its exceptional mechanical, chemical and physical properties, this material holds great potential for various industries, and currently plays an effective role in existing products for corrosive barrier coatings. Pristine graphene is stronger than steel, stiffer than diamond, elastic (up to 20%), and more conductive than copper. Graphene is considered to either be made up of 1-10 atom layers of cabon; known as pristine (1), few (2-5) or multi (3-10) layers of carbon atoms bonded in a hexagonal structure.
Having discussed these innovative polymer/naon-based materials, it was observed that the properties of macro-polymers (PBS and PHA) were more quantifiable, available and reliable, and therefore easily more comparable with PLA than for the nanomaterial (graphene), and natural fibres (cellulose and lignin). Hence, as seen in Figure 14 below, the opportunities for developing new polymer-based composite blends (and filaments) for ME3DP may include the development of PLA/PBS or PLA/PHA due to their complimentary mechanical and glass transition properties [92][93][94], which can be designed to suit a specific industry application. On the other hand, although being more difficult to compare, polymer composite material system developments; incooperating graphene, cellulose and/or lignin into PLA (e.g. PLA/PBS/graphene) also signify great opportunities for innovating for biomedical and structural applications amongst others. These therefore set the right tone as we now go on to look at recent and state of the art research and developments that have been conducted in the area of ME3DP.

![Fig 14](image_url)

**Figure 14** Comparing the glass transition temperature and mechanical properties of the macro-polymers (PLA, PBS and PHA); to support the development of new material (and filament) systems fabrication for ME3DP

3.6 **State of the Art Research Developments in Polymer-based ME3DP**

These will focus on the use of ME3DP techniques as they offer the most cost-efficient approach for AM product fabrication, with great possibilities and convenience for users. Other promising techniques; including BJ and MJ processes; despite their good range of material compatibility, and process efficiency, will not be discussed further, and will enable a better focus on ME3DP processes. Therefore, as we consider a vast range of ME3DP applications in education, packaging, aerospace,
In a recent case using FDM-based technology, PLA and PBS pellets were dried in an oven at a temperature of 80 °C for at least 12 hours, then compounded with a twin-screw extruder to produce a filament with a homogenous PLA/PBS blend. The barrel temperature, set at 140-165 °C, with a screw speed set at 80 rpm were used to control the process. Some ratios of PLA to PBS (PLA: PBS) by weight ratio used in the blends were 90:10, 80:20, 70:30, 60:40 and 50:50 respectively. The PBS/PLA blends were then 3D printed; with the result showing a white luster appearance, with no observable distortion (see Figure 15) when the PBS content was no more than 60% [53]. However, when the weight ratio of PBS exceeded 80%, significant distortion was observed [53]. Q. Ou-Yang et al. [53] further identified that PBS40/PLA60 and PBS60/PLA40 were optimum blends for the ME3DP process when trying to achieve optimum:

- Distortion behaviour
- Dimensional accuracy
- Interlayer bond strength, and
- Material toughness of polymer filament and part

In another study by Wittbrodt and Pearce et al. [66], which aimed to determine the effect of colour and processing temperature on the material properties of PLA (using a Lulzbot TAZ 3D Printer), five colours (grey, white, blue, black, and natural) of commercially available filament processed from PLA...
were tested for crystallinity with XRD; for tensile strength (following ASTM D638); and for the microstructural structure using a SEM machine [66]. The results reflected a strong relationship among tensile strength and percentage crystallinity of a 3D printed sample; a strong relationship between the percentage crystallinity and the extruding temperature [66]. The emerging results ideally reflect on ways in which material choice and material processing route can, through slight changes, affect the resulting part quality. It could also suggest the importance of consistency in experimentation in order to achieve a level of reliability and therefore potential standardisation of processes when attempting to obtain a specified part quality.

Functionalized carbon-based nanomaterials (CBNs) developed from carbon nanotubes (CNTs), have become significant players in the development of advanced material systems that are critically for various high-performance applications [95]. This is ultimately due to their unique combinations of physical/chemical properties as defined by their electrical/thermal conductivity, optical properties and high mechanical strength. Cha et al. [95] predicted that although CNTs have been the focus of research efforts, other types of carbon-based nanomaterials; especially graphene, that has gained significant recognition in recent years; is expected to receive more interest in the near future as various industrial applications can benefit from their extensive research, for applications in high-strength materials, thermally stable materials and electronic products. The beneficial properties of CBNs are also being investigated in potential areas for biomedical engineering applications. They have gained strong traction in biomedical research for applications in cellular sensors, drug delivery systems, and tissue scaffold reinforcements [95]. Despite the fact that it usually takes significant research and numerous validation steps to meet regulations of good manufacturing practices (GMPs), such a development is highly promising for the prospects of future healthcare systems.

Wei et al. [96] were the first to show the possibility of printing graphene composites using the FDM method. In their work, graphene oxide and ABS were dissolved in N-Methyl-2-pyrrolidone solution to achieve a good dispersion of graphene and ABS. following this, the graphene oxide/ABS powder was precipitated from the solution to obtain powder was loaded into an extruder to obtain a filament for FDM printing. These were then used to print freestanding structure with graphene content at no more than 7.4 wt%.

In another experiment, Maurel et al. [96] used dichloromethane as a solvent to dissolve PLA before mixing it with graphite to obtain a graphite/PLA composite disc for lithium ion batteries (see Figure 16). The electrical, electrochemical and flexibility of the resulting composite was further controlled respectively with the use of fillers (carbon nanofibers and carbon black), and plasticizers (e.g. polyethylene glycol). The formed composite was then tape casted to form homogenous films, before being extruded and printed as the anode material for a lithium ion battery; with 60–70 wt% graphite
loading. Consequently, the reversible capacity was found to be capable of reaching 200 mAh g\(^{-1}\) of active material mAg\(^{-1}\) at current density of 18.6 mA g\(^{-1}\) (C/20) after 6 cycles.

In the case of DIW, several composite inks have been designed and developed to address multifunctional applications; graphene-based inks mostly. This is due to their potential for achieving enhanced electrical, mechanical and biological properties that can deliver improved functionalities for numerous 3D printing applications [97]. As seen in Figure 17, Jakus et al. [98] successfully demonstrated a 3D printable graphene composite consisting mostly of graphene, mixed in dichloromethane with a much lesser amount of polylactide-co-glycolide [98]. The ink solution was then stored for several months before being loaded for rapid fabrication via a DIW process as per the user design specifications. A high fidelity scaffold was obtained after printing, and following a controlled
solvent evaporation process. Importantly, the resulting composite scaffold was self supporting and considered potentially suitable for electronic, bioelectronic and biomedical applications.

Figure 17 Use of DIW for fabrication of graphene-based composite for medical and electronic applications. Adapted with permission from [98], Copyright 2015, American Chemical Society.

In another aspect, Matsuzaki et al. [8] experimented with composite fibre materials; i.e. fibres infused into PLA for 3D printing, targeting improved mechanical properties for the printed parts [8]. A modified FDM printer was developed to help impregnate the filament with composite fibres before extrusion. In this experiment, the reinforcing fibre was heated using a nichrome wire before it entered the nozzle head; to enable and enhance the permeation of the fibre bundles into the thermoplastic resin structure. The heater inside the nozzle, further helps to consolidate the heating and promote better mixing of the fibres and the resin in the heating chamber. Critically, the final results showed superior Young’s modulus and strengths compared with other materials fabricated using commercial 3D printers [8]. The safety of such higher temperature processes and process designs may be a concern for use in
certain environment with kids, etc. however, this seems highly controllable. The 3D printed PLA-based composite blend displayed an elasto-plastic and orthotropic mechanical. In an important and similar experiment of 3D printing biocomposites, Le Duigou et al. [10] used a continuous flax fibre composites filament (within PLA matrix) for ME3DP, which suggested that the obtained part showed considerably higher tensile strength and tensile modulus performance when compared to other 3D printed composites (with short and continuous fibre) – see Figure 18.

![Fabrication of Continuous flax fibre filament for 3D printing](image)

Figure 18 Mechanical properties of a 3D printed composite of flax fibre filament (in PLA) – Adapted with permission from [59] under the copyright creative commons attribution license

In a recent study by Chris et al. [99], 3D printed thermoplastic polyurethane (TPU) with differing percentages of multi-walled carbon nano-tubes (MWCNT) were fabricated using the ME3DP technique. In a study by J. Luo et al. [100], PLA/MWCNT composites were found suitable for printing by FDM. In this research, high conductivity was realised in the 3D printed products containing 5% MWCNTs. The conductivity was $0.4 \pm 0.2 \, \text{S/cm}$, its tensile strength was $78.4 \pm 12.4 \, \text{MPa}$, and its elongation at break was $94.4\% \pm 14.3\%$ [100]. In another study by Tekinalp et al. [99], they investigated fibre alignment in
carbon-fibre/ABS composite when the FDM technology was used for printing [60][101]. They identified that using ME3DP; they were able to achieve tensile properties and fibre protrusion lengths that are comparable to samples fabricated with a compression moulding technique[101].

There have also been growing studies that use a fibre alignment technique in ME3DP to functionalize composites for biological purposes [102]. An example is in a study by Bakarich et al. [99], where 3D printed fibre reinforced hydrogel composites with particular fibre orientation, i.e. in the direction of loading, was used to simulate and replicate the structure and loading conditions of the meniscus cartilage in bones [38][7]. Other studies that printed replica’s of biological products like scaffolds, using the ME3DP, were such as in the work by Woodfield et al [99], which involved the use of fibre alignment techniques to fabricate 3D scaffold samples [99]. This gives rise to the potential for using fibre alignment in AM for several commercial biomedical applications in the future; to create more dimensionally-accurate, bio-compatible and functionalized prints. Two of such applications in the biomedical industry includes surface texturing, and scaffold printing amongst others [99][103]. In a case for biomedical applications, it was found that stiffer, denser polymeric networks resulted in better printable bio-inks but led to a poor cell culture microenvironment. Hence, as depicted in Figure 19, bio-inks are being designed to compensate for poor cell culture environment and poor shape fidelity [38].

Figure 19 Developing scaffolds for improved bioactivity and bio fabrication window in extrusion-based 3DP (Adapted with permission from [38], with copyright license number: 4693320664349)
In summary, these scenarios give good coverage of the recent experiments, and key observations that highlight the challenges and opportunities for further justification and improvement of ME3DP techniques for a good range of material and composites systems. Polymer system design, additives or fillers, and processing parameters as they relate to improving functionality, build speed, mechanical properties, accuracy, surface finish, stability, and porosity of final parts; are therefore aspects that require critical review and research in order to support the development of industrially applicable polymer-based ME3DP processes.
43DP of Multifunctional Material Systems: A Concept of 4D Printing (4DP)

This is a good point to freshen the readers’ minds on MFMS; first discussed in the introduction section of this review paper. Essentially, MFMS is an easily understood concept of material systems that reflects on how composites can possess time-dependent multifunctional properties and capabilities [104][105], thereby enabling products to be more effective in their functional requirements while retaining or improving their life-cycle efficiency. More specifically in this review case, multifunctional polymer composites are extensively employed in various industrial applications to offer low density, non-corrosive, high specific strength and modulus, good thermal expansion, and thermal insulation properties [106][107][108][109]. Such multifunctional polymer composite materials have been identified to be material systems that are nano-phased, active (smart/biomimetic), and/or advanced (i.e. with advanced textiles and matrices, and eco-sustainable features) [24]. In another perspective, Narayana & Burela. et al. [110] defines MFMS as material systems that utilize a combination of structural (e.g. strength, stiffness, toughness, etc.) and non-structural (e.g. actuation, energy harvesting, self-healing, sensing, etc.) properties to deliver specific functionalities for the user, such as those highlighted by Yogendra et al. [111], Javaid & Azvaid [109], Yogendra & Rainer [112], Sören et al [113], An et al [114], and Florian et al [115] in their work.

With these in mind, the concept of 4D printing (4DP) is born, directly having a strong relation to the fabrication of MFMS. 4DP currently occurs in either of three paradigms of capabilities for product fabrication [116]; They include:

1. using an individual smart 1D, 2D, or 3D material that changes its shape based on stimuli (like humidity and temperature),
2. using 3DP to construct polymer-based parts that support cell/tissue growth (i.e. bioprinting), or
3. using micro-sized smart particles to self assemble composites or structures, which can alter their patter following stimulation.

From these paradigms, we can more comprehensively explain 4DP as the formation of complex material systems, composites and structures (with the support of 3DP), that have the ability to adopt different functions, shapes and forms when subjected to varying environmental stimuli. Researchers simply view 4DP as an extension of 3DP, with the added constraint of time [116], when considering the mechanical, physical and chemical constraints that already exists within 3DP.

This brief discussion on 4DP/MFMS fabrication is an attempt to help highlight and support the need for wider material adoptions in AM (more specifically, in ME3DP); as a push towards capitalizing on the advantages of AM techniques and any supporting computational frameworks capable of adding to the realisation potential of more unique, robust, and multifunctional product systems. Shape memory
polymers (SMPs) like polyurethanes and hydrogels have been known for their shape changing, multifunctional capabilities [116]. Using FDM, self folding metamaterials have been successfully printed; and while using UV-supported DIW, the printing of highly stretchable self-healing shape memory elastomers have also been achieved for the biomedical industry [116][117]; highlighting the possibilities with ME3DP techniques for future multifunctional products. According to an Ernst & Young report on 3DP, the developments will likely be focused on the industries as presented in Figure 20 below.

The aerospace and defense industries are shown to have the most current applications of 3DP, but also with the highest opportunities for using newly developed 3DP technologies and constructs. Furthermore, according to this chart, mechanical and plant engineering applications will potentially see great adoptions of 3DP technologies and products; based on the low number of applications they currently employ. Some recently 4D printed products are depicted in figure 21 to aid with visualizing some of this revolutionary development that is poised to improve future possibilities of product and service systems within the identified industries.

![Figure 20 Current and future (potential) industrial applications of 3DP [118]]
Figure 21 Showing 4D printed devices for different applications. (a) An actuator system made from porous silicon elastomer, filled with ethanol, (b) A thermo-responsive (30°C to 90°C) liquid crystal elastomer applicable in adaptive optics, (c) A braided tube preform of PLA-based polymer showing shape memory effect over time, (d) A gripper using shape memory behaviour; for potential applications in adaptive manufacturing and robotic systems, (e) A 3D-printed hydraulic robot, using liquid support for bellow actuators. Adapted with permission from [119] under the copyright creative commons attribution license.
5 Major Challenges and Future Perspectives

ME3DP techniques utilizing polymer-based systems have an unprecedented range of opportunities for growth and development especially in the use of biocompatible and biodegradable biomaterials, including fibre reinforced polymers. The automotive, aerospace, biomedical, and packaging industries appeared to be the industries most likely to benefit from these potentially eco-sustainable and multifunctional developments. However, although ME3DP was found to generally offer better potential for achieving cost-efficient, scalable and environmentally-sustainable 3DP processes, they were, alongside other AM techniques found to lack well-established processes, standards, and build-material systems; which are important aspects limiting the reliable adoption of AM for the production of parts and products for the above-mentioned industries. Another challenge that will benefit the interests of investors and users of AM technologies is the security of 3DP systems; considering that several developed 3DP softwares are open-source systems. This should come across to regulators and 3DP system developers as key subjects to consider when designing and creating 3DP systems for the future. Furthermore, in the interest of developing more sustainable supply chains in AM; it was thought that the level and effectiveness of ‘informing and educating’ the masses would remain a challenge for maintaining and improving the global awareness of individuals, businesses and organisations in their decisions that relate to waste management and socio-economic demands.

With regards to future perspectives; it was thought that following the assessment of operational factors including energy, speed, resolution, functionality, and material options for ME3DP techniques; the most useful and prospective area for future research and development surrounds the use of more eco-friendly; bio-based and biodegradable material options that are capable of multifunctionality; with a further consideration of standardizing and improving the speed of ME3DP processes. Already, the wide adoption of PLA suggests a positive development so far and a good starting point. However, materials like PBS, lignin, cellulose, graphene (and other nano-based materials) further serve as great candidates for the development of advanced polymer composite material systems for use in a broad range of industrial areas. Eventually, the hope is to move industries closer to the successful adoption of ME3DP strategies that achieve eco-friendly production of functional/multifunctional and sustainable parts/products for our society at large.
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7 References


[34] Q. Wang et al., Investigation of condensation reaction during phenol liquefaction of waste woody materials, vol. 9, no. 5. 2014.


V. Mazzanti, L. Malagutti, and F. Mollica, “FDM 3D printing of polymers containing natural fillers: A review of their mechanical properties,” *Polymers*, vol. 11, no. 7. MDPI


[80] Nova-Institute, “Biobased Polybutylene Succinate (PBS) – An attractive polymer for
biopolymer compounds Polybutylene Succinate – An interesting building block for biopolymer compounds based on biobased succinic acid,” pp. 1–11, 2015.


[89] M. Drahansky et al., “We are IntechOpen, the world ’s leading publisher of Open Access books Built by scientists, for scientists TOP 1 %,” Intech, vol. i, no. tourism, p. 13, 2016, doi: http://dx.doi.org/10.5772/57353.


[118] F. Thewihsen, S. Karevska, A. Czok, C. Jones-Pateman, and D. Krauss, “If 3D printing has changed the industries of tomorrow, how can your organization get ready today?,” Ernst and Young, p. 24, 2016.

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Fused deposition modeling-based additive manufacturing (3D printing): techniques for polymer material systems

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