Biodegradable Materials Used in FDM 3D Printing Technology: A Critical Review

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Abstract: Three-dimensional (3D) printing is a flexible technique that has attracted increasing interest in recent years. 3D printing has powerful biodegradable materials that are important for environmental protection and emergencies such as COVID-19. To achieve better compatibility for customized and enhanced material characteristics, a variety of ways have been used. Companies and researchers are increasingly interested in biodegradable polymers and composites due to their easy production, eco-friendly, and suitability for a variety of applications. One small step toward protecting the world around us is the use of natural resources to produce fully or partially biodegradable composite materials. PHA (Polyhydroxyalkanoates), PLA (Polylacticacid), High impact polystyrene (HIPS), and PHB (Polyhydroxybutyrates) are examples of bioplastics that are produced and have similar functionality to conventional plastics while also being biodegradable. These materials have the potential to reduce our reliance on petroleum-based plastic, which may present environmental risks. Every country desperately needs to develop bioplastic usage and proper waste management for a pollution-free world. This review is expected to provide a general overview for 3D-printed biodegradable polymer and their applications using fused deposition modelling (FDM) technology.

Keywords: 3D printing, additive manufacturing, FDM, Polymer composites, Biomaterials, Biodegradable.

INTRODUCTION

Polymers have become a very important material in our daily lives. They are used in various fields such as food, industry, medicine, and the automotive industry. Newly, polymers have begun to replace advanced materials due to their superior properties. However, disposable materials account for more than one-third of plastic production, resulting in environmental problems because of waste and plastic emissions [1]. A renewed interest in the research of degradable polymers has been inspired by greater awareness of the pollution problem and its effect on the environment. Because of environmental issues, researchers resort to developing materials that do not have a harmful effect and are environmentally friendly. Most biodegradable polymers belong to thermoplastics (poly (lactic acid), poly (vinyl alcohol, poly hydroxyl alkanoate), or plant polymers (*e.g.*, starch and cellulose). Thermoplastics made from polyolefins are not biodegradable, although some of them contain pro-oxidant additives that make them photodegradable and term degradable. The use of non-biodegradable polyethylene films (PE) on green spaces or soils has caused serious problems in Southeast Asia [2]. Non-biodegradable polymers such as polypropylene (PP), polyethylene (PE), poly (ethylene terephthalate), polystyrene ethylene vinyl alcohol, expanded polystyrene, polyurethane, polyamides, and poly (vinyl chloride) have become widely used in the packaging industry due to their good physical and mechanical properties.

Polymers are commonly utilized in 3D printing, but the raw materials used for 3D printing nowadays consist of different polymer composites to get the desired qualities of the end product [3]. The time it takes for a printer to manufacture a final product is typically a few hours; however, the period varies on the size of the item to be made and the type of printer used for 3D printing [4]. The mechanical and functional qualities of the products can be improved by choosing feedstock with greater mechanical properties and producing polymer composites by adding reinforcements in the form of particles, fibres, or nanomaterials to the composite polymer matrix [5, 6]. Bio-based or natural fillers, which can be made from a variety of agricultural and industrial wastes, have successfully added mechanical strength to base polymers [7]. Additionally, these fillers enable the items' recycling and biodegradability, reducing their negative environmental effects. In order to satisfy customers, 3D printing of bio nanocomposites has recently gotten a lot of attention from a wide range of industries.

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The 3D printing technology known as stereolithography (SLA) was the first commercial application of additive manufacturing (AM) in 1987 [8]. Since then, the AM has evolved very rapidly, particularly in the last decade. There are different methods of this technologies: laminated object manufacturing (LOM) based on plastic lamination [9], stereolithography apparatus (SLA) based on photopolymerization [10], selective laser sintering (SLS) [11], and fused deposition modelling (FDM) [12] based on the melting of plastic filaments. Figure **1** shows various additive manufacturing techniques related to the polymer's 3D printing.

The FDM process is worked by extruding thermoplastic material, which has heated up to its melting point through a nozzle, then depositing the extruded layers of materials on top of each other. Currently, FDM considers the most widely used technology of all types of 3DP technology around the globe due to the low cost of the printer device, sim PLA [13], PVA (polyvinyl alcohol) [14], TPU (thermoplastic polyurethane) [15], nylon [16] It can be considered as one of the most widely used materials in 3D printing technologies, and a variety of cheap filaments [17]. Platform temperature, nozzle size, layer thickness, printing direction, nozzle head temperature, printing speed, and raster angle are parameters that could be controlled to improve the print quality. Other researchers looked at the details of many processing parameters. According to the research, a suitable bed temperature and regulated convective heat transfer conditions can increase the bonding strength of successive layers, improving the mechanical properties of printed objects [18].

FDM technologies are widely used in different applications like aeronautics, automotive, construction,

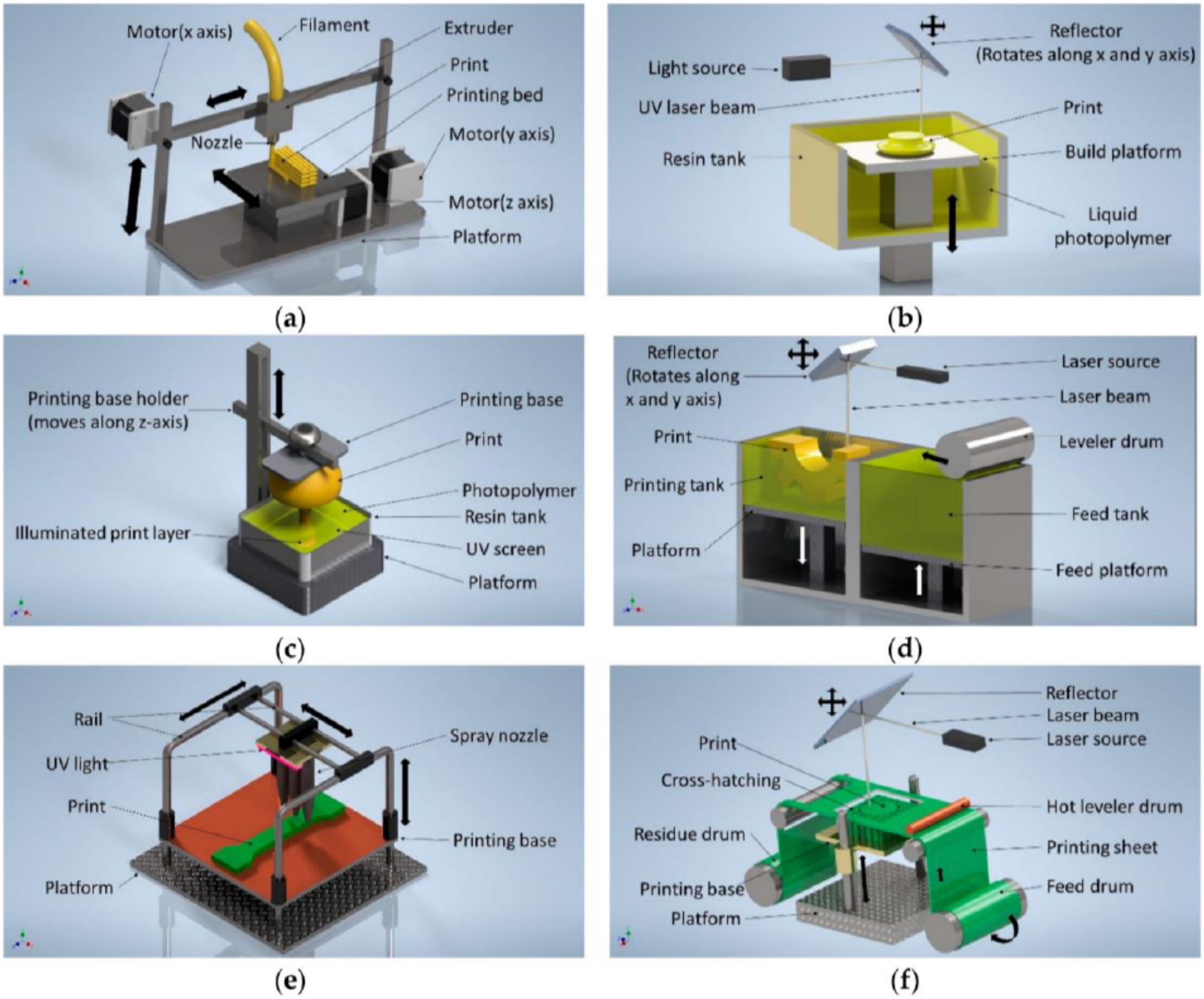

Figure 1: Various techniques for polymer 3D printing (**a**) fused deposition modelling (FDM), (**b**) stereolithography (SLA) technique, (**c**) digital light processing (DLP), (**d**) selective laser sintering (SLS), (**e**) polyjet printing process, (**f**) sheet lamination (LOM) [20].

aerospace, and medicine. Various thermoplastic polymers like acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and polyimide are used as the material of FDM technologies in the shape of filament. ABS material has better elongation, ductility, and flexural strength compared with PLA material, but it has emitted gas in the printing process. On the other hand, PLA material is more environmentally friendly material compared with ABS material because of degrades faster than ABS material and is produced from renewable resources. In addition, it is a biodegradable thermoplastic polymer compound, non-toxic, and ecologically friendly aliphatic polyester made from lactic acid (derived from animals and plants) that is used to make films, textiles, and bottles. PLA has excellent mechanical qualities and, because of its biodegradability, can be used to replace petroleum-based polymers [19].

The use of 3D printing throughout the production process of a product has decreased the extra costs experienced. Furthermore, because of its cheap cost, additive manufacturing can produce a large number of customized products [19]. Furthermore, 3D printed items have improved in terms of resolution, accuracy, usefulness, and reproducibility throughout time. The cost of manufacturing has decreased as a consequence of the growing number of 3D printers and easy access to applications [21]. It is important to note that 4D printing, which combines smart materials and 3D printing, is considered a state-of-the-art technology. 3D printing technology has been utilized to construct static structure in 3D coordinates. Considering how 4D printing's structural reaction changes over time in response to external stimuli, it has recently become more popular [22]. However, the majority of studies published to date have taken into account filaments made of synthetic [23] and bio-based polymers, as well as the characteristics of related 3D printed products [24]. The current area of research focuses on the production of printable biopolymer composites with improved performance [25]. Different biodegradable and non-biodegradable polymers reinforced with organic fillers including wood, sugarcane, hemp, flax, and others were discussed by Mazzanti *et al*. [7] using FDM 3D printing. The authors went into great detail about the printing parameters that have an impact on the mechanical strength of printed items, as well as the mechanical characteristics of both filaments and FDM-produced pieces. Researchers [26] studied 3D-printed bio-inspired spherical-roof cubic cores' compressive properties, failure behavior, and damage patterns are examined. Thence, this paper attempts to present a detailed overview of different bio-based polymers and biodegradable materials and the applications of the bio-based FDM products.

FUSED DEPOSITION MODELLING (FDM)

The FDM process is worked by extruding thermoplastic material, which uses thermoplastic filament as feedstock, the filament has heated up to its melting point, then is extruded through a nozzle in the XY plane creating a layer of solid material on the build plate. Creating a model can be done by depositing a layer contour, The material is then extruded in the XY plane by a nozzle, forming a solid layer on the build plate. By depositing a layer contour and then filling the interior with plasticized material with zigzag head movements, a model could be created. The head moves along the Z-axis after manufacturing one layer, starting the build-up of the next layer. We can make various forms using this method with a minimum of previous step. The manufacturing process begins with the creation of a model in a CAD program then its transfer to software like (Ultra-software) that could control of process parameters such as head movement, feed rate, layer thickness, infill, head and table temperatures, slicing, support application, etc. Then the software creates G-code, which can then be transferred to a 3D printer to create an actual model. The model that was taken from the printer may need requires finishing machining to delete the supports and flaws [27, 28]. Currently, FDM considers the most widely used technology of all types of 3DP technology around the globe due to its low cost of the printer device, simplicity, and variety of inexpensive filaments. Figure **2** shows a procedure of the 3D printing process using the FDM technology.

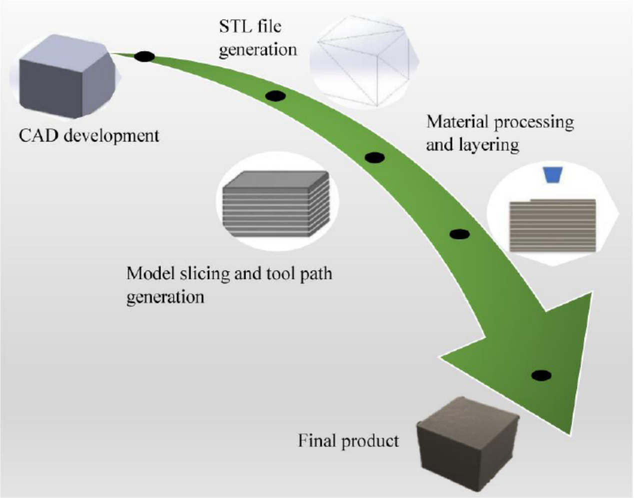

Figure 2: FDM 3D printing procedure [29].

While the support materials may be removed with relative ease for simple designs, it might be challenging for more complicated constructions. A clear part is produced by Ultimaker using a water-soluble support material that leaves no traces in the supporting components. This kind of support material makes it simple to build dynamic structures. The movement of the extruder, the temperature, the speed, and the flow rate of the material during the nozzle all affect how accurately the component was produced. For making anatomical models in dental and surgical training, the FDM technology (Figure **3**) is frequently employed [30].

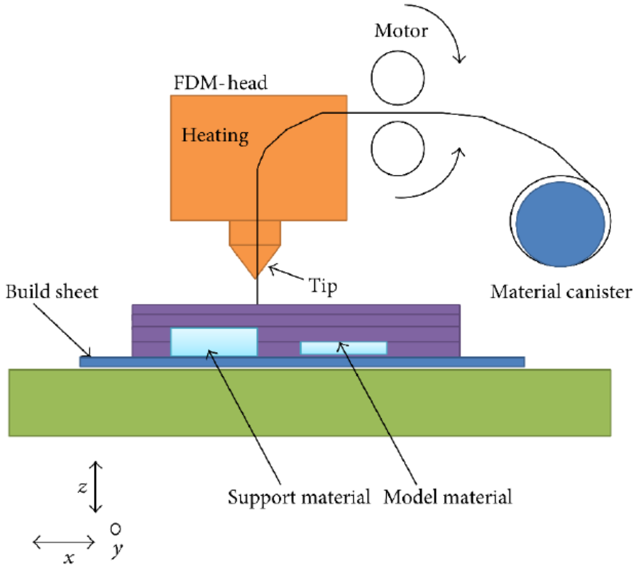

Figure 3: Fusion deposition modelling (FDM) process [31].

THERMOPLASTICS AS FEEDSTOCK MATERIALS FOR FDM

To choose the suitable polymer for the final product, we must first understand the qualities (mechanical and physical properties) and printability of the material. The most prevalent types of thermoplastics are classified by performance in Figure **4a**, and their printability, optical quality, and mechanical qualities are shown in Figure **4b**. In Figure **4b**, impact resistance, heat resistance, and elongation at break are the chemical and mechanical properties that resist higher temperatures, impact energy, and longitudinal deformation before breakage. The simplicity of printing means how easy it is to print a base material in terms of print bed adhesion, maximum print speed, ease of feeding to the printer, and frequency of print defects. These considerations are helpful when selecting materials for FDM [32].

As seen in Figure **4a**, standard thermoplastics (*e.g.*, polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polyethylene (PE), and polypropylene (PP)) are used for ordinary components that are planned to be subjected to minimal stress. However, engineering plastics (*e.g.*, Polycarbonate (PC), nylon (PA), and polyethylene terephthalate (PET)) are utilized in structural parts because they own better wear resistance compared to conventional plastics. Meanwhile, advanced polymers (*e.g.*, polyether-ether-ketone (PEEK) and Polyethyleneimine (PEI)) are resistant to high wear, temperatures, and chemicals. Figure **4b** demonstrates polymer characteristics (*e.g.*, impact resistance, printing ease, elongation break, heat resistance, and visual quality)

The most common thermoplastics for filaments in 3D printing (PEEK, ABS, PET, and nylon 6) are discussed in the next section, and Table **1** compares them in terms of physical and mechanical characteristics, as well as printing circumstances. Heat deflection temperature is a measurement of a polymer's resistance to distortion under a particular load at a higher temperature, and it may be used to

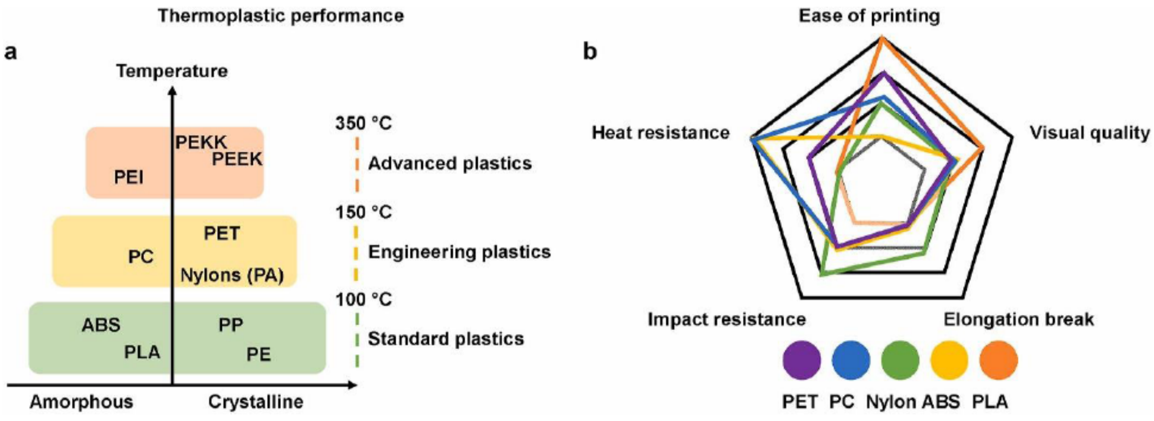

Figure 4: Thermoplastics as materials for FDM 3D printing (**a**) standard thermoplastics, (**b**) polymer attributes [32].

Table 1: Comparison of the Physical and Mechanical Properties, and Printing Conditions of ABS, Nylon, PET, and PEEK for FDM

	ABS	Nylon 6	PEEK	PETG
Glass transition temperature (℃)	102–115	47–57	137–152	70-80
Melting temperature (℃)	-	220	335–343	-
Heat deflection temperature (℃)	100	190	160	71
Modulus (GPa)	1.8–2.39	2.8–3.1	3.56	0.9-1.1
Tensile strength (MPa)	25–65	79	92	55
Printing temperature (℃)	220–250	220–270	360–450	250
Bed temperature (℃)	95–110	70–90	360–450	75-90
Ref.	[37]	[40]	[40]	[37, 41]

figure out what temperature the polymer should be employed at. In Table **1**, heat deflection temperature refers to the temperature at which a certain material specimen bends 0.25 mm under a given strain.

Polyether Ether Ketone (PEEK)

It has high mechanical strength, lightweight, and chemical and heat resistant [10]. PEEK has a rather high printing temperature, about 340 °C [15]. It has a glass transition temperature of about 143 ℃. Furthermore, it has many advantages, such as excellent mechanical and chemical resistance properties (high resistance to biodegradation and thermal degradation), enable it to be used in extreme environments requiring high service temperatures or mechanical properties, such as piston parts, bone, bearings, vehicles, and aircraft [33]. PEEK is a good option alternative feedstock for FDM since it can be handled similarly to an amorphous polymer, resulting in dimensional stability and good layer adhesion.

Acrylonitrile Butadiene Styrene (ABS)

ABS is made by the polymerization of styrene and acrylonitrile in the presence of polybutadiene and is amorphous. ABS is more suitable for use in FDM because it has higher toughness and strength than PLA, as well as better resistance to corrosive chemicals [34]. However, it is somewhat difficult to print on because it tends to warp, which is due to a high shrinkage factor. ABS can produce chemical vapours that affect people with chemical sensitivity. The melting point of ABS is usually between 200-250 ℃ [35]. The automotive, healthcare, and aerospace industries have employed ABS to fabricate a few functional components [36].

Polyethylene Terephthalate (PET)

PET is a polymer that is semi-crystalline and belongs to the polyester family. Rather than raw PET, glycol-modified polyethylene terephthalate (PETG) is more popular in 3D printing filament owing to being less brittle and easy to use. PETG has better printability compared to ABS and enables the production of 3D products with a smooth surface finish and excellent impact resistance, but PETG has a high absorbability of moisture from the air [37].

Nylon 6

Nylon 6 is known for its heat resistance, flexibility, and impact strength. It has good toughness values and is also durable. However, as a hygroscopic material, it absorbs a lot of moisture, which reduces its overall quality [38]. Like ABS, nylon tends to warp. The warping effect can be reduced by keeping the bed temperature at about 75 ℃. However, it is sensitive to moisture and should be stored in a cool and dry place to maintain high-quality products [39].

BIO-DEGRADABLE POLYMER

Depending on their origin, biodegradable polymers are categorized into two categories: natural and synthetic. Synthetic polymers have an advantage over natural polymers in that they are more adaptable, have adjustable mechanical characteristics, and can vary the rate of deterioration as needed. Natural polymers, on the other hand, appear appealing due to their outstanding biocompatibility, but they have not been completely studied due to undesired features including antigenicity and batch fluctuation [42]. Many fascinating uses for biodegradable polymers exist, including drug

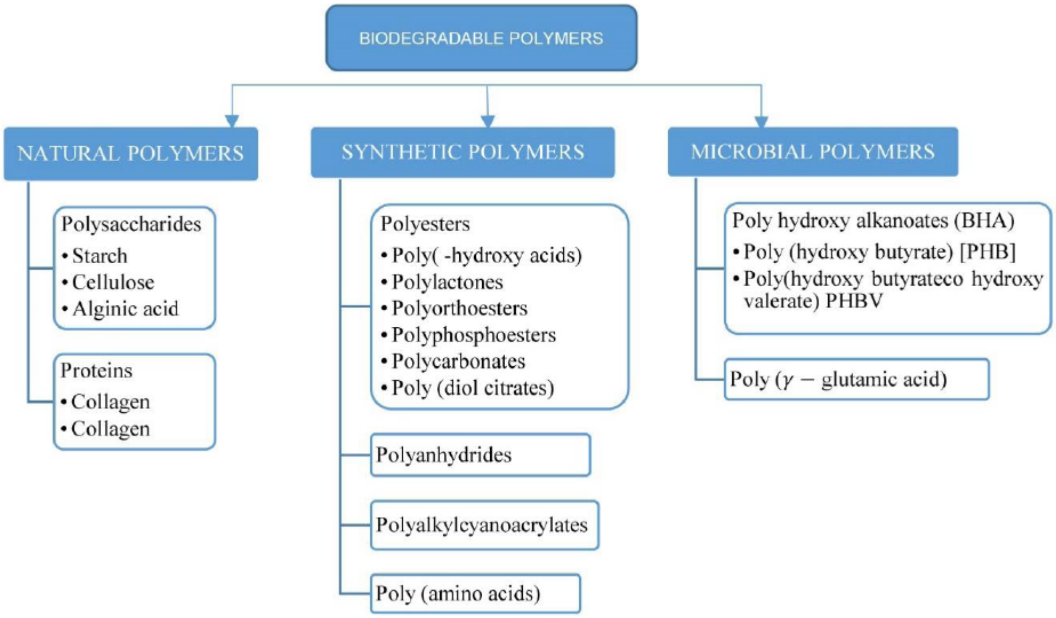

Figure 5: Classification of biodegradable polymers.

administration, tissue engineering, gene therapy, regenerative medicine, temporarily implanted devices, implant coatings, etc. [43, 44]. The basic criteria for selecting a polymer as a degradable biomaterial are matching the mechanical properties and degradation rate to the application requirements, nontoxic degradation products, biocompatibility, durability/stability, processability, and cost [42, 45]. Mechanical properties should be matched to the application to maintain adequate strength until the surrounding tissue has healed [46]. There are many biodegradable polymers available for different applications (Figure **5**), and the choice of the polymer depends on the requirements placed on a particular biomaterial.

On the market, bio-composite filaments consist of a biologically degradable polymer matrix and bio-fillers. The additives are capable of fibers or particles. The percentage of filaments varies from a very small percentage to 40 percent of the amount. The most commonly used thermoplastic is polylactic acid, and sawdust, cellulose fibers, or other natural fibers can be used as fillers. Filament manufacturers use different types of fibers: plum, seaweed, maple, hazelnut, bamboo, wick, mahogany, cedar, walnut, and willow. These are used to give a wood-like feel to the esthetic components [47]. The influenced thermoplastic cellulose derivatives are used on an FDM computer. Additive manufacturing as a key technology will push the design boundaries to more robust elements without the need for an additional cost or process specifications. It makes it especially appropriate for personalized parts and components sized in small batches. However, despite certain AM machine tools for small scale and low external specifications, it can co-locate development and use case venue, reducing the transportation and transport needs. Although FDM devices are being adopted by many consumers and manufacturers because of their minimal cost and effortless application, certain innovations of additive manufacturing should not be overlooked [48]. Table **2** shows biodegradable which is used in FDM manufacturing.

PHA can be used as such or in a blend with polylactic acid. PVA is a biodegradable and water-soluble polymer that is used to support construction. Duran *et al.* [49] PVA is printed as a support structure for ABS. They found that PVA is printable for up to 45 minutes when dried before it absorbs moisture from the air and becomes unprintable. High-impact polystyrene (HIPS) is similar to ABS with good mechanical properties and extrusion temperature. It is used as a substrate for ABS because it dissolves in limonene, but ABS does not. In biocompatible and medical applications, 3D printing filaments are made from polymers with low melting temperatures. These materials can be used in the FDM process to fabricate parts that blend into human tissue, such as scaffolds. Chia *et al*. [50] and Serra *et al*. [51] list some of these materials. Pietrzak *et al*. [52] and Melocchi *et al*. [53] developed capsules for drug delivery systems by using biodegradable 3D-printed hollow hydroxypropyl

Table 2: Bio-degradable Materials for Fused Deposition Modelling Machine

Material	Produced from	Extrusion Temperature	Properties
PLA	Plants starch	160 - 222 ℃	Tough, strong, bio-plastic, nontoxic, odorless, low-warp, Low heat resistance, brittle
PHA	Sugar with biosynthesis	160 ℃	UV-stable, stiffness, elasticity, brittle
HIPS	Petroleum	190 - 210 ℃	High impact resistance, soluble in limonene
PVA	Petroleum	190 - 210 ℃	Water-soluble, good barrier, biodegradable, recyclable, nontoxic, expensive, deteriorates with moisture, special storage
PCL	Crystalline	100 - 140 ℃	Non-toxic slow degradation good resistance to water and oil
High-density polyethylene	Ethylene monomer	180-205 ℃	Biodegradable, stronger intermolecular forces and tensile strength, expensive

cellulose (HPC). These capsules are taken orally and the degradation of the capsule in the stomach releases the drugs concealed in it.

Polylactic Acid (PLA)

PLA is a common thermoplastic known for its biodegradability but also known for its sensitivity to humidity over 60 ℃. PLA has a relatively low melt point of 145–186 ℃ and can be easily formed into filament with a temperature over 185–190 ℃ [54]. It is also characterized with biocompatibility and good mechanical properties (relatively high strength and modulus). The constructed PLA parts have been observed to have lower distortions while printing than ABS. However, they are less resistant and thermally conductive [55, 56]. PLA constructions are most commonly utilized in practical applications that demand a certain level of aesthetics [7, 57]. It is extracted from renewable energy sources like maize starch or cane sugar. It may be produced using existing production equipment (the ones created and utilized in the oil and gas industry for materials). As a result, production process is quite inexpensive. PLA, therefore, has the second biggest production capacity of every bioplastic (most usually referred to as polymer protein) [58]. Polylactic acid has a wide range of applications. Some of the most common applications are eco-friendly medical equipment, disposable films, and containers. PLA is excellent for use as a shrink-wrap sheet because it binds when heated. Furthermore, the ease with which polylactic acid fuses lends itself to some intriguing applications for printing technology [59].

Polyvinyl Alcohol (PVA)

The extent of hydrolysis and the content of the acetate group affect the crystallinity and solubility of the polymer. The melting point for fully hydrolyzed PVA is 230 °C and 180–190 ℃ for partial hydrolysis. PVA biodegrades slowly but decomposes quickly over 200 °C [60]. It has become a more suitable material to create structures and in other construction works owing to its durability, compatibility with natural fibers, chemical, lower cost, and flame resistance. Vinyl polymer materials are formed by polymerizing the corresponding monomers. PVA endures either partial or full thermal decomposition of this polyvinyl acetate to extract acetate groups. PVA is used as innovative inks for the additive manufacturing of objects of various sizes utilizing a layer-by-layer additive fabrication process.

Poly(ε-caprolactone) (PCL)

Poly(caprolactone) (PCL) is the most widely studied in this family [61, 62]. PCL is considered a non-toxic and tissue-compatible material and a semicrystalline polymer with a glass transition temperature of about 60 ºC. The polymer has a low melting temperature (59 to

64 ºC) and is compatible with a range of other polymers. PCL is a valuable base polymer for developing long-term, implanted drug delivery devices since it degrades at a considerably slower pace than PLA. PCL is regarded as a non-toxic and tissue-compatible chemical [63]. PCL has been investigated as a vehicle for the long-term introduction of drugs/vaccines (Capronor) and cell-based treatments due to its delayed degradation feature. Capronor is long-acting contraception that contains the hormone levonorgestrel [64]. PCL has a modest tensile strength (about 23 MPa) and a very high elongation at breakage (>700%) [65]. PCL is well suited for fused deposition modelling (3D melt printing) and it has been used to prepare a variety of 3D scaffolds for tissue engineering [66].

Polyhydroxyalkanoates (PHA)

PHA consists of a class of natural-based polyesters synthesized using microbial fermentation of carbon-based feedstock; which are biodegradable and readily compostable thermoplastics [67]. The polymer shows a glass transition temperature in the range of −5 to 20 °C. PHA are both bio-based and biodegradable, with physical and chemical properties similar to polypropylene, thereby making it a good alternative to PLA in biopolymer system developments. PHA is generally known to be:

- Although resistant to UV radiation, it is weak toward acids and bases.
- Biocompatible and non-toxic, thereby making it suitable for biomedical and food packaging applications [67].
- Insoluble in water, and relatively resistant to hydrolytic degradation

Its biocompatibility and biodegradability by simple hydrolysis of ester bonds in aerobic conditions and piezoelectric properties make them suitable for drug delivery, tissue engineering, and orthopedic applications.

High Impact Polystyrene (HIPS)

HIPS is a biodegradable thermoplastic with low strength and good process technology. The excellent flow characteristics, inexpensive cos, and impact resistance of this FDM filament are all benefits [55]. However, it is prone to wear and requires a high printing temperature and a hot build platform. HIPS has qualities that are comparable to ABS, however, it is less thick. HIPS is preferable for support structures because it dissolves with chemicals such as limonene [68].

High-Density Polyethylene

Polyolefin thermoplastics such as high-density polyethylene (HDPE) are the world's leading manufacturers of plastics, environmentally friendly polymerization processes, recycling, and sustainability. HDPE is an ethylene monomer material made of thermoplastics. When used as HDPE pipe, it is sometimes called " polyethylene" or "alkathene". Higher-density polyethylene is used to make high-density plastic water bottles, plastic lumber, abrasion resistant containers, and geomembranes. An evaluation of the mechanical reusability of HDPE, a raw material widely used for open additive manufacturing, to assess the feasibility of using this recycled plastic in open 3D additive manufacturing [69].

Cellulose and Nanocellulose

Cellulose is an inexhaustible and sustainable polymer. This highly innovative polymeric material is synthesized by numerous living organisms and used extensively in the pharmaceutical and food industries [70]. Its abundance is a consequence of the constant photosynthetic cycles occurring within the cells of plants, which can synthesize several tons a year [70]. They can be obtained from plants or agricultural waste; from husk fiber, bamboo, wood, and sugar cane bagasse [70]. The main characteristics of cellulose include its biodegradability, hydrophilicity, chirality, broad chemical modifying capacity, and capability of forming versatile semicrystalline fiber morphologies [71]. 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 [72]. Bio polymers can be extracted from bio resources like wood cellulose, corn, and so on. Figure **6** illustrates the overall procedure for creating bio-based polymer composite components using FDM.

BIODEGRADABLES IN 3D PRINTING MANUFACTURING

PLA is widely used as a filament for 3D printing. PLA and other biodegradable polymer filaments can be processed with nanoparticles or nanofillers to form a

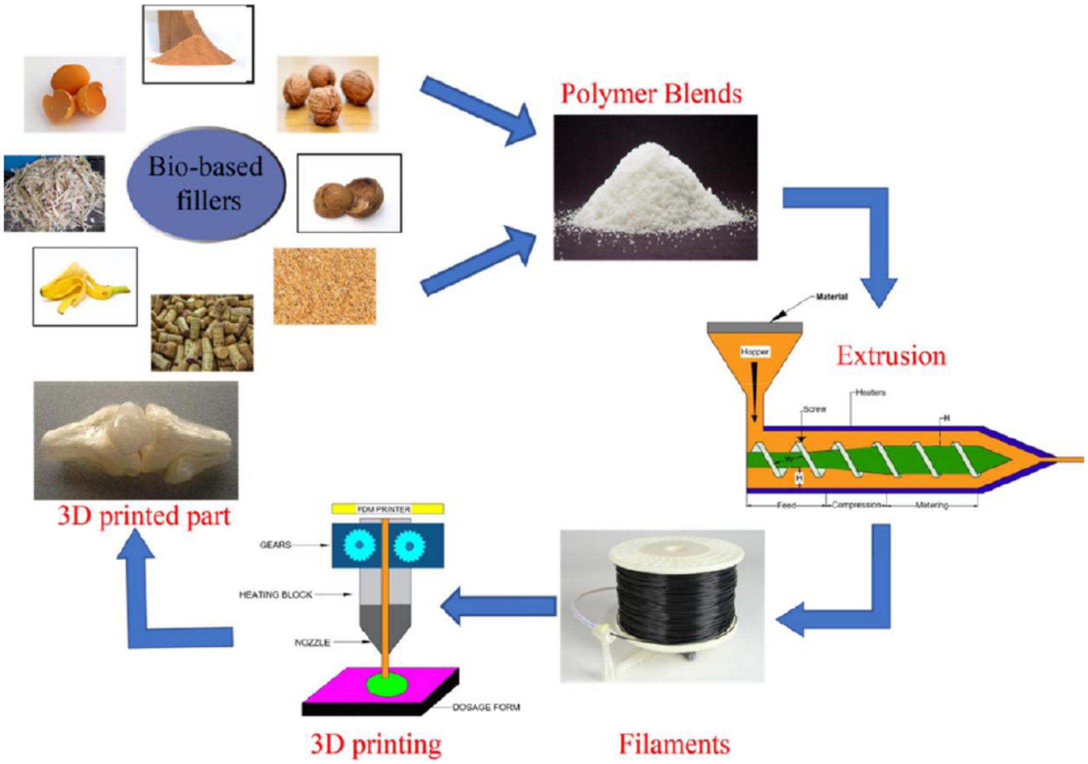

Figure 6: Schematic diagram of the typical 3D printing procedure for bio-based polymer nanocomposites [73].

blend or composite to improve the properties of the filament and the final printed object. 3D printing is primarily used in the fabrication of scaffolds and other tissue engineering applications. Since the scaffolds are made of biodegradable polymer filaments, they are biocompatible and biodegradable under enzymatic action [74, 75]. PLA is the most commonly used bioplastic for FDM filaments. PLA is a biodegradable and biocompatible plastic derived from the fermented starch of plants such as corn, sugar beets, and sugar cane. It also does not emit toxic gases when printed. Polyhydroxyalkanoate (PHA) is a bioplastic produced by the bacterial fermentation of sugars or lipids. Like PLA, PHA is also a thermoplastic aliphatic polyester. The two most frequently used and widely available of PHAs are poly (3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV) and poly(3-hydroxybutyrate) (PHB). PHB has more fracture toughness, strength, and rigidity than PHBV, which is ductile.

A novel electro-hydrodynamic jet printing with FDM technique (E-FDM) was employed by Zhang *et al*. to prepare 3D printed tissue regeneration scaffolds using poly (lactic acid) PLA filaments with different structure sizes. The 3D printing technique gave high speed and high-resolution prints, *i.e*., up to submicron level and directly used PLA filament [76].

FDM 3D printing carried out using graphene incorporated PLA filament also produced patient-specific implants and orthopedic scaffolds with graded porosity and optimum density as reported by Bustillos *et al*. The polymeric chains were restricted by graphene giving a reduction in crystallinity, enhancement in the creep resistance, and other mechanical properties. The 3D sample prepared from these composites exhibited superior wear and creep resistance as compared to that prepared using pure PLA filaments [77].

Foresti *et al*. [78] used the FDM process to produce respirators to support COVID-19 pandemic response by providing safety protection devices. For printing masks utilizing the FDM method, several health-related considerations such as health, consumer safety, virus prevention, regulatory requirements, reusability, and disinfect ability are crucial. Polylactic acid (PLA), advanced polyolefins, and styrene-ethyl butylene-styrene are used in the research work to produce flexible and adaptable masks. Application of continuous fiber-reinforced thermoplastic composites (CFRTPCs) in printing 3D samples which could be used in aviation and aerospace applications was carried out by Tian *et al*.

The developed 3D printed samples were lightweight and an efficiently performing alternative to conventional materials. These CFRTPCs were formulated using a polymer matrix of poly (lactic acid) (PLA) filament and reinforcement of continuous carbon fibers which were fed to fused deposition modelling (FDM) 3D printers simultaneously. The fiber content of 27% gave optimum mechanical properties to the composite. The layer thickness of 0.4 mm to 0.6 mm exhibited optimum bonding between the layers [79].

Ferreira *et al*. [80] investigated the characteristics of PLA composites with pure PLA using short carbon fibres with an average length of 60 μm as reinforcing material. An experimental investigation showed that the tensile modulus, stiffness, Poisson's ratio, and shear modulus of the composite parts increased significantly. In contrast, there were no significant changes in tensile and shear strength. This indicates that the matrix material was stressed during loading and the adhesion between PLA and carbon fibres was insufficient.

Hollander *et al*. employed PCL filaments using a model drug indomethacin in three concentrations using the hot-melt extrusion technique. These modified filaments were used to print T-shaped prototypes of the intrauterine system using the FDM 3D printing technique. The morphology and other properties of the filament and printed samples were dependent on the amount of drug-loaded in the sample [81].

Rymansaib *et al*. [82] used carbon nanotube and graphite flakes as reinforcements at different proportions with different thermoplastics such as PLA, graphene-PLA, ABS, PCL, and HIPS to identify the best material for FDM electrode production. Owing to its improved surface properties and electrical conductivity, HIPS with 10% carbon nanotubes and 10% graphite flakes has been the most suited combination for electrode production, according to different composite compositions.

Many industrial sectors should consider PLA and Poly (3-hydroxybutyrate (PHB) to be biodegradable and biocompatible alternatives to traditional polymers, but both PLA and PHB have drawbacks. PHB has poor processing qualities and is hard, fragile, and brittle. It is recommended that PHB be blended with an amorphous polymer, such as poly(-lactic acid), to minimize its crystallinity and so increase its applicability [83]. Despite this blending, these pure PHB/PLA blends remain brittle and stiff, with poor mechanical characteristics and thermal degradation around the melting point, limiting their processability. The poor ductile properties can be improved by the addition of plasticizers [84].

Blending PLA with polymeric tougheners (such as poly(butylene succinate, PCL, PBS, and PHA) increases its ductility. The outcome can vary depending on the dispersed toughening phase's size, volume fraction, substructure, and intrinsic qualities [85]. To investigate the mechanical characteristics of composite components Kaygusuz and Özerinç [86], mixed 12 wt% PHA with PLA for FDM filaments. When compared to PLA-only components, the ductility improved by around 160 %, while the tensile strength reduced by about 25 %. It was suggested that the printing temperature be regulated between 210 and 240 ℃. Plasticizers such as acetyl tributyl citrate and tributyl citrate can help improve the bonding between PHA and PLA [87].

Ausejo *et al*. [88] also produced parts by the FDM process from PLA/PHA composites at horizontal and vertical build orientations. It was concluded that the build orientation is a significant process parameter for tensile properties, morphology, structure, and surface properties of the composite build parts. The PLA/PHA composite is a potential filament material for bone scaffolds as it is nontoxic and biocompatible.

Chen *et al*. [89] for tissue engineering applications researchers adopted the FDM technique. The filament material is a polymer matrix composite comprising PVA and β-TCP. PVA has the bone-bonding ability and mechanical performance are boosted by the inclusion of β-TCP as reinforcement, in addition to its nontoxicity, tunable hydrophilicity, facile modifiability, and superior biocompatibility. In the creation of composite filaments for the manufacture of porous structures using the FDM technique, micrometer-sized HA was utilized as reinforcement particles with the PLA matrix [90]. In the PLA-HA composite, several quantities of HA were employed, with the highest proportion of HA being 50%. In comparison to PLA-only composite components, PLA-HA composite parts have high porosity, high surface roughness, high cell adhesion, and poor stiffness compared to pure PLA parts.

Other researchers, such as Wu *et al*. [91] have employed PHA composites in the FDM method for filament preparation. Complex shaped items and food-grade packaging may be made with PHA matrix composites [92]. Plasticizers and other additives can be added to composites to increase particular attributes including interlayer bonding and tensile strength.

Wang *et al*. [33] compared a composite of cellulose nanofibers and PLA using polyethylene glycol 600 (PEG600) as a plasticizer to pure PLA in their investigation. With a fiber concentration of 2.5 wt.%, thermal stability, tensile strength, and elongation at the break all increased considerably.

APPLICATION OF 3D-PRINTED POLYMERS USING FDM

Food Packaging Industry

The food packaging business uses current bioplastics. In the past few years, cellulose, starch, and other bio-origin materials have been used in extremely ingenious ways in food packaging [93]. When using biodegradable plastic for food packaging, it is important to take into account things like product shelf life and rules for food safety. Cellophane, PLA, and starch-based plastics are the three most popular bio-based polymers with distinct features [94]. Many bio-based plastics have certificates stating that they will be used in applications involving food contact. Food packaging is the principal application for the recently developed bio-based non-biodegradable polymers (bio-PE and bio-PET). The packaging business is the main application and accounts for 60% of the world's output of biodegradable plastics, according to a segment of the marketplace for these materials based on their expected use [95].

Biomedical Applications

With the potential to produce patient-tailored medical products and equipment, as shown in Figures **7a**,**b**, implantable prostheses with the ideal scale, form, and mechanical qualities are created via 3D printing, which enables the custom manufacturing of products in a compressed timeframe [96]. 3D printing offers considerable advantages in biomedical applications. The fabrication of tissues and organs, customization of prostheses, orthopedic transplants, and anatomical replicas, as well as distribution of medications and drug screening, are among the current and upcoming research priorities of 3D printing in the biomedical and pharmaceutical areas [97]. The ideal characteristics of materials that are regarded suitable for printing for biomedical applications include printability, superior mechanical, thermal, and structural qualities [98].

Agriculture Application

Thermoplastics, especially PLA and ABS, are used to make a variety of agricultural equipment, including irrigation sprinklers and hose manifolds, spare parts for machinery like corn augers and gears, and seed application equipment. Because PLA is recyclable and biodegradable, farmers can also create specialized tools from it, such fruit pickers and shovels [99]. These thermoplastics differ slightly in terms of stiffness and heat resistance, but they are the most widely used filaments for 3D printing due to their low cost and simplicity of usage. It can provide picking up high-hanging fruit without the use of ladders. Three claw fruit picker and 3D printed corn shellers, adapter/garden hose manifold also is an example of water management and irrigation equipment that may be created using PLA material, which are shown in Figure **8**.

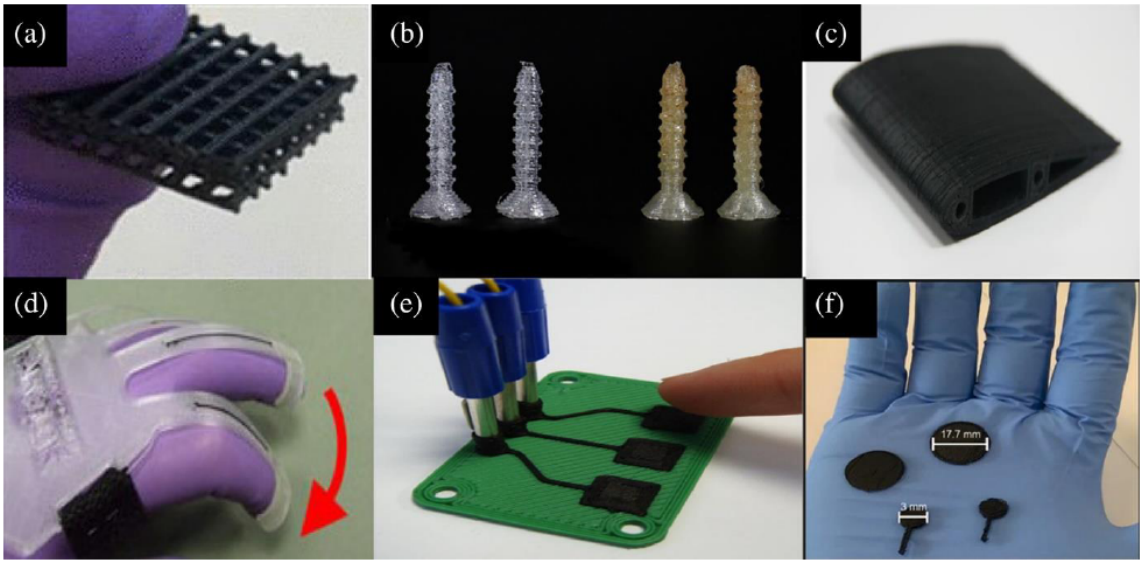

Figure 7: Applications of polymer nanocomposites manufactured by FDM: (**a**) scaffolds, (**b**) screws of orthopaedic, (**c**) aerofoil model, (**d**) flexing glove, and (**f**) 3D-printed disc electrodes [73].

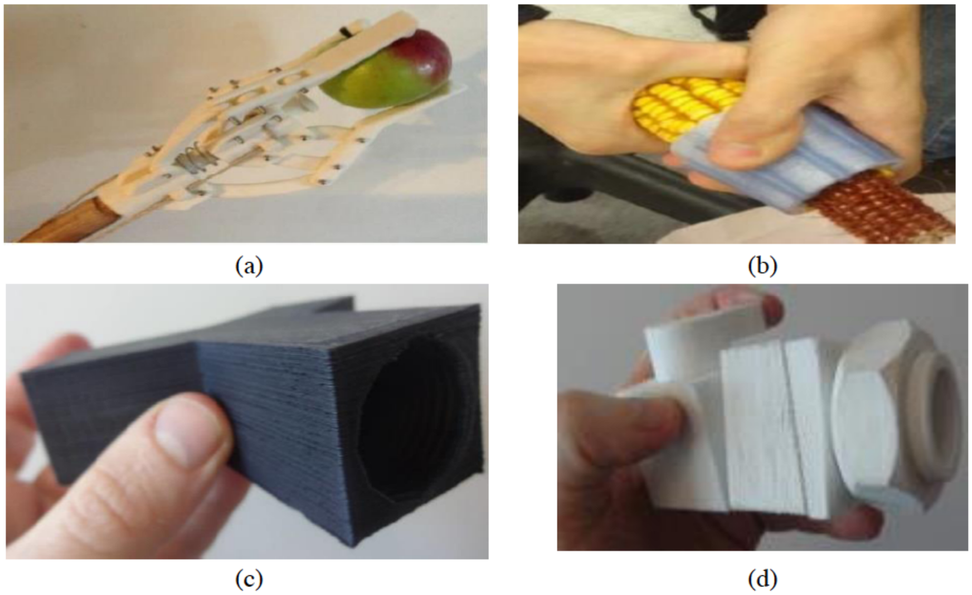

Figure 8: Equipment created using PLA material: (**a**) fruit picker, (**b**) corn-shellers, (**c**) garden hose splitter, (**d**) spigot [99].

Aerospace Application

The majority of aircraft equipment has complex profiles that are time-consuming and expensive to create. The most important aircraft parts, such as engine exhaust and turbine blades, have lately been 3D printed using metal materials since they are more durable and flame resistant than polymers [100]. The aerospace industry has been replacing traditional metal parts with suitably robust FDM-printed parts made of polymer composites such as PLA, the brand name for polyetherimide (PEI), ULTEM, ABS, polycarbonate, and polyphenyl sulfone, as shown in Figure **8c**, to reduce weight and processing time for component maintenance. Recently, printed polymer composites able to endure high temperatures have been developed for use in aircraft applications. These 3D-printed parts can endure temperatures up to 482 °F and are 50% lighter than conventional aluminium parts. The flapping wing, gears for the flapping wing, tail, and structure of unmanned air vehicles all require complex geometry. These can be successfully printed with FDM by using a variety of materials that provide lightweight constructions that offer higher performance [101].

CONCLUSION

This review revealed that there are three different ways in which biobased materials can be employed as feedstock for FDM. Using biobased polymers like PLA or PHA alone, combining them with fillers, and combining petroleum-based polymers like ABS, nylon, and PCL with biobased fillers are the three options. The majority of studies on PLA produced by FDM printing have been on the effects of process variables on the mechanical characteristics. The three most well-known polymer materials for pure thermoplastic FDM filaments and composite FDM filaments are PLA, ABS, and nylon. Other polymers have been utilized as FDM filaments, including PEI, PC, PP, HIPS, and PEEK. The use of 3D printing technology in biomedical applications has expanded the usage of biodegradable polymers in the form of tailored scaffolds and grafts. Biodegradable packaging materials are frequently utilized today since they do not demand high oxygen and water vapor barriers. The biopolymers also exhibit various performance limitations in terms of mechanical, barrier, and cost features, which can be overcome by creative approaches including blending, chemical or physical alterations, coatings, or the application of nanotechnology. The performance of biobased films can be enhanced more effectively by including nanoparticles. As a result, there is extensive scope for more academic and industry research into understanding and commercializing diverse products made from these polymers that are ideal for various uses. Several issues need to be resolved, such as the continued development of science and technology, ongoing funding of pertinent research, updating and altering management and regulatory frameworks, and their successful and practical implementation. Additionally, because of our need to protect the environment, research and development in biodegradable polymers are urgently needed. More intensified research is needed for the large-scale production and commercialization of bioplastic products to be successful worldwide.

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