Composites Science and Technology 213 (2021) 108876

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Review

Polymer-based filament feedstock for additive manufacturing

Soyeon Park [a], Kun (Kelvin) Fu [a,b,*]

[a] Department of Mechanical Engineering, University of Delaware, Newark, DE, 19716, USA
[b] Center for Composite Materials, University of Delaware, Newark, DE, 19716, USA

ARTICLE INFO

Keywords:
A. Polymer-matrix composites (PMCs)
A. Polymers
E. 3D printing
E. Additive manufacturing
E. Extrusion

ABSTRACT

Fused deposition modeling (FDM) or fused filament fabrication (FFF), which is based on polymer melting and extrusion, offers a unique manufacturing method to fabricate objects with complex geometries due to easy process for polymer deformation through melting and solidification and layer-by-layer additive manufacturing. Because of these advantages, FDM has attracted considerable attention over the past decades in a variety of fields including electronics, biomechanical engineering, and sustainable materials. As the demand for functional materials increases, polymer composites with diverse reinforcements such as carbon nanomaterials, metals, biomaterials, and ceramics have been tailored as feedstocks for FDM. Fabrication and printing with polymeric composite filaments require understandings of the physical and chemical properties as well as thermal-rheology behavior of polymer systems, which are crucial to advancing AM development. Herein, we first provide the working mechanism of FDM, the criteria for selecting polymers, and methods for manufacturing polymer and polymer composite filaments. After that, the physical and mechanical properties and printing conditions of the pure polymer filaments, multi-material/structure filaments, and various applications using polymer composite filaments are discussed and summarized. Finally, we share some of our perspectives for the future advance of polymer-based filament for FDM.

1. Introduction

Additive manufacturing (AM), also known as 3D printing, allows the fabrication of customized products with high geometric complexity and good scalability. The first 3D printer, stereolithography, was invented in 1987, and during that time other types of 3D printers were also introduced, including fused deposition modeling (FDM) and selective laser sintering (SLS) [1]. Compared to the traditional manufacturing processes that produces products by cutting materials from solid blocks of material, 3D printing can create 3D objects by adding materials layer by layer. This additive process is attractive as a sustainable manufacturing these days because it saves materials and energy by minimizing the negative impact on the environment. Moreover, 3D printing has greater design flexibility and allows product design modification without any equipment or machine changes, which is required by conventional manufacturing techniques for thermoplastic fabrication including injecting molding, forging, and drawing. Among 3D printing techniques, FDM, or called fused filament fabrication (FFF) is the most popular due to the simpleness of the process and cost-effectiveness [2]. FDM has been widely used in not only rapid prototyping but also many functional applications in biomedical engineering [3], automotive [4], food [5], and construction [6].

These advanced uses require high-performance thermoplastics such as polyether-ether-ketones, polycarbonates, and functional polymer composites. To print the 3D products with these new materials, it is important to understand the rheology of the polymer and polymer composites with FDM. Rheology can be a key part as new filaments are formulated to develop the versatility of FDM. In addition, it is essential to know the characteristics of polymers and fillers to establish FDM material selection criteria, and how to manufacture filaments from polymers and polymer composite.

In this review, we focus on the materials of the polymer composite filaments, filament fabrication and printing processes, and applications using the polymer composite filaments. First, we will provide FDM working mechanisms for polymer and polymer composites and the overall filament fabricating procedure. Second, it will be explored that functional filaments to handle the challenges in FDM as well as the applications (e.g., biomedical fields, sustainable materials, electrical energy storage, and electronics) using the composite filaments with numerous filling materials (e.g., carbon nanomaterials, metal,

* Corresponding author. Department of Mechanical Engineering, University of Delaware, Newark, DE, 19716, USA.
E-mail address: kfu@udel.edu (K.(K. Fu).

https://doi.org/10.1016/j.compscitech.2021.108876
Received 25 January 2021; Received in revised form 8 May 2021; Accepted 24 May 2021
Available online 3 June 2021

biomaterials, and ceramic). Finally, we share our thought on the key challenges and future development of polymer-based filament feedstock and AM system.

2. Fused deposition modeling (FDM)

2.1. Working principle of FDM along with polymer filaments

FDM is an extrusion-based 3D printing technology that prints 3D products using solid filaments made of thermoplastic. A FDM printer has a printer head made up of several components, such as an extruder motor, a heater, a nozzle, and other auxiliary parts like a temperature sensor and a filament guide, as shown in Fig. 1. The extruder motor applies enough pressure to push out a filament through the nozzle, and the heater changes physical state of the filament by creating a high temperature around the melting point of the material. The working principle of the FDM is simple like below. Once the filament is inserted into the guide and pushed down by an extruder motor, it turns into the semi-liquid state at a hot end. The molten filament is extruded through the nozzle and deposited layer by layer on the platform or previously printed layers. However, when printing polymer and polymer composite filaments, there are several things to consider. As illustrated Fig. 1, the first is the state of the filament when printing a composite filament. Depending on the filler materials, shape, and loading, the print qualities vary due to inconsistent extrusion, filament deterioration during printing, and improper properties (e.g., inadequate viscosity and too high brittleness) for printing, which will be covered in section 2.1. The second is the parameters in a nozzle and hot end. The shape of the nozzle and temperature of the hot end affects the surface quality of the products and determine printability of the polymer and polymer composites, respectively. The third is mechanical properties of the printed objects. Due to the layer-by-layer printing process, the printed products have anisotropic mechanical properties (higher properties in printing directions). Therefore, when printing objects for applications, especially structural applications, we should consider the printing directions. In recent, there are several methods to improve the mechanical properties in perpendicular to layers, which will be discussed in section 3. The last is the functional abilities of the printed composite filaments. By using smart polymers, such as shape memory polymers, the printed objects are able to have advanced functional abilities that change shape over times under the stimulus (e.g., electricity [7] and temperature [8,9], etc.). It is called 4D printing. Compared to 3D printing, 4D printing focuses more on the material design and provides new insights in many applications, including medical industries [10] and robotics [11]. Moreover, when using post-treatment, the printed composite can be converted functional products. The details on functionality of composite filaments will be discussed in the section from 3.2.1 to 3.2.5.

The key part of FDM is the hot end where polymer's physical state change takes place. At the hot end, the temperature control needs lots of attention. In order to melt the material, the temperature of the hot end must be high enough to keep the material molten, but not too high for the material to deteriorate [12]. For printing the high performance of polymers such as polyether-ether-ketone (PEEK), it is challenging to create a high temperature, since the surrounding components can degrade due to high temperature. Besides the hot end, there are also several factors that determine the quality and mechanical properties of printed products, including printing speed and environmental conditions (humidity and temperature of the chamber and bedplate). For instance, too high temperature of the bed plate and chamber prevents the natural cooling of the extruded filaments, but if the temperature is too low, the printed filament crystallizes prematurely, which can cause component distortion and warping [13].

In the FDM printing process, it is important to understand the rheology of molten filaments affected by flow rate and temperature. This is because rheology becomes a key factor in determining printability when using new materials. In Fig. 2a, the fiber with a diameter D_f (2.85 mm) is melt by heat transfer from the barrel, and when the molten filament passed the nozzle with a small diameter d (0.3–0.5 mm), shear and elongation flow is generated. The molten filament should have shear-thinning characteristics at elevated temperatures to have the adequate filament flow. At low shear rates, the viscosity is high to avoid premature extrusion, but at a high shear rates the viscosity decreases enough for the filament to be extruded [14]. However, the appropriate viscosity range for FDM is unable to measure because of difficulty in measuring the actual shear stress generated during printing [15]. For this reason, there is no indicator viscosity range for successful FDM. In addition, the viscosity is related to the die swell. When the viscosity is low, it allows the molecules in molten polymer to slide easily, reducing the elastic energy retained in the extruded polymer. As a result, die swell is reduced after printing. During the extruding process, the polymer chains become aligned with the flow direction, attributed to the shear stress generated along the barrel wall. At the small area of the nozzle, the maximum shear stress is produced, resulting in the higher alignment of the polymer chains. After the filament exits the nozzle, the filament cools down via through heat transfer between the hot filament and environment. At the same time, the diameter of the extruded filament increases by an amount of b (~300 μm), and the aligned polymer chains tend to return to their original state because of the elasticity of the polymer. Details of the changes in polymer chains (randomly distributed in initial state, aligned by passing the nozzle, returned to original state by swelling) during FDM printing are illustrated in Fig. 2b.

There is also another type of extrusion-based 3D printing technique, which is screw-based 3D printing. As shown in Fig. 3a, the most common filament-based printing, FDM, uses solid filaments as feedstock. It is able to fabricate functional composite products with reinforcement aligned along the printing direction. However, when using solid filament, clogging may occur due to changes in diameter, and buckling and slipping of the filament in the extruder motor may result in printing failure due to improper flow of the filament [18]. To overcome these limitations, screw-based 3D printing has been studied. As illustrated in Fig. 3b,

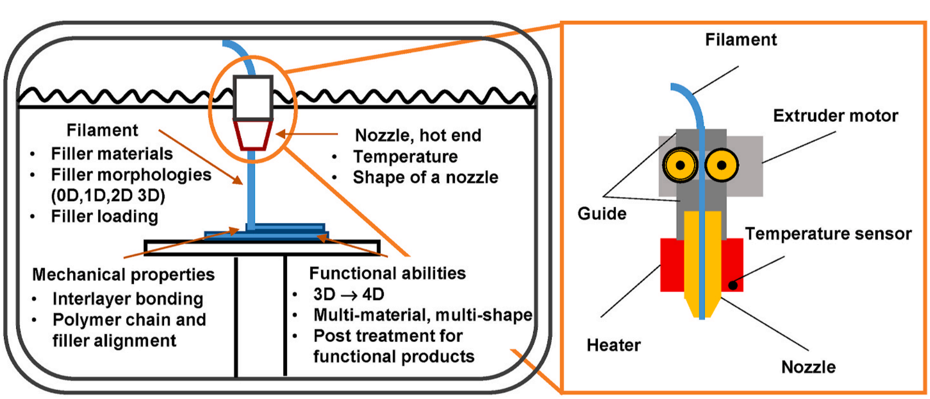

Fig. 1. The schematic and parameters of the FDM printer. The solid filament is melted into the semi-liquid state at the hot end, extruded through the nozzle, and then deposited layer by layer on the platform or previously printed layers to form three-dimensional structures. When printing the composite filaments, there are a few factors to be pointed out in terms of filament components, parameters for nozzles and hot ends, and mechanical enhancement and functionality of the printed product.

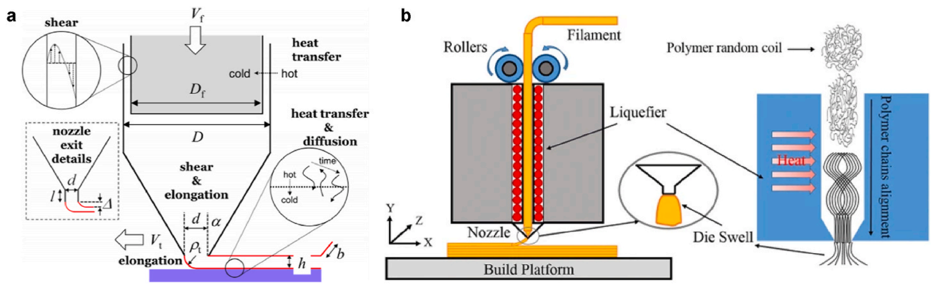

Fig. 2. Rheology-controlled polymer molecular distribution in fused filament fabrication. (a) The extrusion process with polymer behavior [16]. After heat transfer from the barrel melts the filament, the molten filament exhibits shear and elongation flow in the conical nozzle. (b) An overall FDM printing mechanism by showing the polymer chain [17]. When filament is extruded, the polymer chains become aligned with the flow direction due to the generated shear stress along the barrel wall. After exiting the nozzle, the filament swells and the aligned polymer chains have tendency to return to their original state.

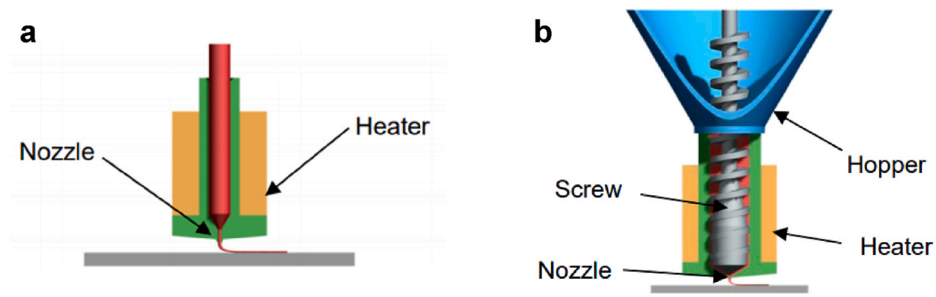

Fig. 3. Schematic of extrusion-based 3D printing [18]. (a) Filament-based printing and (b) screw-based printing.

the fillet shape of the raw material is used, and this printing is commonly used to manufacture products with continuous fixed shape. In this printing system, the fillets in the hopper are transported to the nozzle by the screw and melted by the heater during transfer. This printing system have several benefits, such as few restrictions on the shape of the feedstock and less clogging, but trapped air should be removed for continuous printing.

2.2. Polymer feedstocks for FDM

As materials for FDM, the standard and engineering levels of thermoplastic such as polylactic acid (PLA), polycarbonate (PC), polyethylene terephthalate (PET), nylon (PA), and acrylonitrile-butadiene-styrene (ABS) have been widely used. As the hot end develops the capability to create high temperature, the advanced plastic such as polyether-ether-ketone (PEEK) and polyetherimide (PEI) are becoming printable. Due to the wide selection of feedstocks, it is important to know material properties (physical and mechanical properties) and printability when choosing the right polymer for the finished product. Fig. 4a shows the most common types of thermoplastics, which are classified according to performance, and Fig. 4b presents their printability, visual quality, and mechanical properties. In Fig. 4b, heat resistance, impact resistance, and elongation break are the chemical and mechanical properties that resist higher temperatures, impact energy, and length deformation before breaking, respectively. The ease of printing means how easy it is to print a feedstock in terms of bed adhesion, maximum print speed, ease of feeding to the printer, and the frequency of print failures, and visual quality refers to how good the printed part looks, which is determined by the surface quality such as smoothness of the surface. These points of view will be helpful to choose materials for FDM. Nowadays, as the demand for multifunctional materials increases, research has been conducted to make polymer composite filaments by mixing carbon nanomaterials, biomaterials, metals, and ceramics into the polymers, which will be discussed in section 3.

2.3. Hot-melt extrusion for 3D printing filament manufacturing

Polymer raw materials for FDM are made into continuous filaments after raw materials are processed into polymers and transformed into pellets. For example, Fig. 5a shows the overall material processing for PLA filaments, which are commonly used in FDM technology. The process begins with corn fermentation (corn to Lactic Acid), condensation (Lactide) and polymerization (Polylactic acid; PLA). After that, the material is pelletized and extruded into filaments for final use. From the point of view of the filament manufacturing process, it consists of three steps: hot-melt extrusion, cooling, and winding stage, as shown in

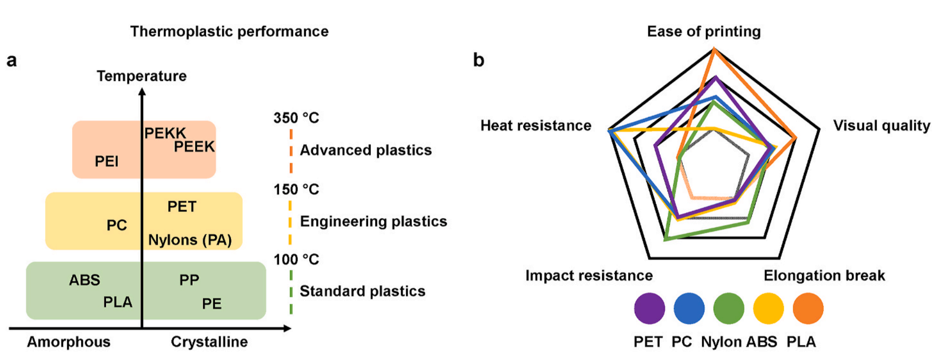

Fig. 4. Thermoplastics as feedstock materials for FDM. (a) Categories of thermoplastics: Standard plastics (Acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polypropylene (PP), and polyethylene (PE)) are used for general parts operated under low stresses. Engineering plastics (Polycarbonate (PC), polyethylene terephthalate (PET), nylon (PA)) have good wear resistance compared to standard plastics and are applied to structural parts. Advanced plastics (Polyethyleneimine (PEI), polyether-ether-ketone (PEEK)) have high temperature resistance as well as high wear and chemical resistance. (b) A Rader plot graph showing polymer properties in terms of ease of printing, visual quality, elongation break, impact resistance, and heat resistance.

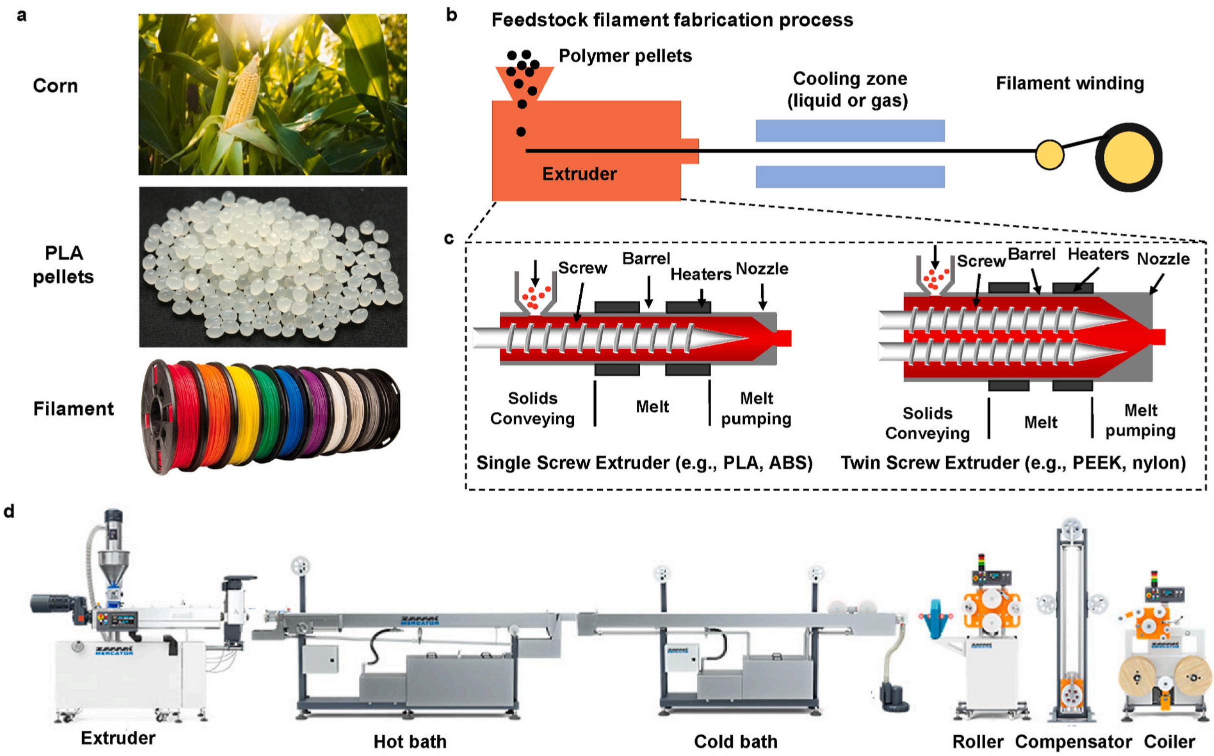

Fig. 5. The process for fabricating a filament. (a) The material processing for the polylactic acid (PLA) filaments. The process begins with corn fermentation, condensation and polymerization, and the material is pelletized and extruded into filaments. (b) An overall process in the fabrication of a filament. (c) Schematic representation of single-screw and twin-screw extruder. (d) Figure of the filament production line for FDM, including extruder, hot bath, cold bath, roller, compensator, and coiler [22].

Fig. 5b. Hot-melt extrusion is a technology for manufacturing polymer filaments and has a good ability to dispense two or more solid materials homogeneously [19]. This process uses heat and pressure to melt or soften materials and produces products with uniform shape and density through a die. The heater in an extruder melts the materials, and the rotating screw mixes the materials and passes the softened materials along the barrel to the end of the screw. The extrusion step is important as it can manipulate the orientation of the particles while extruding the composite filament [20]. For example, when extruding the composite with carbon nanotubes (CNTs), which have high electrical conductivity and tensile strength, CNTs tend to be aligned in the direction of the extrusion, resulting in high mechanical properties and electrical conductivity in the aligned direction [21]. This process can be controlled with several parameters such as temperature, screw speed, and feed rate. Once the filaments are extruded, they are cooled by fixing their shape in the cooling stage and wound for the filament bundle in the winding stage.

Typically, the extruders used for hot-melt extrusion are divided into two types depending on the number of the screws: single-screw extruder and twin-screw extruder, as shown in Fig. 5c. The single screw and the twin-screw have some advantages and disadvantages, which are summarized in Table 1. The single-screw extruder has one screw and is mainly used to produce homogeneous polymers in a continuous shape [23]. When the screw rotates, frictional forces are generated between the rotating screw and the barrel surface, which make a flow that moves the materials to the die [24]. As screw speed increases, higher friction and thermal energy are generated, making single screw extruders unsuitable for heat sensitive materials. Also, high pressure occurs during the extrusion process and compresses the materials to produce filaments. However, the lack of shear deformation may tend to cause agglomeration and poor mixing. Therefore, it will be suitable for fabricating pure polymer filament, but it is difficult to extrude high-quality polymer composite filaments that require mixing two or more materials. In the case of the twin-screw extruder, it has two screws, which are parallel to the barrel. Unlike the single-screw extruder, a twin-screw extruder creates a higher shear force not only in the gap between the screws and the barrel, but also between the rotating screws, helping to mix the materials well [19]. Moreover, when the molten material is squeezed between the screws, it stretches and causes a viscous flow by dissipating heat. Therefore, the speed and heat generation of the screw are independent. The other difference is that the shear forces can be increased by manipulating the rotating direction of the two screws: co-rotating whereby the screws rotate in the same direction, and counter-rotating whereby the screws rotate in the opposite direction. Compared to the co-rating system, the counter-rotating system is more useful for dispersing the fillers in the polymer matrix, because it produces higher shear forces when the materials are squeezed in the gaps between the screws [25]. For these reasons, the twin-screw extruder is more efficient to mix two or more materials homogeneously and is widely used to make polymer composite filaments [26].

After the filaments are extruded from the extruder, they pass through a hot and cold bath to have a certain diameter (1.75 or 2.85 mm), which is the typical size of FDM filament. A roller, compensator, and coiler make the filaments to be wounded for filament bundle, as shown in

Table 1
Comparison between single-screw and twin-screw.

Types of extrusion	Advantages	Disadvantages
Single-screw extrusion	Low cost, mechanical simplicity, low maintenance	Poor mixing, and not suitable for heat-sensitive materials
Twin-screw extrusion	High dispersing capacity, resulting in better mixing, better control of process parameters, easy material feeding, and high productivity and flexibility	Relatively high cost, high input energy, and not suitable for shear-sensitive materials

Fig. 5d.

3. Filaments

Various thermoplastics including PLA, ABS, PC, PET, nylon, and PEEK are used as feedstocks for FDM technology. As physical, mechanical, and chemical properties of thermoplastics are different, it is essential to know the physical and mechanical properties and printability of a material to choose an appropriate material according to its function and purpose. In this section, we will address the most popular thermoplastics (PLA, ABS, PC, PET, nylon, and PEEK) for the filaments in 3D printing, and Table 2 compares them in terms of physical and mechanical properties, and printing conditions. In general, heat deflection temperature measures polymer's resistance to distortion under a given load at elevated temperature, and it can be used as an indicator for the service temperature of the polymer materials. In the table, heat deflection temperature refers the temperature, at which a given material specimen is bended of 0.25 mm under a given load (0.46 MPa or 1.8 MPa for PEEK).

1) Polylactic acid (PLA). PLA is the most widely used as a filament material due to its low cost and ease of print. PLA has a relatively low melt point around 145–186 °C and can be easily formed into filament with a temperature over 185–190 °C [27]. Biocompatibility and good mechanical properties (relatively high strength and modulus) of PLA make it popular in the industrial packing and biomedical field [28].
2) Acrylonitrile butadiene styrene (ABS). ABS is an amorphous and synthesized by polymerizing styrene and acrylonitrile in the presence of polybutadiene. Not only does it have better strength and toughness than PLA, but it also has better resistance to corrosive chemicals, making ABS more attractive for use in FDM [29]. However, it is slightly difficult to print due to the tendency to warp, attributed to a high shrinkage factor.
3) Nylon 6. Nylon 6 is a popular synthetic polymer and used in many industries due to its good strength, flexibility, and durability. But it is sensitive to moisture and should be kept in a cool, dry place for high-quality products [30].
4) Polycarbonate (PC). PC is one of the engineering plastics and has carbonate groups in their chemical structure. PC is popular in 3D printing owing to its excellent mechanical properties (toughness, flexural strength, and impact resistance) and wide heat resistance ranging from −150 °C to 140 °C [31]. Therefore, it is widely used for tough applications such as functional testing and tooling [32]. However, PC is one of hygroscopic plastics, meaning that it absorbs moisture in the air. To prevent the degradation of the filament, it should be stored in dry or airtight environment. It is also prone to occur warping between the filaments and the build plate or between filaments. When the PC is printed without heated environment, residual stress can be created in the polymer, and as printing proceeds, the residual stress eventually overcome the bed or inter-layer adhesion, causing distortion. Therefore, it is important to ensure sufficient bed adhesion by controlling the bed and environmental temperature (Bed temperature: 90–105 °C, environmental temperature: ~250 °C) and adjusting the gap between nozzle and the bed.
5) Polyethylene terephthalate (PET). PET is a semi-crystalline polymer and one of the polyester family. Rather than raw PET, glycol-modified polyethylene terephthalate (PETG) is more popular in 3D printing filament owing to less brittle and easy to use. PETG has better printability compared to ABS and enables the production of 3D products with smooth surface finish and excellent impact resistance, but PETG has the high absorbability of moisture from the air.
6) Polyether-ether-ketone (PEEK). PEEK is a semicrystalline polymer in the Polyaryletherketone (PAEK) family and one of the advanced plastics, which has a high melting temperature. PEEK was difficult to print due to the high melting temperature around 343 °C, but as the hot end in FDM printer has recently progressed, it has led to the development of PEEK filaments for more general FDM. Moreover, many advantages of PEEK, including excellent mechanical and chemical resistance properties (high resistance to biodegradation and thermal degradation), allow the applications of the polymer in extreme conditions requiring high service temperatures or mechanical properties such as bone, bearing, piston parts, vehicle, and aircraft [33].

Polyether-ketone-ketone (PEKK) is also a semicrystalline polymer in PAEK family. PEKK is a rising material in aerospace and tooling industries due to its high mechanical and chemical resistance properties like PEEK. The melting temperature of PEKK is around 385 °C, slightly higher than PEEK [34]. The main difference between PEEK and PEKK is that PEKK has a much lower crystallization rate (about 3 orders of magnitude) [35] and is less sensitive to cooling in a low-temperature build chamber below 200 °C. Thus, PEKK is popular as an alternative feedstock for FDM, because it can be processed like an amorphous polymer, providing good layer adhesion and dimensional stability.

One of the challenges in FDM is that the bond between the printed layers is weak, resulting in lower strength and toughness. Several attempts have been made to solve this problem by locally heating the printed layers and promoting a crosslinking network between the intermediate layers. A simple method is using a laser or infrared ramp to locally heat the surface of the printed layer prior to the deposition of the new layer [42,43]. Modifying the filament by adding thermal conductive fillers is another method. These fillers help to generate heat between interlayers and entangle the polymer on the surface under external stimulus like a microwave and infrared lamps. For example, thermoplastic filaments coated with carbon nanotube (CNT)-rich layer were used to weld the printed interfaces using microwave irradiation [44]. CNTs were selected since they are known to quickly generate heat on exposure to microwave radiation. The thermoplastic coated CNT layer was made via the bath coating process, as shown in Fig. 6a. Once the printed coaxial composite filaments were exposed to the micro irradiation, the CNT-rich layers were selectively heated, and the entanglement of polymers across the interface was enhanced, resulting in increased fracture strength, as shown in Fig. 6b.

Table 2
Comparison of the physical and mechanical properties, and printing conditions of PLA, ABS, Nylon, PC, PET, and PEEK for FDM.

	PLA	ABS	Nylon 6	PC	PETG	PEEK
Glass transition temperature (°C)	53–64	102–115	47–57	140–151	75–80	137–152
Melting temperature (°C)	145–186	–	220	220–260	–	335–343
Heat deflection temperature (°C)	56	100	190	190	71	160
Modulus (GPa)	1.2–3.0	1.8–2.39	2.8–3.1	2.34	0.9–1.1	3.56
Tensile strength (MPa)	28–50	25–65	79	62	55	92
Printing temperature (°C)	190–220	220–250	220–270	260–310	230–250	360–450
Bed temperature (°C)	45–60	95–110	70–90	80–120	75–90	120–150
Ref.	[36,37]	[37,38]	[36,37]	[36,37]	[37,39,40]	[36,41]

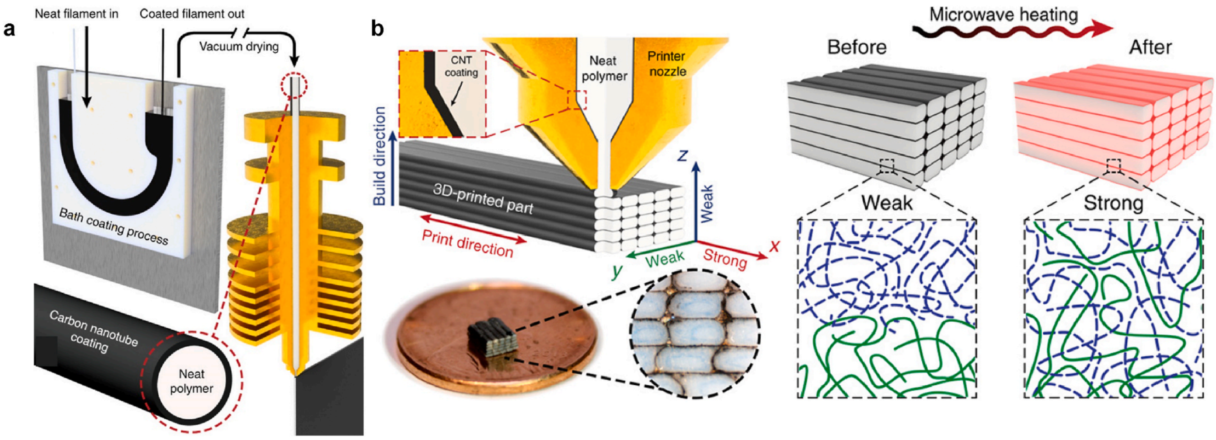

Fig. 6. Strategies to increase interfacial bonding of printed filaments. (a) Thermoplastic filament coated with CNT/polymer ink [44]. (b) Schematic of 3D printing using thermoplastic filaments coated with a CNT-rich layer to locally heat the interface between the printed layers [44].

3.1. Multi-material/structure filaments

Multi-material/structure filaments such as core-shell filament have been also studied to improve printing quality and mechanical properties, including impact resistance and fracture toughness. For example, the semi-crystalline polymers are difficult to be printed with high quality because of the large volume change on crystallization [45]. But these challenges can be overcome using multi-material/structure filaments. For instance, a core-shell filament was manufactured using the conventional filament fabrication method for enhanced mechanical properties, such as impact resistance and toughness [46]. In the fabrication of the filaments, two single screw extruders were used by connecting them to a core-shell coextrusion die with a circular opening, as shown in Fig. 7a. As materials, PC/ABS mixture was used as core and either high-density polyethylene (HDPE) or low-density polyethylene (LDPE) was used as an outer shell. This core-shell filament exhibited higher toughness than those of PC/ABS blend filament. As shown in Fig. 7b. and 7c., the core-shell filament had lower modulus than the PC/ABS blend filament because of the less stiffness of polyethylene, but better toughness because of the high ductility of polyethylene. Another multi-material/structure filament is dual-material filaments using a novel thermal draw process [47]. The dual-material filaments were composed of PC and ABS in a core and an outer, respectively. The filaments were printed using FDM and then thermally drawn into continuous filaments, as shown in Fig. 7d. Different from the previous example, this manufacturing method can manipulate the core shape of the filaments.

3.2. Polymer composite filaments

As the demand for custom-shaped functional products increases, 3D printing for composites has also been developed, which has advantages in terms of cost and optimized structure. Depending on the purpose of the final product, such as electronic products and artificial bone implants, different types of fillers including carbon nanomaterials [48–50], metals [51,52], biomaterials [53–55], and ceramics [56–58] are employed.

3.2.1. Composite filaments using carbon nanomaterials

Carbon nanomaterials such as graphene/graphite and carbon nanotube (CNT) are actively utilized as reinforcement materials due to high electrical and thermal stability, low density, and good mechanical properties (strength, stiffness, and toughness) [59–61]. The carbon composites with high electronic conductivity are attractive in many potential applications especially in the field of electronics including energy storage devices, sensors, and electrically conductive structures [62]. Compared to electronics and electrochemical devices manufactured by the conventional manufacturing techniques, such as slurry casting and coating nanomaterials on the substrate, 3D printing provides a simplistic, rapid, and low-cost approach to producing these electronics with complex structure. In addition, 3D printing allows to manipulate the structure of the components by overcoming limitations of electronics and electrochemical devices (i.e., the trade-off between power and energy of conventional electrode, a lack of scalability and high cost for producing high-resolution sensors). As 3D printing for these products have been actively studied, they exhibit better performance in terms of high areal energy and power density and high sensitivity, compared to the conventional electrodes and sensors, respectively [63,64]. One example is a solid-state supercapacitor using commercial filament, a graphene-based-PLA filament [48]. The graphene composites with a circular disk shape were printed via an FDM printer and then coated with gold. They were used as a working electrode and current collector, as shown in Fig. 8a. The 3D printed supercapacitor exhibited good capacitive performance (specific capacitance with 98.37 F g^{-1} at a current density of 0.5 Ag^{-1}) and stable cycling stability up to 100 charges/discharge cycles (81.94% in capacitance retention). Another example is 3D disc electrodes for the lithium-ion anode and the solid-state graphene supercapacitor using graphene-based commercial filament [49]. The filament was comprised of only 8% graphene and 92% PLA, but it had a conductivity of 2.13 S/cm. Fig. 8b shows the printing process for 3D disc electrodes with the graphene-based-PLA filament and the coin cell assembly for the lithium-ion battery. In addition to the energy storage devices, force sensors can be manufactured with FDM using functional nanocomposite filament, which is CNT/polyurethane (TPU) filaments [50]. CNTs were dispersed in a TPU matrix using a shear melting process with a twin-screw extruder to manufacture the composite filaments, and the resistivity of the extruded filaments was about 0.143 Ω m. The two discrete parts (structural part and sensing part) were fabricated via FDM with multi-nozzles capable of individually printing pure TPU and CNT/TPU composite filaments, as shown in Fig. 8c. In a bending test, the force sensor with the 2.4 mm thickness of the TPU beam and 0.6 mm thickness of the CNT/TPU beam exhibited piezoresistive properties with 0.55% resistance changes at 2 mm deflection.

In addition to improving the functional abilities, the use of carbon nanomaterials as reinforcements can enhance mechanical properties. This is because that these nanomaterials, including graphene-nanoplate (GNP) and CNT, have a large aspect ratio and excellent mechanical properties. In the literature, there are examples of using carbon nanomaterials such as GNP [65] and CNT [66] to improve mechanical properties of the printed products. The composites using GNP showed higher Young's modulus (158.4%), ultimate tensile strength (43.2%),

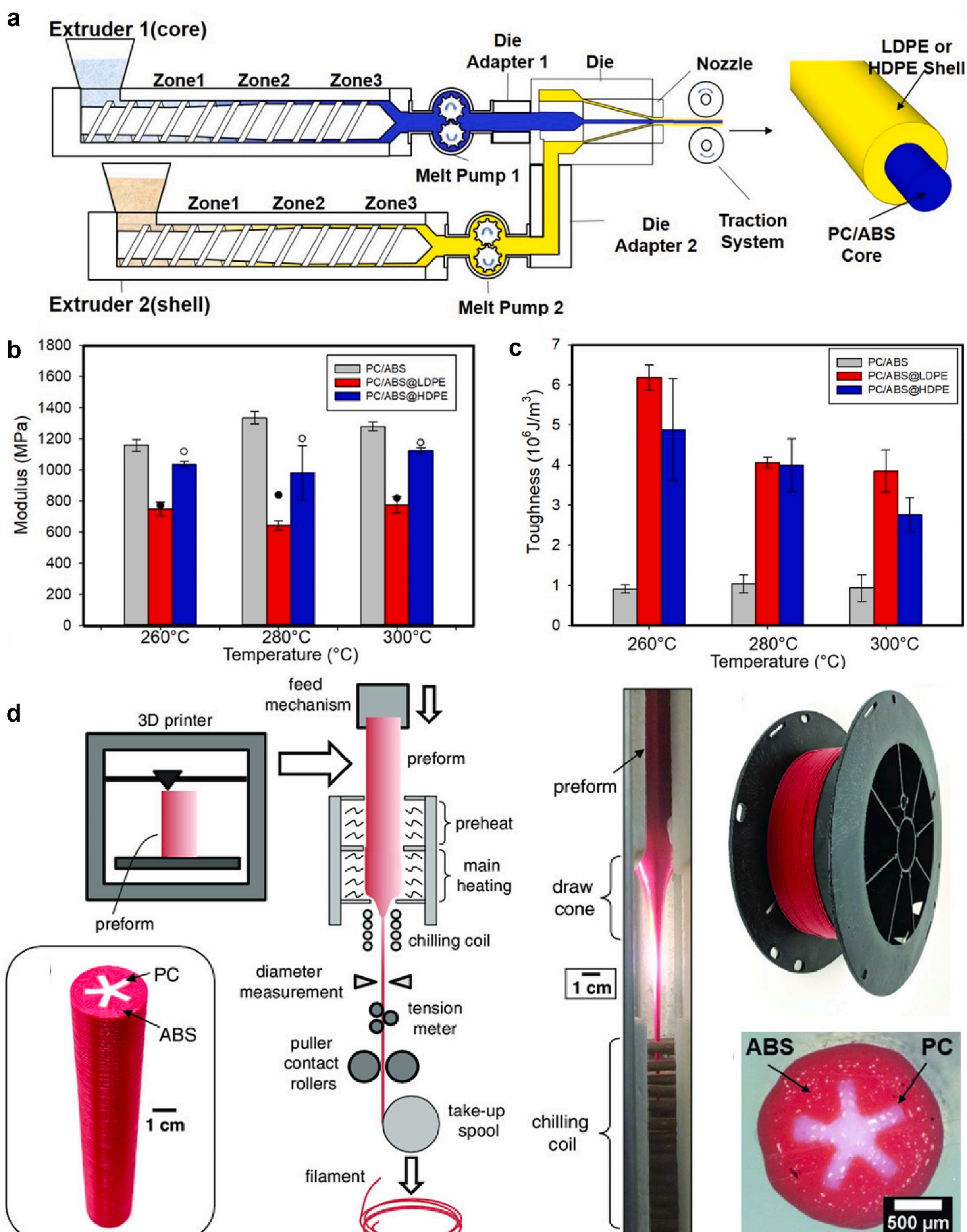

Fig. 7. Multi-material/structure filament design and manufacturing. (a) Schematic of co-extrusion process for core-shell filaments (PC/ABS with LDPE or HDPE) [46]. (b), (c) Modulus, and toughness of the printed samples at various temperatures, respectively [46]. (d) The filament fabrication procedure using 3D printing and thermal draw process [47].

and lower elongation at break (495.9%) in the printed direction, compared to the Poly (vinyl alcohol) (PVA) [65]. For CNT-reinforced composite, the composite had improved tensile strength (~130%) in an aligned orientation, compared to the ABS object [66].

3.2.2. *Composite filaments using metals*

Metal/polymer filaments are also actively used in energy storage devices, semiconductors, and circuits. The filaments come in diverse materials ranging from copper and bronze to iron and stainless steel

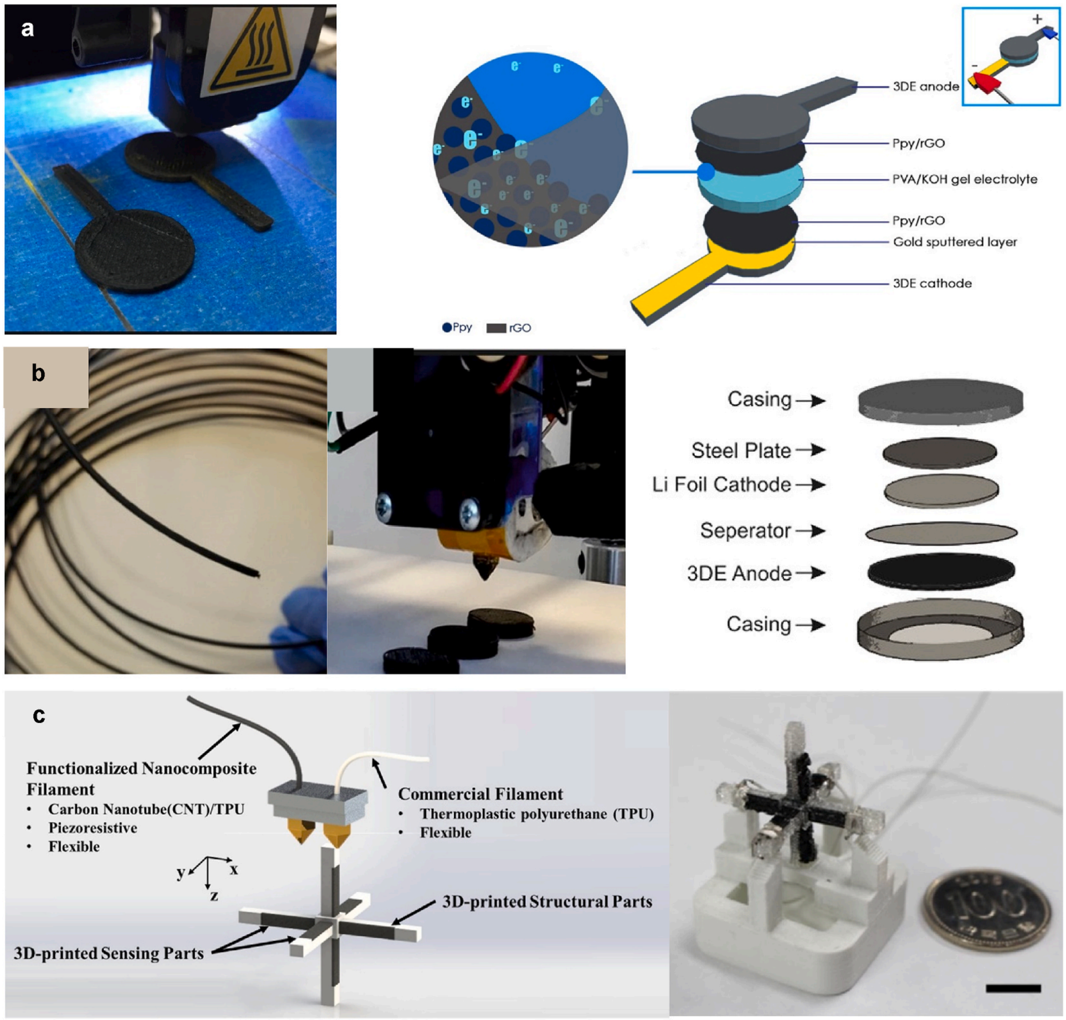

Fig. 8. Applications of the composite filaments using carbon nanomaterials. (a) 3D printed electrode in a solid-state supercapacitor using commercial graphene-based conductive filament [48]. (b) 3D disc electrode for solid-state battery with commercial graphene-based-PLA filament [49]. (c) Force sensor produced by CNT/TPU filaments [50].

[67–69]. A commercial metal/PLA filament, shown in Fig. 9a, was actively used for electronic devices, because the metal filament showed more flexibility and lower electronic resistivity (0.006 Ω cm) and lower impedance (around 3 Ω over a range of frequencies from 1 Hz to 1 MHz), compared to those of carbon black and graphene-based filaments [51]. Using the copper-based filament as conductive materials, bronze-fill PLA filament as dielectric materials, and pure PLA filament as insulating materials, a variety of conductive traces, resistors, inductors, and capacitors with optimized shape were fabricated. Fig. 9b shows the embedded circuits for lightning LED and capacitor. Meanwhile, research to make their own copper/PLA filament for semiconductor printing has been done. The polymer composites were prepared by mixing 80 wt% of copper particles into the PLA matrix, and the filaments were fabricated by the extrusion method under the controlled pressure [52]. After that, the printed samples using FDM were sintered and calcined at 900 °C to convert the copper models to copper oxide (CuO) models, as shown in Fig. 9c. The printed semiconductor can be used as a multifunctional semiconductor device responding to light, pressure, and temperature.

Metal is a good reinforcement material in structure parts due to their higher mechanical properties such as hardness, toughness, and strength. Compared to metal printing, the metal-reinforced composites are easy to print because they do not need high-temperature extruder and cost-effective due to no requirement of a specific power distribution. Among many types of metals, copper [70,71], aluminum [70], and stainless steel [72] in powder form are actively used as reinforcement for filaments. For example, the copper or aluminum-based PLA composite showed higher tensile modulus (104.8% or 134.5%, respectively) [70].

3.2.3. *Composite filaments using biomaterials*

Filaments containing biomaterials seek to not only fabricate customized implants such as artificial bone but also mitigate the environmental impact of plastic waste on the earth. Instead using petroleum-derived plastic such as nylon and PET, biobased materials, come from carbon-neutral feedstock like lignin, can help to reduce environmental pollution. The eco-friendly filament can be fabricated by adding lignin into PLA [53]. In particular, lignin is abundant in the fibrous parts of various plants. Compared to petroleum-based polymers, PLA, which has a lower carbon footprint in production, can be mixed with lignin to make composite filaments more environmentally friendly without mechanical degradation. Fig. 10a shows the PLA/lignin filament with 5 wt% of lignin contents. With the addition of lignin, PLA filaments became environmentally friendly without compromising the modulus of elasticity. In a thermogravimetric analysis of kraft lignin, thermal decomposition occurred over a wide temperature range starting from 216 °C. Another eco-friendly filament is bio-composite filament through twin-screw extrusion using PLA and microcrystalline cellulose (MCC) [54]. Fig. 10b shows the PLA/MCC filament and 3D printed porous circle using the filament. Processing PLA/MCC filament is a little bit

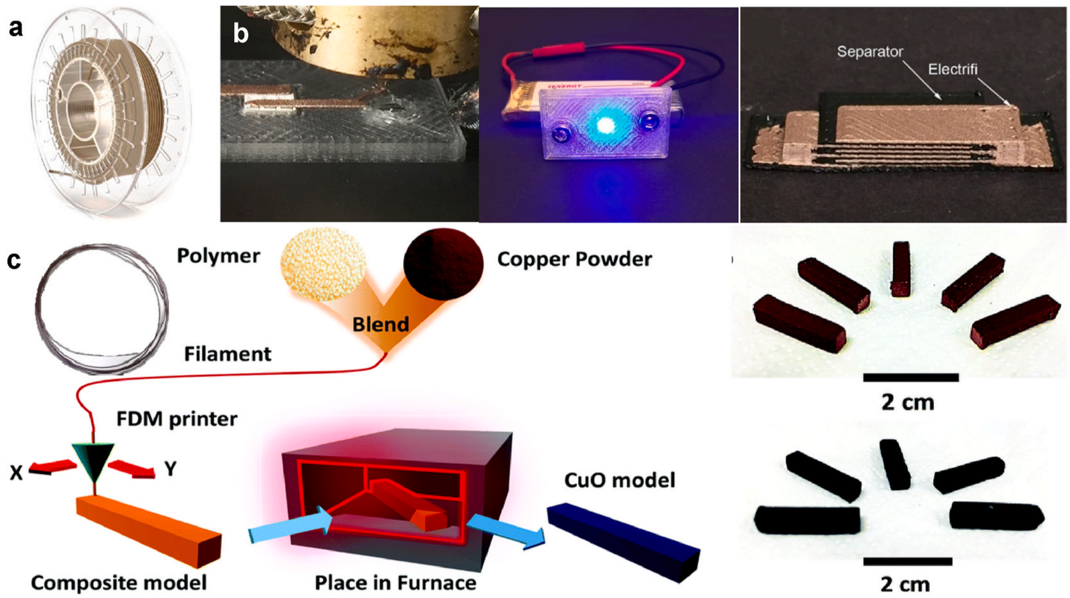

Fig. 9. Applications of the composite filaments using metals. (a) The commercial PLA/copper filament. (b) The printed embedded circuit and five-layer parallel plate capacitor using commercial PLA/copper filament and pure PLA separator [51]. (c) The process to make 3D printed CuO semiconductor using copper/PLA filament [52].

challenging as the cellulose is prone to creating bubbles within the filaments. The printed bio-composites under the optimized printing conditions exhibited a higher storage modulus, compared with pure PLA. O-acetyl galactoglucomannan (GGM), a wood-derived biopolymer, can also be used to replace the PLA as bio-feedstock in 3D FDM printing [55]. GGM is a common derivative of hemicellulose from spruce wood and prominent as cost-effective biomaterials. The PLA and hemicellulose (up to 25% ratio) were mixed through a solvent blending approach. The mixtures were extruded into filament via hot-melt extrusion (using a single-screw extruder), and the 3D scaffold samples were printed via FDM printing, as shown in Fig. 10c. These biocompatible and biodegradable scaffolds have significant potential in various biomedical applications (e.g., tissue engineering and drug-eluting scaffolds).

3.2.4. *Composite filaments using ceramics*

The high mechanical strength and hardness, good thermal and chemical stability, and feasible optical and electrical performance of ceramics make ceramics versatile materials [73]. Ceramic components are generally produced using conventional technologies, such as injection molding, die pressing, and gel casting, but takes long time to process and limits design flexibility. For these reasons, 3D printing for ceramics has been prominent as alternative manufacturing method, some 3D printing techniques, including stereolithography and laminated object manufacturing, have printed composites with mechanical properties similar to those produced by conventional process [73]. Ceramics are widely used as fillers for FDM printing to apply various applications including biomedical fields [56,74] and electronics [57,58,75]. Ceramic composites produced with FDM can achieve high quality (e.g., homogeneity, dimensional accuracy, and mechanical properties) when printed with optimized parameters, including layer thickness and building orientation. For instance, 3D artificial bones were manufactured to mimic natural goat femurs through computed tomography (CT)-guided FDM using polycaprolactone (PCL)/hydroxyapatite (HA) filament, as shown in Fig. 11a [56]. CT-guided FDM uses X-ray CT to scan the goat leg and the CT data is converted into a 3D model. This printing method is a simple, relatively low-cost for artificial bones. The PCL/HA filament was fabricated using a twin-screw, and the bone made from the filament had mechanical properties close to that of natural bone (adult goat femur: >18.17 MPa and >132.22 MPa, and 3D printed bone: 15.43 MPa and 80.16 MPa in compressive strength and modulus, respectively), good biocompatibility, and biodegradation ability. Another example is dielectric devices using ABS and barium titanate (BT) [57]. The composites exhibited a shear thinning behavior as the ceramic content increased but showed brittle behavior. The ABS/BT composites were prepared by kneading the ABS pellets with the BT particles (up to 74.2 wt% BT powder), and the filaments were made using a melting shear process with a single screw, and then the electrodes were printed via normal FDM machine, as shown in Fig. 11b. and c. Fig. 11d shows the manufactured ABS/BT filaments and the printed electrodes. The ABS/BT with 35 vol% sample had a relative permittivity of 11.5 at 200 kHz, and the relative permittivity of the composites increased as the amount of BT filler increased. 3D structures for actuators, transducers, and sensors can also be printed using piezoelectric ceramics such as lead–zirconate–titanate (PZT) and lead-magnesium-niobate-lead-titanate (PMN-PT) [58]. For the green ceramic filament, ECG9 was used as a polymer binder, and silver-palladium powders and piezoelectric materials were added for the functional use. The printing process was same with normal FDM process, as shown in Fig. 11e. After printing the 3D structure, the binder was removed through sintering. With the composite filament, various transducers with different shape were manufactured for actuator, broadband resonant transducer, and sensor applications, as shown in Fig. 10f.

3.2.5. *Composite filaments using fibers*

Fiber-reinforced polymer composites have great potential in structural industries, including aerospace, automotive, and energy applications, due to high mechanical properties with lightweight. Both discontinuous fibers (e.g., chopped glass fibers [76], chopped carbon fibers [77], and short basalt fibers [78]) and continuous fibers (e.g., glass [79], carbon [79,80], and aramid fibers [81]), are used as reinforcements for the composite, but continuous fiber-reinforced composites exhibit high performance compared to the discontinuous fiber-reinforced ones. Because continuous fibers have long aspect ratio and normally have aligned orientation in composites. Nowadays, 3D printing for fiber-reinforced composites has actively studied to manufacture structural applications using high mechanical properties and design flexibility of 3D printing.

One example using continuous fiber composite is 3D printing of

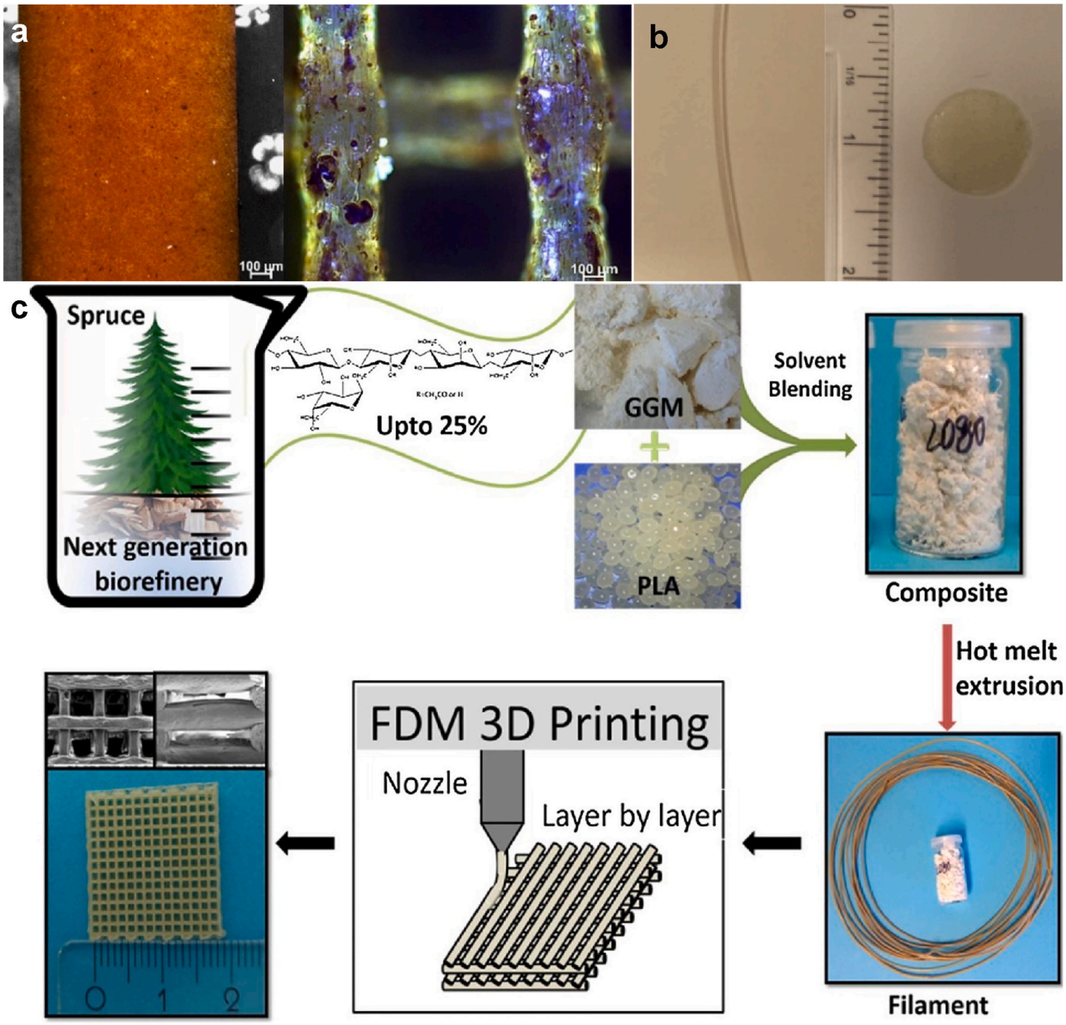

Fig. 10. Applications of the composite filaments using biomaterials. (a) Reflected light micrographs of PLA/5 wt% of lignin [53]. (b) The filament and the 3D printed circle of PLA/MCC filament with 3 wt% MCC [54]. (c) Overall process to manufacture bio-composite products from the preparation of the filaments using GGM and PLA to FDM 3D printing [55].

carbon fiber-reinforced filament (CFF) for steering blades, elevators, and rudders in aircraft [80]. FDM printer has successfully printed light-weight and high-performance composites using a sandwich structure that provides both light weight in the core and high mechanical properties (tensile and compressive strength) in the outer skin. Using commercial CFF, the sandwich structures with various core shapes (honeycomb, rhombus, rectangle, and circle) were printed, as illustrated in Fig. 12a. The mechanical properties of the sandwich structures showed large difference in three-point bending tests depending on the core shape. The corners of each core have different angles from the side of the outer skin, such as 60° in honeycomb and 45° in rhombus, and it affects the reinforcement effect of each composite. The structures with rhombus exhibited the highest flexural modulus per density ($E/\rho = 18$ GPa/(g/mm^3)), followed by circle (17.8), honeycomb (15), and rectangle (14.3).

Short fiber is also attractive because of their ease of processing, cost-effectiveness, and good mechanical properties. As an example, the circular honeycombs of PLA-Polycaprolactone (PCL)/KH550-treated basalt fiber (KBF) were printed with FDM [78]. Basalt fiber-reinforced composites are prominent as an alternative to carbon fiber-reinforced composite in terms of cost, and PLA/KBF has good printability and comparable mechanical properties with PLA/CFF composites. In addition, by mixing soft phase PCL with hard phase PLA, the composites had both stiffness and toughness. In this example, the composites were printed with different weight fraction of PCL from 0% to 40%. As shown in Fig. 12b, with the addition of PLC, side surface became smooth, and the printed composite had improved printing interlayer adhesion, resulting in high compressive strength and energy absorption. The printed sample with 30 wt% of PLC showed the highest mechanical properties, but the modulus of the specimen was lower than that of pure PLA/KBF due to lower modulus of PCL. This experiment showed the potential of the PLA-PCL/KBF structures for energy absorption.

4. Perspective and conclusion

This paper presents an overview of the polymer-based filament feedstocks for FDM from material and process to applications. FDM technology has been considered a promising technology due to its various choice of materials. For example, in the case of stereolithography (SLA), it is difficult to add black fillers such as carbon nanomaterials into the liquid resin, because the dark color of the materials can interfere with the light absorption of the resin, resulting in poor solidification. Due to these advantages, FDM technology has been actively used in many applications with the development of the polymer composite filaments. In this section, we will share our view on the key challenges and future development of FDM for polymer-based filament. This is summarized in Fig. 13 and the relevant contents are discussed below.

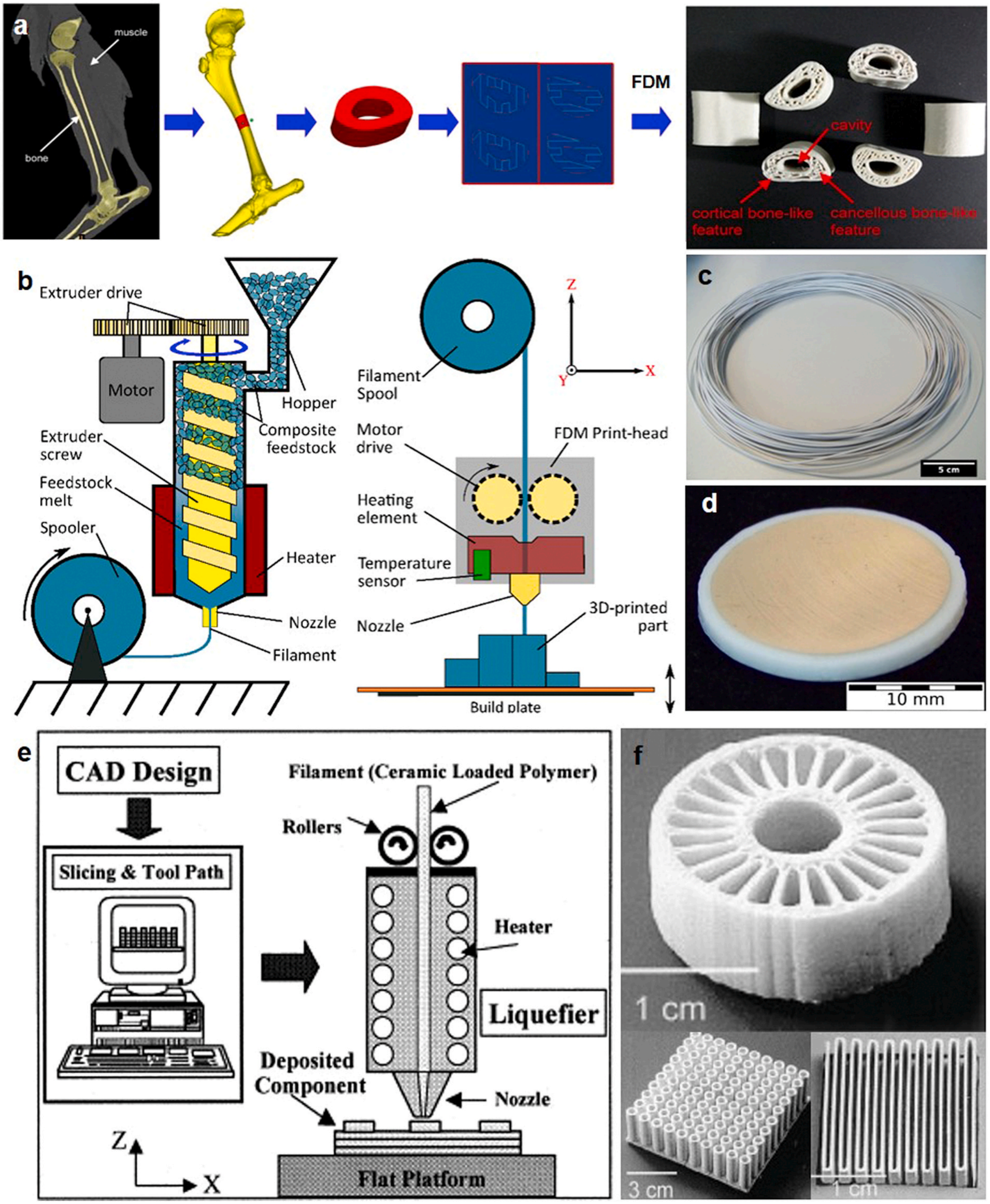

Fig. 11. Applications of the composite filaments using ceramics. (a) The 3D artificial goat femurs made of PCL/HA filament through computed tomography (CT)-guided FDM [56]. (b) A schematic of melting shear process with a single screw for the ceramic filament and FDM techniques for printing electrodes. The kneaded composite chunks were used to fabricate the ceramic filament [57]. (c) The fabricated ABS/BT composite filament [57]. (d) The printed electrode using ABS/BT filament with sputtered gold on the top surface for dielectric devices [57]. (e) A schematic of fused deposition of ceramics to manufacture the advanced ceramic components [58]. (f) Transducers with tube, curved, radical shape made of piezoelectric ceramics [58]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.

1) Filament. A lot of research has been done to develop higher performance polymer composites by incorporating diverse fillers and thermoplastics. Before making the thermoplastic composite filaments, we should consider the type and shape of the fillers you need for a specific purpose. For example, the carbon nanomaterials are actively used as reinforcements for the composite filaments to manufacture lightweight and conductive 3D products. In carbon materials, there are various choices from carbon black (0-dimensional shape), CNT (1-dimensional shape), and graphene (2-dimensional shape) to 3D hybrid networks such as 3D CNT networks and

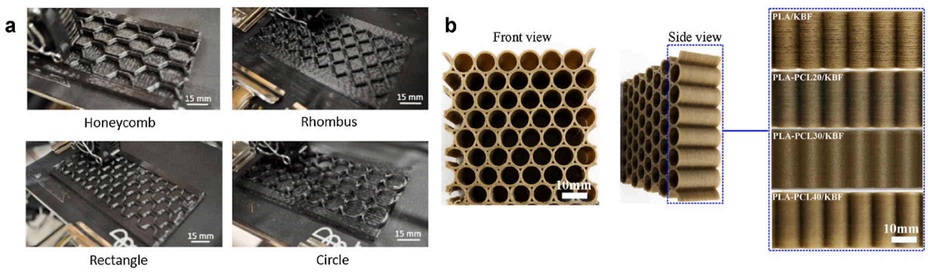

Fig. 12. Applications of the fiber-reinforced composite filaments. (a) The sandwich structure with various course shapes (honeycomb, rhombus, rectangle, and circle) [80], and (b) The 3D printed circular honeycombs of PLA-PCL/KBF with varying ratios (from 0 wt% of PCL to 40 wt% of PLC) [78].

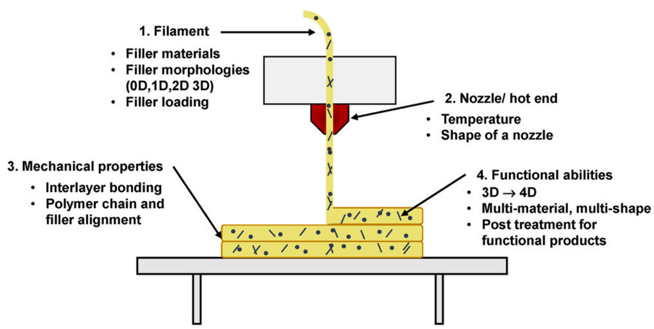

Fig. 13. Several factors to consider for FDM printing of the thermoplastic composites.

graphene-CNT hybrids. In the case of the 3D network carbon nanomaterials, they have several advantages like high surface area, minimized agglomeration or re-stacking, and enhanced thermal and electrical transport. Another thing to consider when manufacturing composite filaments is the thermal decomposition of the fillers. In the case of the polymer composites using microcrystalline cellulose, it needs to pay attention to set the parameters including temperature, backpressure, and extrusion speed to prevent the formation of bubbles within the filament [54]. Moreover, we should take into account the loading of fillers and filler size. If a high content of fillers is added to the polymer, the filaments can become brittle due to particle clustering and may break during printing, resulting in clogged nozzle. Also, if the ratio of filler diameter to a nozzle diameter is greater than 6.2 under an extrusion force less than 42 N, complete clogging occurs [82]. To overcome these limitations, a higher extrusion force or smaller size filler is required.

2) Nozzle and hot end. An important part in a FDM printer is the hot end including a nozzle. There are different shape styles of nozzle depending on the length and the width. For the nozzle length, a shorter nozzle gives shorter cooling time and reduces heat loss before the filament leaves the nozzle, providing good adhesion to the previously printed layer. Longer nozzle, on the other hand, has more distance and gives more time for the filament to cool, making printed filament harder before bonding the printed layer. In the case of nozzle width, it can affect the surface quality of the object. For example, the narrow one may cause bulge outwards and upwards, especially when layer height is low. Also, the temperature at the hot end is the essential parameter to print out the filaments. When printing the high performance of polymer composites, the hot end requires a high temperature to melt the materials, but the temperature of the hot end is kept as low as possible to prevent the material degradation. The last thing to consider when printing polymer composites is the wear of the nozzles due to rigid reinforcements, including ceramics and metals. These fillers can wear down the nozzle, so it is better to use wear-resistance nozzle, such as steel nozzle, instead of a standard brass nozzle that is relative soft.

3) Mechanical properties. The main issue in FDM printing is the anisotropic mechanical properties of the printed parts. One of reasons is the weak interlayer bonding between printed layers in the thickness direction, resulting in the limited strength of the printed objects. As mentioned in section 3, there are several attempts to handle this challenge by locally heating the printed layer using a laser, microwave, and infrared lamps. Another factor that causes anisotropic properties depending on the printing direction is the arrangement of polymer chains and fillers. The polymer chains and fillers in the filaments are aligned in the direction of flow within the nozzle, resulting in high mechanical properties in printed direction, compared to the those in the transverse direction or the direction perpendicular to the layers.

4) Functional abilities. With the recent introduction of smart materials, including shape memory polymers, smart hydrogel composites, and liquid crystal polymers and elastomers, 3D printing has been developed into 4D printing to get advanced functional abilities. The process of 4D printing is the same as 3D printing, but 4D printing is based on the materials system for the desired state and movement. 4D printing produces 3D objects that change their shape and properties as a function of time under external stimuli such as heat [8,9] and water [83]. Another way to manufacture functional objects is utilizing post-treatment like thermal treatment. Metal oxides, for example, have excellent optical, electrical, thermoelectric, and chemical properties, and are most often studied as inorganic semiconductors. For copper oxide semiconductors, sintering process can be applied to convert the printed ceramic composite products made of PLA and copper into copper oxide products [52].

5) Sustainability and recycling. With the growing interest in the environment, there are many attempts to reduce and recycle plastic wastes in 3D printing. One of the ways to increase the suitability of 3D printing is making the filament environmentally friendly. As discussed in section 3.1.4, research has been conducted to use bio-based materials instead of petroleum-derived plastics, such as nylon and PET, to mitigate the environmental impact of plastic waste on the earth. Another way for 3D printing sustainability is the use of filaments made from recycled waste plastics. Most of filaments are made of thermoplastics and thermoplastics are easier to recycle than thermosets due to no or low degradation of the polymer chain when they melted. For example, the polyethylene terephthalate bottles and packaging have been recycled as filaments for 3D printing [84]. The recycled filaments showed the potential to replace commercial filaments by showing similar tensile strength and elongation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is supported by the University of Delaware startup funding.

References

[1] T. Wohlers, T. Gornet, History of Additive Manufacturing, 2016.
[2] D. Kazmer, Three-dimensional printing of plastics, in: Appl. Plast. Eng. Handb. Process. Mater. Appl. Second Ed., Elsevier Inc., 2017, pp. 617–634, https://doi.org/10.1016/B978-0-323-39040-8.00029-8.
[3] C. Lee Ventola, Medical applications for 3D printing: current and projected uses, P T., December 20, 2020, www.thingiverse.com, 2014, 39, 704-711.
[4] L.E. Murr, Frontiers of 3D printing/additive manufacturing: from human organs to aircraft fabrication, J. Mater. Sci. Technol. 32 (2016) 987–995, https://doi.org/10.1016/j.jmst.2016.08.011.
[5] F. Yang, M. Zhang, B. Bhandari, Recent development in 3D food printing, Crit. Rev. Food Sci. Nutr. 57 (2017) 3145–3153, https://doi.org/10.1080/10408398.2015.1094732.
[6] C. Gosselin, R. Duballet, P. Roux, N. Gaudillière, J. Dirrenberger, P. Morel, Large-scale 3D printing of ultra-high performance concrete - a new processing route for architects and builders, Mater. Des. 100 (2016) 102–109, https://doi.org/10.1016/j.matdes.2016.03.097.
[7] S.T. Ly, J.Y. Kim, 4D printing – fused deposition modeling printing with thermal-responsive shape memory polymers, Int. J. Precis. Eng. Manuf. - Green Technol. 4 (2017) 267–272, https://doi.org/10.1007/s40684-017-0032-z.
[8] Q. Zhang, K. Zhang, G. Hu, Smart three-dimensional lightweight structure triggered from a thin composite sheet via 3D printing technique, Sci. Rep. 6 (2016) 1–8, https://doi.org/10.1038/srep22431.
[9] T. Van Manen, S. Janbaz, A.A. Zadpoor, Programming 2D/3D shape-shifting with hobbyist 3D printers, Mater. Horizons. 4 (2017) 1064–1069, https://doi.org/10.1039/c7mh00269f.
[10] C.Y. Cheng, H. Xie, Z. yuan Xu, L. Li, M.N. Jiang, L. Tang, K.K. Yang, Y.Z. Wang, 4D printing of shape memory aliphatic copolyester via UV-assisted FDM strategy for medical protective devices, Chem. Eng. J. 396 (2020), 125242, https://doi.org/10.1016/j.cej.2020.125242.
[11] A. Zolfagharian, A. Kaynak, A. Kouzani, Closed-loop 4D-printed soft robots, Mater. Des. 188 (2020), 108411, https://doi.org/10.1016/j.matdes.2019.108411.
[12] I. Gibson, D.W. Rosen, B. Stucker, I. Gibson, D.W. Rosen, B. Stucker, Extrusion-based systems, in: Addit. Manuf. Technol., Springer US, 2010, pp. 160–186, https://doi.org/10.1007/978-1-4419-1120-9_6.
[13] S. Berretta, R. Davies, Y.T. Shyng, Y. Wang, O. Ghita, Fused Deposition Modelling of high temperature polymers: exploring CNT PEEK composites, Polym. Test. 63 (2017) 251–262, https://doi.org/10.1016/j.polymertesting.2017.08.024.
[14] M. Elbadawi, Polymeric additive manufacturing: the necessity and utility of rheology, in: Polym. Rheol., InTech, 2018, https://doi.org/10.5772/intechopen.77074.
[15] T.N.A.T. Rahim, A.M. Abdullah, H. Md Akil, Recent developments in fused deposition modeling-based 3D printing of polymers and their composites, Polym. Rev. 59 (2019) 589–624, https://doi.org/10.1080/15583724.2019.1597883.
[16] M.E. Mackay, The importance of rheological behavior in the additive manufacturing technique material extrusion, J. Rheol. 62 (2018) 1549–1561, https://doi.org/10.1122/1.5037687.
[17] N. Shadvar, E. Foroozmehr, M. Badrossamay, I. Amouhadi, A.S. Dindarloo, Computational analysis of the extrusion process of fused deposition modeling of acrylonitrile-butadiene-styrene, Int. J. Material Form. (2019) 1–11, https://doi.org/10.1007/s12289-019-01523-1.
[18] H. Valkenaers, F. Vogeler, A. Voet, J.P. Kruth, Screw Extrusion Based 3D Printing, a Novel Additive Manufacturing Technology, (n.d).
[19] D.K. Tan, M. Maniruzzaman, A. Nokhodchi, Advanced pharmaceutical applications of hot-melt extrusion coupled with fused deposition modelling (FDM) 3D printing for personalised drug delivery, Pharmaceutics 10 (2018), https://doi.org/10.3390/pharmaceutics10040203.
[20] G. Spinelli, R. Kotsilkova, E. Ivanov, I. Petrova-Doycheva, D. Menseidov, V. Georgiev, R. Di Maio, C. Silvestre, Effects of filament extrusion, 3D printing and hot-pressing on electrical and tensile properties of poly(lactic) acid composites filled with carbon nanotubes and graphene, Nanomaterials 10 (2019) 35, https://doi.org/10.3390/nano10010035.
[21] G.L. Goh, S. Agarwala, W.Y. Yeong, Directed and on-demand alignment of carbon nanotube: a review toward 3D printing of electronics, Adv. Mater. Interfaces. 6 (2019), 1801318, https://doi.org/10.1002/admi.201801318.
[22] Production lines - zamak mercator, n.d. http://www.zamakmercator.com/en/oferta-8/linie-produkcyjne-2.html#1. (Accessed 16 January 2021).
[23] H.G. Geus, Developments in manufacturing techniques for technical nonwovens, in: Adv. Tech. Nonwovens, Elsevier Inc., 2016, pp. 133–153, https://doi.org/10.1016/B978-0-08-100575-0.00005-X.
[24] H. Patil, R.V. Tiwari, M.A. Repka, Hot-melt extrusion: from theory to application in pharmaceutical formulation, AAPS PharmSciTech 17 (2016) 20–42, https://doi.org/10.1208/s12249-015-0360-7.
[25] M.M. Crowley, F. Zhang, M.A. Repka, S. Thumma, S.B. Upadhye, S. Kumar Battu, J. W. McGinity, C. Martin, Pharmaceutical applications of hot-melt extrusion: Part I, Drug Dev. Ind. Pharm. 33 (2007) 909–926, https://doi.org/10.1080/03639040701498759.
[26] A. Shrivastava, Plastics processing, in: Introd. To Plast. Eng., Elsevier, 2018, pp. 143–177, https://doi.org/10.1016/b978-0-323-39500-7.00005-8.
[27] D. Garlotta, A literature review of poly(lactic acid), J. Polym. Environ. 9 (2001) 63–84, https://doi.org/10.1023/A:1020200822435.
[28] V. DeStefano, S. Khan, A. Tabada, Applications of PLA in modern medicine, Eng, Regen 1 (2020) 76–87, https://doi.org/10.1016/j.engreg.2020.08.002.
[29] C.C. Kuo, L.C. Liu, W.F. Teng, H.Y. Chang, F.M. Chien, S.J. Liao, W.F. Kuo, C. M. Chen, Preparation of starch/acrylonitrile-butadiene-styrene copolymers (ABS) biomass alloys and their feasible evaluation for 3D printing applications, Compos. B Eng. 86 (2016) 36–39, https://doi.org/10.1016/j.compositesb.2015.10.005.
[30] B.-G. Cho, S.P. McCarthy, J.P. Fanucci, S.C. Nolet, Fiber reinforced nylon-6 composites produced by the reaction injection pultrusion process, Polym. Compos. 17 (1996) 673–681, https://doi.org/10.1002/pc.10659.
[31] J.Y. Lee, J. An, C.K. Chua, Fundamentals and applications of 3D printing for novel materials, Appl. Mater. Today. 7 (2017) 120–133, https://doi.org/10.1016/j.apmt.2017.02.004.
[32] F. Fischer, Thermoplastics: the Best Choice for 3D Printing, 2011.
[33] L.O. Dandy, G. Oliveux, J. Wood, M.J. Jenkins, G.A. Leeke, Accelerated degradation of Polyetheretherketone (PEEK) composite materials for recycling applications, Polym. Degrad. Stabil. 112 (2015) 52–62, https://doi.org/10.1016/j.polymdegradstab.2014.12.012.
[34] D.J. Blundell, A.B. Newton, Variations in the crystal lattice of PEEK and related para-substituted aromatic polymers: 2. Effect of sequence and proportion of ether and ketone links, Polymer 32 (1991) 308–313, https://doi.org/10.1016/0032-3861(91)90019-F.
[35] W. Wang, J.M. Schultz, B.S. Hsiao, Dynamic study of crystallization-and melting-induced phase separation in PEEK/PEKK blends. https://pubs.acs.org/sharingguidelines, 1997. (Accessed 12 April 2021).
[36] Polymer Data Handbook - James, n.d., E. Mark - Oxford University Press, https://global.oup.com/academic/product/polymer-data-handbook-9780195181012?cc=us&lang=en&. (Accessed 9 September 2020).
[37] Heat deflection temperature (HDT) at 0.46 MPA (67 psi), n.d. https://omnexus.specialchem.com/polymer-properties/properties/hdt-0-46-mpa-67-psi. (Accessed 19 April 2021).
[38] Handbook of Polymers, second ed., Knovel, https://app.knovel.com/web/toc.v/cid:kpHPE00012/viewerType:toc/root_slug:handbook-polymers-2nd. (Accessed 9 September 2020). n.d.
[39] P. Latko-Durałek, K. Dydek, A. Boczkowska, Thermal, rheological and mechanical properties of PETG/rPETG blends, J. Polym. Environ. 27 (2019) 2600–2606, https://doi.org/10.1007/s10924-019-01544-6.
[40] X. Wang, W. Liu, H. Zhou, B. Liu, H. Li, Z. Du, C. Zhang, Study on the effect of dispersion phase morphology on porous structure of poly (lactic acid)/poly (ethylene terephthalate glycol-modified) blending foams, Polymer 54 (2013) 5839–5851, https://doi.org/10.1016/j.polymer.2013.08.050.
[41] Heat deflection temperature: definition & values at 1.8 Mpa (264 psi), n.d, https://omnexus.specialchem.com/polymer-properties/properties/hdt-1-8-mpa-264-psi. (Accessed 19 April 2021).
[42] A.K. Ravi, A. Deshpande, K.H. Hsu, An in-process laser localized pre-deposition heating approach to inter-layer bond strengthening in extrusion based polymer additive manufacturing, J. Manuf. Process. 24 (2016) 179–185, https://doi.org/10.1016/j.jmapro.2016.08.007.
[43] V. Kishore, C. Ajinjeru, A. Nycz, B. Post, J. Lindahl, V. Kunc, C. Duty, Infrared preheating to improve interlayer strength of big area additive manufacturing (BAAM) components, Addit. Manuf. 14 (2017) 7–12, https://doi.org/10.1016/j.addma.2016.11.008.
[44] C.B. Sweeney, B.A. Lackey, M.J. Pospisil, T.C. Achee, V.K. Hicks, A.G. Moran, B. R. Teipel, M.A. Saed, M.J. Green, Welding of 3D-printed carbon nanotube–polymer composites by locally induced microwave heating, Sci. Adv. 3 (2017) 1–7, https://doi.org/10.1126/sciadv.1700262.
[45] T.M. Wang, J.T. Xi, Y. Jin, A model research for prototype warp deformation in the FDM process, Int. J. Adv. Manuf. Technol. 33 (2007) 1087–1096, https://doi.org/10.1007/s00170-006-0556-9.
[46] F. Peng, H. Jiang, A. Woods, P. Joo, E.J. Amis, N.S. Zacharia, B.D. Vogt, 3D printing with core–shell filaments containing high or low density polyethylene shells, ACS Appl. Polym. Mater. 1 (2019) 275–285, https://doi.org/10.1021/acsapm.8b00186.
[47] K.R. Hart, R.M. Dunn, E.D. Wetzel, Tough, additively manufactured structures fabricated with dual-thermoplastic filaments, Adv. Eng. Mater. 22 (2020), 1901184, https://doi.org/10.1002/adem.201901184.
[48] C.Y. Foo, H.N. Lim, M.A. Mahdi, M.H. Wahid, N.M. Huang, Three-dimensional printed electrode and its novel applications in electronic devices, Sci. Rep. 8 (2018) 1–11, https://doi.org/10.1038/s41598-018-25861-3.
[49] C.W. Foster, M.P. Down, Y. Zhang, X. Ji, S.J. Rowley-Neale, G.C. Smith, P.J. Kelly, C.E. Banks, 3D printed graphene based energy storage devices, Sci. Rep. 7 (2017) 1–11, https://doi.org/10.1038/srep42233.
[50] K. Kim, J. Park, J. hoon Suh, M. Kim, Y. Jeong, I. Park, 3D printing of multiaxial force sensors using carbon nanotube (CNT)/thermoplastic polyurethane (TPU) filaments, Sensors Actuators, A Phys. 263 (2017) 493–500, https://doi.org/10.1016/j.sna.2017.07.020.
[51] P.F. Flowers, C. Reyes, S. Ye, M.J. Kim, B.J. Wiley, 3D printing electronic components and circuits with conductive thermoplastic filament, Addit. Manuf. 18 (2017) 156–163, https://doi.org/10.1016/j.addma.2017.10.002.
[52] A. Salea, R. Prathumwan, J. Junpha, K. Subannajui, Metal oxide semiconductor 3D printing: preparation of copper(II) oxide by fused deposition modelling for multi-functional semiconducting applications, J. Mater. Chem. C. 5 (2017) 4614–4620, https://doi.org/10.1039/c7tc00990a.

[53] E. Gkartzou, E.P. Koumoulos, C.A. Charitidis, Production and 3D printing processing of bio-based thermoplastic filament, Manuf. Rev. 4 (2017), https://doi.org/10.1051/mfreview/2016020.
[54] C.A. Murphy, M.N. Collins, Microcrystalline cellulose reinforced polylactic acid biocomposite filaments for 3D printing, Polym. Compos. 39 (2018) 1311–1320, https://doi.org/10.1002/pc.24069.
[55] W. Xu, A. Pranovich, P. Uppstu, X. Wang, D. Kronlund, J. Hemming, H. Öblom, N. Moritz, M. Preis, N. Sandler, S. Willför, C. Xu, Novel biorenewable composite of wood polysaccharide and polylactic acid for three dimensional printing, Carbohydr. Polym. 187 (2018) 51–58, https://doi.org/10.1016/j.carbpol.2018.01.069.
[56] N. Xu, X. Ye, D. Wei, J. Zhong, Y. Chen, G. Xu, D. He, 3D artificial bones for bone repair prepared by computed tomography-guided fused deposition modeling for bone repair, ACS Appl. Mater. Interfaces 6 (2014) 14952–14963, https://doi.org/10.1021/am502716t.
[57] B. Khatri, K. Lappe, M. Habedank, T. Mueller, C. Megnin, T. Hanemann, Fused deposition modeling of ABS-barium titanate composites: a simple route towards tailored dielectric devices, Polymers 10 (2018) 666, https://doi.org/10.3390/polym10060666.
[58] M. Allahverdi, S.C. Danforth, M. Jafari, A. Safari, Processing of advanced electroceramic components by fused deposition technique, J. Eur. Ceram. Soc. 21 (2001) 1485–1490, https://doi.org/10.1016/S0955-2219(01)00047-4.
[59] V. Choudhary, B.P. Singh, R.B. Mathur, Carbon nanotubes and their composites, in: Synth. Appl. Carbon Nanotub. Their Compos., InTech, 2013, https://doi.org/10.5772/52897.
[60] Q. Chen, J.D. Mangadlao, J. Wallat, A. De Leon, J.K. Pokorski, R.C. Advincula, 3D printing biocompatible polyurethane/poly(lactic acid)/graphene oxide nanocomposites: anisotropic properties, ACS Appl. Mater. Interfaces 9 (2017) 4015–4023, https://doi.org/10.1021/acsami.6b11793.
[61] M. Caminero, J. Chacón, E. García-Plaza, P. Núñez, J. Reverte, J. Becar, Additive manufacturing of PLA-based composites using fused filament fabrication: effect of graphene nanoplatelet reinforcement on mechanical properties, dimensional accuracy and texture, Polymers 11 (2019) 799, https://doi.org/10.3390/polym11050799.
[62] K. Gnanasekaran, T. Heijmans, S. van Bennekom, H. Woldhuis, S. Wijnia, G. de With, H. Friedrich, 3D printing of CNT- and graphene-based conductive polymer nanocomposites by fused deposition modeling, Appl. Mater. Today. 9 (2017) 21–28, https://doi.org/10.1016/j.apmt.2017.04.003.
[63] Z. Lyu, G.J.H. Lim, J.J. Koh, Y. Li, Y. Ma, J. Ding, J. Wang, Z. Hu, J. Wang, W. Chen, Y. Chen, Design and manufacture of 3D-printed batteries, Joule 5 (2021) 89–114, https://doi.org/10.1016/j.joule.2020.11.010.
[64] Y. Ni, R. Ji, K. Long, T. Bu, K. Chen, S. Zhuang, A review of 3D-printed sensors, Appl. Spectrosc. Rev. 52 (2017) 623–652, https://doi.org/10.1080/05704928.2017.1287082.
[65] L. Yang, Y. Chen, M. Wang, S. Shi, J. Jing, Fused deposition modeling 3D printing of novel poly(vinyl alcohol)/graphene nanocomposite with enhanced mechanical and electromagnetic interference shielding properties, Ind. Eng. Chem. Res. 59 (2020) 8066–8077, https://doi.org/10.1021/acs.iecr.0c00074.
[66] B. Podsiadły, P. Matuszewski, A. Skalski, M. Słoma, Carbon nanotube-based composite filaments for 3D printing of structural and conductive elements, Appl. Sci. 11 (2021) 1272, https://doi.org/10.3390/app11031272.
[67] A.R. Torrado Perez, D.A. Roberson, R.B. Wicker, Fracture surface analysis of 3D-printed tensile specimens of novel ABS-based materials, J. Fail. Anal. Prev. 14 (2014) 343–353, https://doi.org/10.1007/s11668-014-9803-9.
[68] M.A. Ryder, D.A. Lados, G.S. Iannacchione, A.M. Peterson, Fabrication and properties of novel polymer-metal composites using fused deposition modeling, Compos. Sci. Technol. 158 (2018) 43–50, https://doi.org/10.1016/j.compscitech.2018.01.049.
[69] E. Cantı, M. Aydın, Effects of micro particle reinforcement on mechanical properties of 3D printed parts, Rapid Prototyp. J. 24 (2018) 171–176, https://doi.org/10.1108/RPJ-06-2016-0095.
[70] Z. Liu, Q. Lei, S. Xing, Mechanical characteristics of wood, ceramic, metal and carbon fiber-based PLA composites fabricated by FDM, J. Mater. Res. Technol. 8 (2019) 3743–3753, https://doi.org/10.1016/j.jmrt.2019.06.034.
[71] M. Mohammadizadeh, H. Lu, I. Fidan, K. Tantawi, A. Gupta, S. Hasanov, Z. Zhang, F. Alifui-Segbaya, A. Rennie, Mechanical and thermal analyses of metal-PLA components fabricated by metal material extrusion, Inventions 5 (2020) 44, https://doi.org/10.3390/inventions5030044.
[72] D. Godec, S. Cano, C. Holzer, J. Gonzalez-Gutierrez, Optimization of the 3D printing parameters for tensile properties of specimens produced by fused filament fabrication of 17-4PH stainless steel, Materials 13 (2020) 774, https://doi.org/10.3390/ma13030774.
[73] Z. Chen, Z. Li, J. Li, C. Liu, C. Lao, Y. Fu, C. Liu, Y. Li, P. Wang, Y. He, 3D printing of ceramics: a review, J. Eur. Ceram. Soc. 39 (2019) 661–687, https://doi.org/10.1016/j.jeurceramsoc.2018.11.013.
[74] H. Yang, S. Yang, X. Chi, J.R.G. Evans, Fine ceramic lattices prepared by extrusion freeforming, J. Biomed. Mater. Res. B Appl. Biomater. 79 (2006) 116–121, https://doi.org/10.1002/jbm.b.30520.
[75] Y. Chen, D. Bartzos, Y. Lu, E. Niver, M.E. Pilleux, M. Allahverdi, S.C. Danforth, A. Safari, Simulation, fabrication, and characterization of 3-D alumina photonic bandgap structures, Microw. Opt. Technol. Lett. 30 (2001) 305–307, https://doi.org/10.1002/mop.1297.
[76] W. Zhong, F. Li, Z. Zhang, L. Song, Z. Li, Short fiber reinforced composites for fused deposition modeling, Mater. Sci. Eng. 301 (2001) 125–130, https://doi.org/10.1016/S0921-5093(00)01810-4.
[77] R.T.L. Ferreira, I.C. Amatte, T.A. Dutra, D. Bürger, Experimental characterization and micrography of 3D printed PLA and PLA reinforced with short carbon fibers, Compos. B Eng. 124 (2017) 88–100, https://doi.org/10.1016/j.compositesb.2017.05.013.
[78] L. Sang, S. Han, X. Peng, X. Jian, J. Wang, Development of 3D-printed basalt fiber reinforced thermoplastic honeycombs with enhanced compressive mechanical properties, Composer Part A Appl. Sci. Manuf. 125 (2019), 105518, https://doi.org/10.1016/j.compositesa.2019.105518.
[79] J. Justo, L. Távara, L. García-Guzmán, F. París, Characterization of 3D printed long fibre reinforced composites, Compos. Struct. 185 (2018) 537–548, https://doi.org/10.1016/j.compstruct.2017.11.052.
[80] K. Sugiyama, R. Matsuzaki, M. Ueda, A. Todoroki, Y. Hirano, 3D printing of composite sandwich structures using continuous carbon fiber and fiber tension, Composer Part A Appl. Sci. Manuf. 113 (2018) 114–121, https://doi.org/10.1016/j.compositesa.2018.07.029.
[81] A.N. Dickson, J.N. Barry, K.A. McDonnell, D.P. Dowling, Fabrication of continuous carbon, glass and Kevlar fibre reinforced polymer composites using additive manufacturing, Addit. Manuf. 16 (2017) 146–152, https://doi.org/10.1016/j.addma.2017.06.004.
[82] T. Beran, T. Mulholland, F. Henning, N. Rudolph, T.A. Osswald, Nozzle clogging factors during fused filament fabrication of spherical particle filled polymers, Addit. Manuf. 23 (2018) 206–214, https://doi.org/10.1016/j.addma.2018.08.009.
[83] D. Raviv, W. Zhao, C. McKnelly, A. Papadopoulou, A. Kadambi, B. Shi, S. Hirsch, D. Dikovsky, M. Zyracki, C. Olguin, R. Raskar, S. Tibbits, Active printed materials for complex self-evolving deformations, Sci. Rep. 4 (2014) 1–9, https://doi.org/10.1038/srep07422.
[84] N.E. Zander, M. Gillan, R.H. Lambeth, Recycled polyethylene terephthalate as a new FFF feedstock material, Addit. Manuf. 21 (2018) 174–182, https://doi.org/10.1016/j.addma.2018.03.007.