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REVIEW

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A short review on fused deposition modeling 3D printing of bio-based polymer nanocomposites

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Abstract
Fused deposition modeling (FDM), one among the most commonly used additive manufacturing (AM), techniques has been widely used in recent years to produce customized parts with intricate geometries, especially from thermoplastics. This method was limited in its ability to produce parts for industrial applications due to inferior properties and the poor quality of fabricated parts. Hence, researchers are being driven to discover novel materials that are viable for FDM in order to keep up with enormous demand for functional products. In the recent years, it is widely recognized that the emphasis was placed on the bio-based polymer composite matrices rather than conventional thermoplastics due to its vital advantages that aid in the replacement of synthetic and perilous materials. On this context, this review focuses on the recent advancements in FDM printing with biomaterials. Specifically, attempts have been made to investigate and provide nutshell of 3D printing of current bio-based nanocomposites which consist of either bio-derived filler or polymer matrices in order to make 3D printing sustainable. The effect of fillers on the filaments and FDM based products, evolution of novel characteristics of bio nanocomposites, the printability of the developed composites and their development in leading applications were also investigated and summarized.

KEYWORDS
biodegradable, biomaterials, biopolymers and renewable polymers, manufacturing, thermoplastics

1 | INTRODUCTION

A product prior to reaching the end-users, has to undergo various inherent manufacturing processes which are time-consuming and expensive.[1] The challenges accompanying the progress of the tailored products and the need to enable the flexible production of these vendibles steered the advancement of rapid technologies, specifically additive manufacturing (AM).[2] Additive manufacturing, colloquially named as three dimensional (3D) printing has revolutionized the design and fabrication sectors and thus garnered a lot of attention from researchers during the past few decades due to its versatility and low operational costs for rapid prototyping.[3] AM can effectively fabricate a wide array of 3D structures with complex geometries by printing successive layers of materials from 3D model data utilizing direct digital manufacturing processes.[4–7] Thus, the foremost positive aspects of AM technology lies within the development of complex, customized, and prototype models with the elimination of tooling, reduced production time, material wastes, and cost as compared to the traditional subtractive process.[8] In the recent years, AM technology has advanced rapidly and has become a well-integrated area of research.[4,9] Owing to the evolution in AM technology and the characteristic benefits, 3D printing has multitude of applications such as medical,[6,10,11] automobile,[12] electronics,[13] structural,[14–17] and aerospace.[18]

Various AM technologies such as ink jet 3D printing,[19] selective laser sintering (SLS),[20] and fused deposition modeling (FDM),[21] have emanated over the years following the stereo lithography (SLA).[22,23] The choice of suitable technique relies on the type of materials fabricated, creation of layers, speed of processing, cost, accuracy, and applications.[24] Among all the existing techniques, the extrusion based FDM also known as fused filament fabrication (FFF) is one of the most affirmative techniques of 3D printing. Under the aegis of its simple fabrication process, reliability, dimensional stability, low maintenance, and cost effectiveness in producing objects with high resolution, FDM has become the most favored technique for researchers, industrialists, and academicians.[8,25] Furthermore, FDM eliminates limitations on complex geometries allowing for the manufacturing of a wide array of complex parts and by customizing microstructure and the distinctive features of each layer.[26–28] Hence, the development of the FDM technique as well as the feedstock materials that can be adapted to FDM has become the prominent area of interest for research and is thus making swift progress.

FDM as shown in Figure 1 is a melt extrusion process where the filament on the spool is continuously passed through a liquefier head and is heated slightly beyond the melting point such that it becomes a semi liquid.[29] The thermoplasticity of the filaments has a substantial impact on the printing process allowing them to melt at the time of printing and thereafter to solidify resulting in the desired products.[5] The molten filament extrudes through a nozzle as semi liquid which is then deposited into thin layers sequentially on the platform parallel to the XY plane. The layer deposition is followed by the movement of either platform or nozzle head along Z direction precisely following one layer thickness for the successive layer assemblage.[30] The layer deposition follows the pattern from the typical stereo lithography (STL) format file which consists of the geometry of the object to be printed.[31] The CAM software results in the deposition of the layers which will fuse together and then solidify to form the model.[31,32] The printers that can accommodate two or three print heads enable the machine to deposit the layers simultaneously from the nozzles.[29]

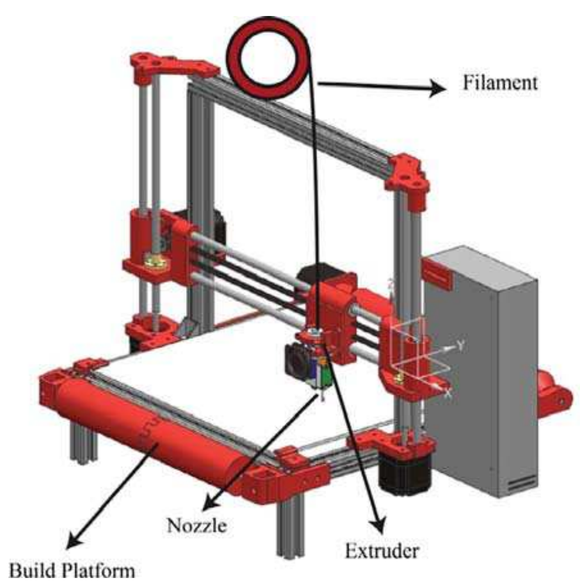

FIGURE 1 A schematic of FDM set up [Color figure can be viewed at wileyonlinelibrary.com]

Regardless of the great benefits offered by FDM, the fabricated parts have a number of downsides and shortcomings. The paramount issues that still persists from the FDM technique are the degraded mechanical characteristics resulted by the interfacial bonding strength and porosity of the printed objects which requires compelling attention.[32,33] The following parameters significantly influence the performance and functionalities of the product: extruder geometry (nozzle and filament diameters), processing parameters (hot melt and hot bed temperatures, printing speed), and work piece depositing parameters (number and thickness of layers, infill geometry and density, number of layers, raster angle, gap, and width patterning).[29,31,34]

The consistency of the FDM product depends primarily on two key factors; choice of suitable materials and the choice of optimum process parameters.[31] FDM is generally compatible with a variety of polymers for fabricating the products in various forms because of its adaptability to wide range of industrial techniques.[35–37] The choice of polymers varies from common plastics, namely polypropylene (PP), polyethylene (PE), and polyethylenetetrapthylate (PET), to engineering plastics such as polycarbonate (PC) and polysulfone (PSU).[31] The thermoplastic filaments from acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) are employed as the primary feed for FDM-based 3D printers.[38]

Fossil-based fuels are the main source for large number of conventional plastics and thus end up as massive solid wastes after usage. The adoption of sustainable plastics is the most efficacious solution to replace the nondegradable plastics as they are ecofriendly and are more reliable for human usage.[39–41] The most commonly used biopolymers are PLA, poly(hydroxyalkanoates) (PHAs), poly(ethylene glycol) (PEG), poly(caprolactone) (PCL), and so on, 3D-printed polymer products made from the materials lack mechanical strength which limits their usage to prototype models. Proper selection of feedstock with higher mechanical properties and developing polymer composites by the incorporation of reinforcements in the form of particle, fiber or nanomaterial into the composite polymer matrix improves the mechanical and functional properties of the products.[7,21,42,43] Multifarious materials such as metals, ceramics, bio-based deposits can be chosen for the reinforcements into material matrices to enhance the desired properties.[44]

Bio-based or natural fillers obtained from various industrial and agricultural wastes proved to be successful fillers imparting mechanical strength to the base polymers.[31] Furthermore, these fillers allow for the recyclability as well as the biodegradability of the products thus decreasing the environmental impact. Hence, recently, the production of 3D printing of bio nanocomposites has received considerable attention in diverse sectors to fulfill the demands of the consumers. In this process, the reinforcement of natural fillers unearths some specific challenges which need to be addressed.

However, most reviews to-date have considered filaments from synthetic polymers,[45,46] bio-based polymers and the properties of corresponding 3D printed parts.[47–49] The development of printable biopolymer composites with increased performance is now the focus of research.[50,51] Mazzanti et al.[31] discussed about the FDM 3D printing of various biodegradable and non-biodegradable polymers reinforced with natural fillers like wood, sugarcane, hemp, flax, and so on. The authors discussed about the mechanical properties of both filaments and FDM-printed parts and also about the printing parameters which affects the mechanical strength of the printed products extensively. Aida et al.[52] has provided an extensive review based on the FDM filaments that can be prepared with the fiber reinforced polymer bio composites by replacing harmful synthetic fibers with natural fibers by applying proper surface modifications. Deb et al.[53] has explored various natural fillers derived from agricultural by products, plant leaves, barks, and so on that can be used with PLA for making the FDM filaments in their review. They concluded that among all the filaments the PLA/flax fiber filament has good strength compare to wood/PLA, Hemp/PLA, and so on. The aforementioned reviews were focused on polymer composites with natural fillers for FDM which are in the form of fiber or particles.[31,52,53] These reviews were not focused on the size of the reinforcements. Relatively limited research has been done on bio-based nanocomposites which consist of fiber or particle as a reinforcement having one dimension in nanometer scale which enhances the properties of printed parts.[54] Thence, this paper attempts to present a detailed overview on development of different polymer composites incorporated with nanosize bio-based fillers for FDM process to accentuate the physiochemical properties, the challenges encountered by the bio-based polymer nanocomposites and the applications of the bio-based FDM products.

2 | MATERIALS

The layer-by-layer approach followed by FDM-printed neat polymer parts causes anisotropy that resulted in poor mechanical, electrical, and thermal properties compared to traditional manufacturing methods.[8,55] Modern printing materials with enhanced properties are obtained by reinforcing small amounts of nanomaterials into polymer matrix.[56,57] Thus, polymer nanocomposites have become the focus of research in the recent years. Essentially, substantial attempts were made to develop bio-based polymer nanocomposites to overcome the limitations of environmental and printer friendly materials.[48] Besides the required thermomechanical properties, the developed materials are expected to be printable, biocompatible, and biodegradable.[48]

In general, the diameter of the 3D printable filament is considered as 1.75 mm. While the larger filament needs high pressure to be extruded, the filament with small diameter results in failure due to improper pressure grips. Compared to the printing process parameters, the diameter of the filament will have negligible effect on the printing quality.[32]

The nozzle diameter of FDM printer is generally 0.4 mm. Printing temperature and printing speed are also the key factors in the quality of the product. Printing speed is the velocity with which the material is deposited on the work plate. Optimum printing speed should be selected as it directly affects the printing time of the component. The printing speeds which are too high or too low would result in warping of the product due to the deposition of excessive or insufficient material during printing process.[58] Nozzle temperature is the temperature inside the heating nozzle which should be maintained optimum as it affects the flow of the molten metal.[31] The nozzle temperature when optimized will result in good quality print with sufficiently strong bonding between layers. The layer thickness is the thickness of the layer deposited by the nozzle and is related to the number of layers recommended which specifies the manufacturing cost for the given printed part. The effect of layer thickness on the quality of the product also depends on the build orientation of the sample.[59] Infill density is the percentage volume of material printed on the component. Raster angle is also one of the important process parameter which affects the quality of the product. It generally

TABLE 1 Printing process parameters of FDM printed polymer biocomposites

Polymer	Filler	Filler size	Filler wt%	Filament process	Filament Dia mm	FDM printer	Nozzle temperature °C	Printing speed mm/s	Layer thickness mm	Printing bed temperature °C	Raster angle	Infill ratio %	Reference
PLA	CNT	0.5–2 μm length 5–10 nm (inner dia) 20–30 nm (outer dia)	0.5–8	Double screw extruder	1.40–1.75	Self-developed	210	40	0.2	50	45°	100	Yu et al.[61]
PLA	Graphene	<10 μm	0.5–2	Double screw extruder	1.40–1.75	Self-developed	210	40	0.2	50	45°	100	Yu et al.[61]
PLA	CNT	–	0.25–4	Twin screw extruder	1.75	Creator Pro Flash Forge 3D printer	220	45	0.2	65	–	100	Mora et al.[62]
PLA	MWCNTS	7–15 nm in diameter, 5–10 mm in length	1%–9%	Double screw extruder	1.75	FDM printer from Chengdu Pulian Co	210	9	0.3	–		100	Luo et al.[63]
PLA	CNT	Diameter: 13 nm, length: 10 μm	2–8	Double screw extruder	1.75	Raise3D N2 Plus 3D printer (Raise3D)	215	50	0.2	–	–	–	Yang et al.[64]
PLA	Nano Graphite	1.5–2.0 μm	5–30 pbw (part by weight)	Single screw extruder	1.75	–	210	15	0.4	40	–	–	Guo et al.[65]
PLA	Graphene Carbon black	–	–	–	–	MakerGearM2 version-4	220	–	0.25	70	–	100	Daniel et al.[66]
PLA	Graphene	–	10	–	1.75	Makerbot Replicator 2	210	30	0.2	60	−45° and +45°	100	Prashantha et al.[67]
PLA	Wood particles	14 μm	5	Desktop-class plastic extruder	1.75	Self-assembled	210	–	–	–	–	–	Tao et al.[68]
PLA	Graphene nanoplates (GNP)	–			1.75	WitBox desktop 3D printer	210	50	0.12	–	0°		Caminero et al.[69]
PLA	Nano silica	20–30 nm in dia		Single screw extruder	1.75	(Raise 3D Pro 2	215	70	–	–	–	–	Seng et al.[70]
PLA	CNC	5–20 nm wide and 150–200 nm long	1, 2, 5, 10	Single screw extruder	1.75	Ultimaker 3.0 3D printer feed	230	–	0.2	60	0°	100	Dinesh Kumar et al.[71]
PLA	CNF	–	1, 2.5, 5	Wellzoom desktop extruder	1.75	M3036 FDM desktop	–	40	–	–	–	100	Wang et al.[72]
PLA/PBH	NC	–	10	Friul Filiere TCM 500 single screw extruder	1.7	Sharebot Next Generation desktop 3D printer	210	–	0.2	40	±45°	100	Rigotti et al.[73]
PHBH	Fibrillated nanocellulose (NCF)		0.5.1.3	Single screw extruder	1.72	Sharebot NG 3D printer	180–200	–	–	75	±45°	100	Valentini et al.[74]

TABLE 1 (Continued)

Polymer	Filler	Filler size	Filler wt%	Filament process	Filament Dia mm	FDM printer	Nozzle temperature °C	Printing speed mm/s	Layer thickness mm	Printing bed temperature °C	Raster angle	Infill ratio %	Reference
PLA	Lignin		20, 40	Noztek Xcalibur extruder	1.75	Prusa i3 MK3S	200–210	35	–	–	45°	–	Tanase-Opedal et al.[75]
PLA	Kraft pine lignin	–	0, 5, 10, 15, 20	Twin screw extruder	1.78	–	205	20	0.1 mm	–	90°	100	Gkartzou et al.[76]
PLA	Wood particles	–	10–50	Single screw extruder	1.45–1.75	Zortrax M200 3D printer	230	–	0.19 mm	–	–	–	Kariz et al.[77]
TPU/PLA	Graphene oxide	–	0.5, 2, 5	Mini extruder	–	–	210	20	0.1 mm	60	–	100	Chen et al.[78]

varies from 0° to 90°. The suitable printing process parameter along with appropriate selection of materials[60] will result in quality products with desirable strength. The process parameters of some of the bio-based polymer composites are shown in Table 1.

Bio-based polymer nanocomposites are hybrid materials which consist of either filler or polymer matrices that have been obtained from biological resources.[79] In this section, these two possibilities of bio-based polymer nanocomposites will be contemplated.

2.1 | Nanocomposites with bio-based polymers

Bio polymers can be extracted from bio resources like wood cellulose, corn, and so on. The general process of obtaining bio-based polymer composite parts from FDM is shown in Figure 2. They can also be obtained from mixed sources of biomass and petroleum. The commonly used biopolymers are PHAs, PEG, PCL, PLA, and so on. Among all these PLA has recently been paid lot of attention because it is derived from starch sources and PLA shows good thermal processibility.[80] The filler material can be metal nanoparticles,[54] ceramic nanoparticles,[81] carbon nanoparticles.[55]

PLA is a common filament feedstock material used in FDM. PLA is a biodegradable and biocompatible highly versatile thermoplastic aliphatic polyester produced through fermentation of sugar feedstocks such as beets and by converting starch in corn, potatoes, or other starch sources.[82,83] Owing to its remarkable mechanical and thermal properties, PLA has been well-recognized in 3D printing.[84] Despite these advantages PLA has poor impact strength, thermal resistance, brittle nature thus exhibiting small elongation before break, low crystallization rate, and heat distortion temperature akin to most bio-based materials.[85] The inclusion of polymer blends, composites and plasticization using biocompatible plasticizers can overcome these disadvantages.[21,80,86,87] Carbon nanotube (CNT)/graphene/carbon nanoparticles (NC)/carbon black is anticipated to ameliorate the electrical attributes of the FDM-based PLA composites to be more effective in electrical applications.[61] The electrical conductivity (σ) is in the vicinity of 10^{-16} S m^{-1} for PLA, making it an excellent insulator in electronic packaging applications. Nevertheless, with the incorporation of carbon nanofillers electrical conductivity increases exponentially suggesting the creation of penetrable conduction routes and charge dispersion on the composite surface.[62–66,88,89] By reinforcing graphene into PLA, improves the mechanical and thermal properties.[54,61] The thermal conductivity of PLA/graphene composites improves with the filler content because the interferences of the filler iotas result in the formation of a conductive network through the polymer.[66–68,88]

The CNT/graphene serves as effective reinforcement in polymer composites, allowing better filler dispersion and improved interfacial strength. This results in the improvement of mechanical properties.[63,64,69,90,91]

PLA is exceedingly hygroscopic in nature which causes bubble formation subsequently resulting in deformed printed parts. Additionally, moisture absorption reduces the shelf life of filaments. Because of its excellent hydrophobicity for extending the shelf life of filaments, silica gel or fumed silica is commonly employed as a siccative in various applications.[70] The reinforcement of treated nanosilica decreases hygroscopicity and improves thermal stability and mechanical properties.[70]

Poly(butylene adipate-*co*-terephthalate) (PBAT), a copolyester of adipic acid and is biodegradable has superior toughness with high resistance to breakage and outstanding thermal stability.[92] PLA/PBAT mixtures are profoundly alluring blends as the PLA provides noteworthy mechanical strength while PBAT administers elevated toughness and flexibility.[39,86] On the contrary, their incongruence and insolubility have been the major limitations that extenuate the ductile properties, driving to a negative impact to utilize these mixtures in applications with high mechanical strength. To enhance the interfacial bonding (i.e., improve the compatibility) between both the biopolymers, plasticizers like, glycidyl methacrylate (GMA),[93] organoclay (OC)[81,94] can be added.

The ductility of PLA is enhanced by blending it with polymeric tougheners (e.g., PCL, poly(butylene succinate) (PBS), and PHA) and the variation in size, volume fraction, substructure, and intrinsic properties of the dispersed toughening phase can influence the outcome.[95]

PBS is an aliphatic, semicrystalline, and biodegradable polyester which has low melting point (less than 120°C). However, because of its outstanding ductility, it is regarded as a suitable choice for FDM filaments.[96] But due to the low melting strength of PBS it is difficult to extrude monofilament continuously. Furthermore, product defects may emerge from the distortion caused by the substantial volume shrinkage during cooling. Hence, PBS has to be modified to overcome these impediments and thus make it suitable for FDM printing. The PBS/PLA are one of such blends which exhibited superior mechanical properties with outstanding elongation of 90%–300% and making it viable for FDM printing.[81,95]

Cellulose is widely abundant sustainable biopolymer and is found in tunicates, plants, and some bacteria.[97] Cellulose nanofibrils (CNFs) and nanocrystals (CNCs) have been extensively adopted as a modernistic collection of nanomaterials in 3D printing.[98]

In addition to the PLA, other polyesters like PCL and PHAs also has gained a significant amount of consideration due to the wide range of biomedical and food packaging applications.

2.2 | Nanocomposites with bio-based fillers

Often, the polymers are reinforced with the fillers to enhance the thermomechanical properties. Especially, if the fillers are derived from the natural resources, they aid for optimal qualities like biodegradability and biocompatibility which are more predominantly applicable in the biomedical field. Furthermore, increased urbanization has resulted of massive growth in agro, industrial, and domestic wastes. Synthesis of bio-based fillers from these resources at nanoscale makes it feasible for the hybridization of bio-based fillers with synthetic as well as natural polymers.[21] Hence, in this section recent research focusing on the development of polymer nanocomposites synthesized from bio-based materials were discussed exclusively.

The inclusion of CNCs into PLA improves mechanical and thermal properties, as the cellulose nanoparticles act as crystallization nucleating agents. The load is absorbed by the CNC particles that are oriented within the polymer chains and consequently resulted in the improvement of tensile properties.[71,72,99] Cellulose nanocrystals yielded by acid hydrolysis of plum seed shells were effectively incorporated into the PLA/PHB matrix via a reactive blending process which resulted in the improved adhesion followed by thermal stability and mechanical properties.[85] Nanocellulose was acquired from microcellulose with ultrasonication treatment to disrupt the arranged structure in such a manner to come up with completely biodegradable 3D-printed nanocomposites based on biopolyesters like PLA, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH), and nanocellulose. The inclusion of nanocellulose in the filament samples improved thermomechanical characteristics of the composites.[73,74] The filaments for 3D printing with improved mechanical strength were fabricated from low density polyethylene reinforced with nanofibrillated cotton (NFC) particles which are synthesized from cotton material obtained from recycled T-shirts.[100] PLA/lignin biocomposites for 3D-printing applications have been developed using lignin, synthesized from cooking liquor of Norway spruce chips by using a soda cooking technique.[75] The PLA/lignin biocomposites thus developed exhibited good printability with no agglomerations. Owing to the antioxidant activity of lignin, these composites also have shown enhanced scavenging activity. Carbon nanoparticles synthesized from waste coconut shell powder is incorporated into Bioplast for the development of biodegradable 3D printable filaments.[101]

In addition to the aforementioned nanofillers, various other industrial and plant by products are being served as fillers for polymer composites. Some of the plant-based fillers include biomass (cellulose, lignin, hemicellulose etc.),[76,102] sugarcane bagasse,[103] husks from rice and wood,[104–106] fibers from banana,[44] pine, hemp, harakeke,[107] jute, flax,[108] bamboo,[109] thermomechanical pulp,[110] cork powder,[111] saw dust,[68] cardboard dust, wood flour,[112,113] cocoa shells,[114] walnut shell powder,[115] almond skin powder,[116] and so on. The inclusion of fillers causes shrinkage which makes printing more accurate.[117] The filaments thus developed exhibited superior properties compared to that of the neat polymer.

3 | THERMOMECHANICAL PROPERTIES OF THE NANOCOMPOSITE FILAMENTS AND FDM PRINTED PARTS

In an effort to obtain the 3D-printed parts by FDM, effective polymer nanocomposite filaments have to be developed. Despite the efforts made in developing the filaments, the subsequent layer deposition of the materials in FDM results in the microstructural change of the 3D-printed part in comparison to that of the filaments that are extruded from bio-based polymer nanocomposite blends. Predominantly, the void formation becomes the major drawback of the 3D-printed parts which consequently results in the mediocre mechanical abilities. Hence, it is crucial to analyze the properties of the filaments such that the inducement of the processing parameters of 3D printing can be performed effectively. The thermal properties obtained from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are discussed in this section. Additionally, the mechanical properties from tensile and flexure tests are discussed.

3.1 | Thermal properties

Although various thermoplastic-based polymer nanocomposite filaments are available in the literature, this study specifically highlights the distinctiveness of the bio-based polymer nanocomposites. PLA being a green polymer has been extensively wielded as a base polymer matrix with innumerable reinforcements for the formulation of 3D printable filaments. The glass transition temperature of PLA and graphene/CNT composites has been reduced by 5% and also lowered the crystallinity of the filaments.[61] Furthermore, the addition of the CNT degraded the thermal decomposition temperatures along with crystallization and melting behavior.[61,63,64] Reinforcement of graphene in lower quantities decreased the thermal decomposition temperature compared to neat PLA. However, with the filler content the thermal stability also increased which might be due to restricted thermal conductivity caused by the inhomogeneous dispersion of large quantities of graphite in the polymer matrix.[65] Wood flour filled PLA filaments also have shown decrement in the decomposition temperature and increment in the amount of residue left compared to neat PLA filaments as the thermal decomposition temperature wood flour is lower than that of PLA.[68]

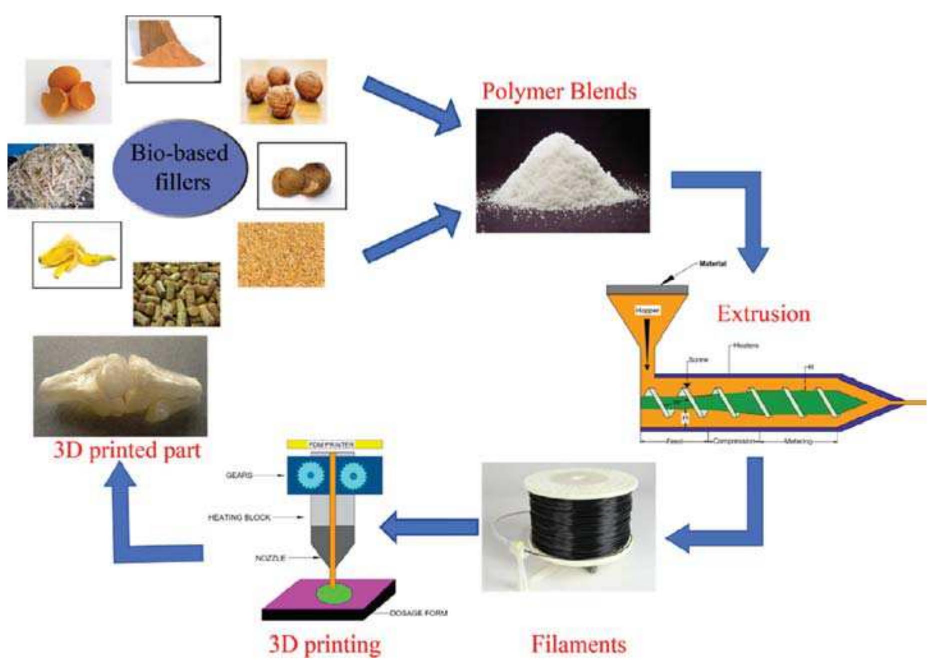

FIGURE 2 Schematic for general process of 3D printing of bio-based polymer nanocomposites [Color figure can be viewed at wileyonlinelibrary.com]

The reinforcement of plum shell based nanocellulose into PLA/PHB blends have shown nucleating activity and improved the recrystallization of PLA.[85] Additionally, the composites have also exhibited improved onset temperatures from TGA compared to the pure PLA/PHB blends. Similar behavior was observed when nanocellulose is incorporated into polymer results were observed when kraft lignin is reinforced in PLA where lignin promoted the crystallization of PLA and it's double melting behavior being a nucleating agent.[75,76,102] The decomposition of PLA/lignin has started around 216°C and has occurred over a broad range of temperature.[76] However, with the increase in filler percentage the thermal properties tend to deteriorate because of the constraint motion of polymer chains and reduced crystallization.[71,76] Furthermore, few research studies have reported that due to the incorporation of fillers, the thermal properties have very minute to no significant effect.[73,101] Despite these effects, the presence of nanofillers was found to enhance the stiffening effect. A summary of DSC and TGA results are tabulated in Table 2.

3.2 | Mechanical properties

The literature related to the mechanical properties of the bio-based polymer nanocomposite filaments was scantily available. An appreciable number of filaments were based on a PLA matrix where various nanomaterials are reinforced to augment the mechanical properties. Overall, the reinforcement of the fillers at low proportions has enhanced the stiffness and the toughness of the filaments.[50] Table 3 summarizes the tensile strength and young's modulus of the various bio-based polymer nanocomposite filaments and printed parts. The cellulose nanofibrils, when infused in PLA/PEG have increased the mechanical properties suggesting the formation of hydrogen bonds which resulted in an improvement in the tensile properties.[72] Similar outcomes were observed when cellulose nanocrystals were reinforced in PLA matrix which confirmed the matrix and filler interaction.[71,73,85,99] In addition to these, the carbon synthesized from coconut shell powder has considerably enhanced the tensile properties of the PLA/Bioplast filaments at lower loadings. An increase in the amount of filler resulted in the agglomeration of the particles which caused the deterioration of mechanical properties.[101] Similar results were observed for PLA composite filaments with carbon nanofillers. The tensile and flexure strength was improved to certain extent of loading for the filaments and when the filler loading is further increased, the matrix is subjected to high stress concentration which changes the matrix continuity resulting in the toughness deterioration of the composite.[65]

Though lignin resulted in reduced tensile properties, this may be partially compensated by changing the 3D printing temperature.[75] The ultimate tensile strength (UTS)

TABLE 2 Thermal properties of bio-based polymer nanocomposites

Polymer	Filler	Filler (wt%)	Onset temperature °C	Glass transition temperature, Tg °C	Reference
PLA	CNT	4	287.0 (<neat PLA)	–	Yu et al.[61]
	CNT	2	–	54 (neat PLA)	
	Graphene	2	282.4 (<neat PLA)	–	
	MWCNT	0.75	–	64.74	Cobos et al.[118]
	(Halloysite nanotubes) HNT derived from clay	1		65.77	
	CNC	2	–	62.90	Dinesh Kumar et al.[71]
	Lignin	20–40	347–339.7	56–71	Tanase-Opedal et al.[75]
PLA/PHB	Cellulose nanocrystals derived from plum seed shells	1	273	–	Frone et al.[85]
PLA/PEG	CNF	1	320	–	Wang et al.[72]
PHBH	NCF	3	288	2.0 (<PHBH)	Valentini et al.[74]
Printed parts					
PLA	CNT	8	–	61.04	Yang et al.[64]
	Lingnin	20–40	347–339.7	56–71	Ji et al.[102]
PHBH	NCF	3	264	0.8	Valentini et al.[74]

TABLE 3 Mechanical properties of bio-based polymer nanocomposites

Polymer	Filler	Filler Wt %	Tensile strength MPa	Youngs modulus MPa	Reference
PLA	MWCNT	5	78.4	134.4	Luo et al.[63]
	CNT	6	64.12	1.9 GPa	Yang et al.[64]
	Wood flour/Nano graphite	10	30	–	Guo et al.[65]
	Cellulose	10	9.92	3.48 GPa	Hyvärinen and Kärki[99]
	Wood flour particles	10	57	3.63 GPa	Kariz et al.[77]
TPU/PLA	GO	0.5	–	80	Chen et al.[78]
PLA/PEG	CNF	2.5	57.5	–	Wang et al.[72]
PHBH	NCF	0.5	23.1	1259	Valentini et al.[74]
Printed samples					
PLA	Lignin	20–40	27–46	1746–2843	Tanase-Opedal et al.[75,102]
	Lignin	5	2.19 GPa	41.9	Gkartzou et al.[76]
	Graphene	10	40.2	2454	Prashantha and Roger[67]
			66.8	3752	Caminero et al.[69]
PHBH	NCF	0.5	18.0	807	Valentini et al.[74]

and young's modulus of PLA/lignin composites remained similar irrespective of road width and were observed to be 18% (UTS) and 6% (Young's modulus) lower than that of neat PLA. Dissimilar fracture behavior can be exhibited by the specimens that are fabricated under similar conditions which might be due to laminar failures caused by the extrusion or the weak adhesion among the fibers, particularly at the fusion points.[76] The mechanical properties of the resultant material revealed that the lignin containing filaments had lower resistance to load than neat PLA. Yet, for composites containing 3% (*w*/*w*) of lignin, this effect was not noticeable. In this scenario, the materials exhibited substantial increase in the ultimate load prior to fracture.[119]

The printing parameter settings, namely number of layers and thickness, raster angle and gap, printing speed, filament diameter, and so on, influence the mechanical strength of the FDM-printed products. PLA incorporated with graphitic nanofiller has exhibited poor mechanical properties at low percentage of filler loadings due to the influence of poor parameter settings which dominated the filler effect. However, at high loadings the filler effect becomes significant and the mechanical properties have improved.[61] However, the tensile properties of the 3D-printed objects have improved compared to the properties of the filaments before subjected to FDM as the filaments undergo huge stress which caused deformation and layer slippage during FDM. The flexure properties of the printed products have improved with the increase in filament diameter suggesting that the processing parameters contribute significantly in determining the mechanical properties. The 3D-printed PLA composites incorporated with multi-walled carbon nanotubes (MWCNTs) have shown increment in tensile strength in comparison to the neat PLA up to 5% loading.[63] The enhancement of the properties is attributed to the homogenous dispersion of MWCNTs and the similar melt flow rate of the PLA and the composites that are suitable for 3D printing. As the filler percentage increases, the continuity in the extrusion process becomes challenging. Similarly, the 3D-printed dog bone specimens from PLA infused with carbon nanoparticles have revealed an increase in stiffness compared to the extruded filaments due to layer-by-layer deposition.[89] PLA/CNT specimens of $15 \text{ mm} \times 15 \text{ mm} \times 2 \text{ mm}$ were 3D printed with a nozzle diameter of 0.8 mm, liquefier temperature of 215°C, filling velocity of 50 mm/s, and with a layer thickness of 0.2 mm.[64] The tensile strength improved by 64.12% for 6% filler loading and flexure strength increased by 24.29%. The effect of layer-by-layer deposition is dominated by the interfacial bonding between PLA and CNT which resulted in the substantial enhancement in mechanical properties of the PLA/CNT composites. Nonetheless, some PLA/CNT specimens have shown 30% improvement in tensile modulus for 5% filler loading whereas strength and toughness were decreased which is influenced by the alignment of CNTs.[90] The young's modulus and tensile strength of FDM-printed PLA/graphene nanocomposites exhibited significant improvement in comparison to the pure PLA 3D-printed samples.[67,69] The samples are printed by using Makerbot Replicator 2[67] and WitBox desktop 3D printer[69] with nozzle diameter 0.4 mm and nozzle temperature of 210°C for both type of printers. The feed rate, layer height is 50 mm/s, 0.12 mm for WitBox desktop 3D printer and 30 mm/sec, 0.2 mm for Makerbot Replicator 2, respectively. The voids due to the multilayer deposition have slightly reduced the strain at break for flat specimens. The specimens developed by on-edge orientation have illustrated superior mechanical properties compared to the flat and upright specimens. These results suggest that the build orientation of the specimens significantly influences the mechanical properties. However, the properties of horizontally built specimens are still inferior to the properties exhibited in injection molded samples which suggest that the quality and dimensional stability of FDM products are yet to be improved.[67] The PLA/wood flour (WF) specimens have shown an increment in the initial deformation resistance with the addition of the wood flour.[68] Although tensile modulus was increased for PLA/WF composites, the tensile strength decreased with the increase in strain suggesting that these composites could better serve in the structures that requires high compressive strength. Addition of silk powder as filler in PLA/PBAT composites have reduced the tensile strength and flexure properties of the 3D-printed specimens. However, these specimens have exhibited high impact strength with the presence of Joncryl which is a compatibilizer that have promoted esterification.[92] The PLA/PBAT/nano talc 3D-printed specimens have exhibited superior tensile characteristics against the neat PLA and composite filaments.[86] However, at higher loadings of nano talc, the voids between the layers have increased resulting in the deterioration of mechanical properties.

4 | APPLICATIONS

4.1 | Biomedical applications

3D printing imparts noteworthy advantages in biomedical applications with the ability to manufacture patient customized medical products and equipment as shown in Figure 3a,b. Present and forthcoming research priorities of 3D printing in biomedical and pharmaceutical fields primarily includes: (1) manufacturing of tissues and organs; personalization of prostheses, orthopedic transplants, and anatomical replicas; (2) customized ways of drug delivery, distribution of drugs and drug screening.[48] Printability, excellent mechanical, thermal, and structural properties are the ideal attributes of materials that are considered worthy being printed for biomedical applications.[6,124] A summary of various biomedical applications of bio-based polymer nanocomposites are listed in Table 4.

3D printing has evolved as an ingenious source for the scaffold development in tissue engineering due to its abundant benefits, which includes rapid fabrication, greater accuracy, and custom-made manufacturing.[138] Several degradable polymers such as PCL, poly(glycolic acid), PLA, chitosan, and their copolymers were employed to manufacture scaffolds.[139–141]

Chen et al.[78] manufactured polyurethane (TPU)/PLA/graphene oxide (GO) nanocomposite filaments and scaffolds. With the inclusion of 0.5 wt% GO tensile modulus, yield point and compression modulus has increased by 75.50%,

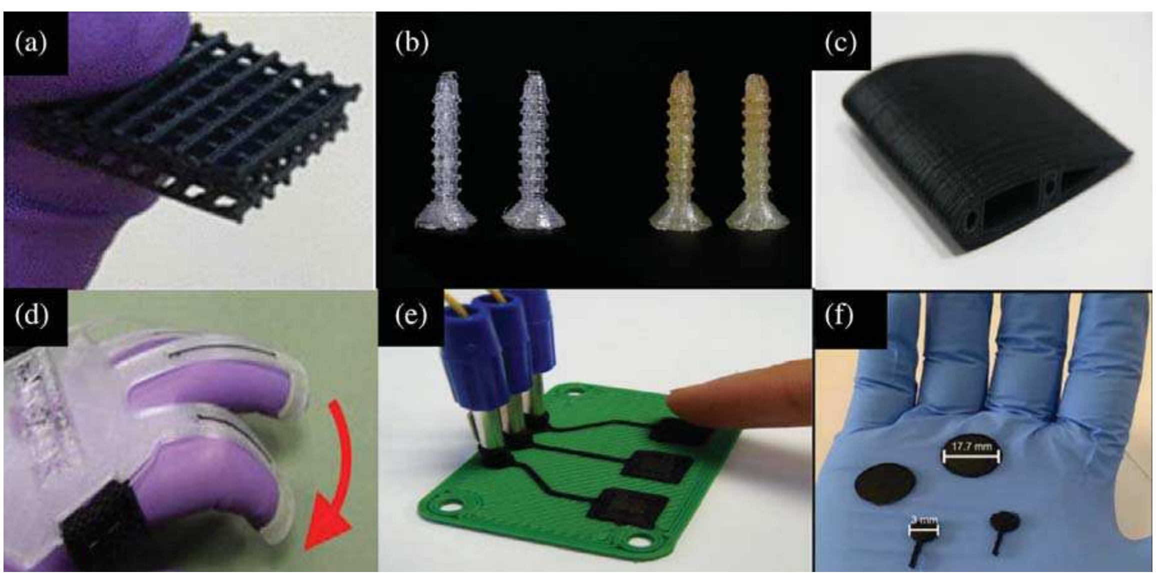

FIGURE 3 Applications of FDM from polymer nanocomposites: (a) scaffolds (reproduced with permission from Chen et al.[78]), (b) orthopedic screws (reproduced with permission from Dehghani et al.[120]), (c) aerofoil model (reproduced with permission from Olasek[121]), (d) glove undergoing flexing (reproduced with permission from Leigh et al.[122]), (e) capacitive interface device (reproduced with permission from Leigh et al.[122]), and (f) 3D printed disc electrodes (3DEs; reproduced with permission from Foster et al.[123]) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Bio medical applications of bio-based polymer nanocomposites

Polymer	Filler	Application	Reference
PLA	nHA	Anatomical model, molar teeth, bone scaffolds with microvascular mimicking channels improves vascularized cell growth	Esposito Corcione et al.[125–127]
	Collagen derived CQD	Luminescent scaffolds with improved photostability and non-photo bleaching characteristics	Dehghani et al.[128]
	Hydrogel with gold nanoparticles	Scaffolds with enhanced stiffness and cell behavior	Heo et al.[129]
	HA + CNT	Scaffolds for bone regeneration with improved compressive strength, electrical conductivity, protein adsorption, and cell attachments	Gonçalves et al.[130]
	Lingnin	Meshes for wound dressing with antioxidant properties which enhances the wound healing	Domínguez-Robles et al.[119]
	Graphene oxide	Scaffolds for bone tissue engineering	Belaid et al.[131]
	EBN	Scaffolds for bone tissue engineering	Belaid et al.[132]
TPU/PLA	Graphene oxide	Tissue engineering scaffolds with improved mechanical properties, thermal stability, and cell viability	Chen et al.[78]
PLA-g-MA	Chitosan	Strips with improved tensile strength, water resistance, and bacterial properties	Wu[133]
PCL	HA + Nano MgO	Scaffolds with increased hydrophilicity and cell behavior	Roh et al.[134]
	Silver nanoparticles (AgNps)	Antimicrobial scaffolds for tissue engineering with increased mechanical properties and enzymatic stability	Radhakrishnan et al.[135]
	Hydrogel with alginate, gelatin	Scaffolds that heal bone deformities with a bioactive hybrid system	Hernandez et al.[136]
1,6-Hexanediol l-phenylalanine-based poly (ester urea) (PEU)	Hydroxyapatite (HA)	Scaffolds for bone regeneration with enhanced bioactivity	Yu et al.[137]

69.17%, and 167% respectively. As the GO loading increases, the strain at break constantly decreases which indicates that reinforcement of GO decreases the elasticity of polymer matrix. The printing orientation also leads to different mechanical properties due to the weak adhesive strength between layers during 3D printing. The 3D-printed scaffolds unveil outstanding thermomechanical properties in addition to cell growth and proliferation, enabling them to be extensively applied in various fields, particularly as an impending source in tissue engineering for developing scaffolds.

Beladi et al.[131] developed PLA/graphene oxide scaffolds for bone tissue engineering applications and investigated their mechanical, thermal biocompatibility properties. With the inclusion of graphene oxide, the surface roughness and hydrophilicity of the scaffolds were improved which promoted the cell adhesion and proliferation on scaffold surface and differentiation for bone regeneration. Graphene oxide loading of 0.3% has shown significant rise in young's modulus which is improved by 30%. Beladi et al.[132] developed PLA/exfoliated boron nitride (EBN) scaffolds for tissue engineering applications. With the reinforcement of EBN, polymer crystallinity has been decreased. Although the thermal and mechanical properties were not influenced considerably, surface roughness and hydrophilicity were improved with the infusion of EBN.

Corcione et al.,[125] fabricated polylactic acid-nanohydroxyapatite (nanoHA) composite filaments and prepared specimens with simple geometry which can be used for the characterization anatomical details. The addition of nanoHA which was homogeneously distributed throughout the PLA matrix has improved the mechanical properties without altering the rheological performance. The homogenous dispersion of HA particles has resulted in reduced agglomeration defects. Scaffolds made of PLA/15%HA that have a higher crack resistance have the potentiality to be employed as trabecular bone replacement transplants which are capable to withstand cyclic loading.[126,138]

The PCL/HAp/MgO scaffolds made-up of using 3D printing of PCL combined with 1–15 wt% of MgO and HAp. Cell viability of preosteoblast (MC3T3-E1) cells in PCL scaffolds was improved by adding MgO/HAp nanoparticles and plasma treatment. The hydrophilicity of these scaffolds has improved by treating them with oxygen and nitrogen plasma this is because of nitrogen and oxygen functional groups.[134] The antibacterial properties of Maleic anhydride-grafted polylactide (PLA-g-MA) composites were improved by infusing chitosan (CS) and by promoting strong adhesion between the CS and the PLA-g-MA matrix.[133] Consequently, improved water resistance was observed for PLA-g-MA/CS composites in addition to the enhanced mechanical strength.

Gonçalves and coworkers have found that PCL/HA/CNT scaffolds developed from FDM has porous structure with pore sizes ranging across 450–750 μm and has become electrically conductive for 2 wt% CNTs. The infused CNTs has improved protein adsorption and cell adhesion.[130] The customized antimicrobial scaffolds were prepared by incorporating silver nanoparticles (AgNps) into the PCL matrix which improves scaffold stiffness and enzymatic stability which can be utilized for bone tissue engineering application.[135] PLA filaments were immersed in carbon quantum dots (CQD) obtained from pig skin were developed and were used to print a cube of 5 mm side and 300 μm layer thickness which were used in cell and tissue imaging.[128]

4.2 | Aerospace applications

Greater part of the aviation components has complex profiles which are laborious and expensive to be produced. To recently, the foremost aerospace components, such as exhaust of the engine and turbine blades, have been 3D-printed with metal materials as they are harder and have more flame retardancy than polymers.[142] To minimize weight and processing time for component maintenance, the aerospace sector has been substituting traditional metal parts with suitably robust FDM-printed parts of polymer composites such as PLA, ULTEM the branded name for polyetherimide (PEI), ABS, polycarbonate, and polyphenylsulfone,[143] as shown in Figure 3c. Polymer composites capable of withstanding high temperatures have recently been printed for aerospace applications. An inlet guide vane is fabricated by Glenn Research Center using FDM with ULTEM 1000 reinforced with short carbon fibers which can withstand 400°F operating temperature. The polyether ether ketone (PEEK) was reinforced with carbon fiber and these composites were successfully used to print aero components like aerofoil, support arm for rotor and air intake. These 3D-printed parts are relatively light in weight by 50% compared to conventional aluminum parts and can withstand temperature up to 482°F.[144] Unmanned air vehicles have complex parts like flapping wing, gears for flapping wing, tail, and frame which requires complex geometries. These can be effectively printed with FDM by utilizing various composites which gives light weight structures which gives better performance.[145,146] A summary of various aerospace applications of bio-based polymer nanocomposites is listed in Table 5.

4.3 | Electronic applications

Electronic prototypes that are geometrically suitable and have a shorter development time can be produced using

3D printing technology.[1,7] 3D-printed polymer composites can be used as electronic devices in wide array of applications by inducing electrically conductive nanoparticles as filler, as shown in Figure 3d,e. Various electronic applications of bio-based nanocomposites are summarized in Table 6. Carbon black/PCL composites were used to produce electronic sensors ranging from piezoresistive to capacitive using FDM.[7] Piezoresistive sensors can be 3D printed by CNT and thermoplastic polymer.[149] Efforts have been made to create electronic 3D-printed parts by encasing metallic wires such as copper, nickel, and nickel-chromium in polymer matrices. These structures are used for making electromechanical devices namely loudspeaker, LVDT, rheostat, and membrane switches.

FDM is used to fabricate high quality electrodes and devices for electrochemical storage typically batteries and supercapacitors.[156] The graphitic amount in the filament, which serves as an active material, was amplified as much as conceivable to improve electrochemical efficiency despite retaining adequate mechanical properties required for printing. A variety of disc electrodes (3DE) as shown in Figure 3f is printed by graphene/PLA filaments.[123,150–153] The graphene/PLA circular electrodes which consists of 8 wt% graphene and 92 wt% PLA with hole are printed and tested which are used as an anode in Lithium-ion batteries and as supercapacitors.[123] Though very little amount of graphene present in the electrode this PLA/graphene material can be effectively work as a battery anode/capacitor material. Such non-modified graphene-based electrodes, exhibited hydrogen evolution reaction (HER) current densities of 0 and $-1.5\ \text{mA cm}^{-2}$ at an overpotential of -1 V.[150,151] The PLA/graphene filaments were used to 3D print the electrodes which were further used to fabricate super-capacitor that has exhibited good performance with a specific capacitance of $98.37\ \text{Fg}^{-1}$.[152,153] A negative electrode of 250 μm and 11 mm diameter 3D structures were printed with PLA/graphite filaments and used as negative electrodes in Li-ion batteries.[155]

A corrosion free, lightweight current collector was fabricated by using PLA and 10 wt% of nanocarbon. With these collectors a prototype of metal free super capacitor is assembled with the graphite oxide reduced by microwave exfoliation (MEGO) electrodes and graphite oxide (GO) membrane as the separator.[154]

4.4 | Emerging applications

In addition to the above mentioned applications, the FDM has found its way into unconventional applications such as filtration and packaging applications. However, the applications of FDM in these areas are still under-explored and are emerging.

It has also begun to pique the interest of researchers in the water and wastewater treatment sectors for the production of complex components in membrane modules, such as membranes and feed channel spacers for the spiral wound module (SWM).[157] Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO), electrodialysis (ED), membrane distillation (MD) are the numerous membrane-based processes which consists of membrane spacers.[158] Membrane/feed spacers have mesh like structure and are utilized to separate membranes and enable for the formation of flow channels in the SWM resulting in a higher

TABLE 5 Aerospace applications of bio-based polymer nanocomposites

Polymer	Filler	Application	Reference
ULTEM 1000	Chopped carbon fiber	Inlet guide vane	Najmon et al.[143]
PEEK	Carbon fiber	Airfoil, rotor support arm	Objects Impossible[144]
PLA	Carbon fiber	X-plan, a vertical take-off and landing UAV	Reisinger[147,148]

TABLE 6 Electronic applications of bio-based polymer nanocomposites

Polymer	Filler	Application	Reference
PCL	Carbon black	Piezoresistive sensors	Wang et al.[7]
TPU	CNT	Multiaxial force sensor	Kim et al.[149]
PLA	Graphene	Disc electrodes used in batteries and supercapacitors	Foster et al.[123,150–153]
	Nanocarbon	Collectors for super capacitors	Baskakov et al.[154]
	Graphite	Disc electrodes for batteries	Maurel et al.[155]

yield of clean water.[159] Pressure loss and fouling are two major issues with traditional feed spacers. 3D printing of feed spacers has proved to be more beneficial compared to traditional methods by improvizing the mass transfer while minimizing the pressure loss.[160] Siddiqui et al.[161] fabricated feed spacers using FDM, polyjet 3D printing and SLA and compared the outcomes concluding that FDM produced spacers are unsuitable due to the difficulty in fabricating thin spacer filaments. In addition, the prototype proved fragile and unsuited for SWM. Although the FDM prototypes have exhibited high mass transfer and greater pressure loss, surprisingly the FDM spacers exhibited poor affinity toward bacterial attachment. Tan et al.[162] compared solid (FDM), liquid (Polyjet), and powder form (SLS) of 3D printing techniques for fabrication of spacers. Among, Polyjet has the superior part-to-model accuracy while FDM has the lowest accuracy. Overall, compared to the FDM-printed spacers, polyjet and SLS-printed spacers have high degree of accuracy and are more viable for water treatment.

Now a days 3D printing was also used for air filtration to remove toxic gases, biological aerosol particles which include viruses, bacteria cells, and so on.[163] Personal protective masks can act as a barrier against some pollutants; however, conventional procedures make it difficult to produce a highly effective barrier. The FDM 3D printing technique can be effectively utilized to fabricate these protective devices. Goswami et al.[164] fabricated facial protective mask by using PLA with functionalized graphene-coated air filters. A 3D-printed mask may be customized easily and quickly according to the needs of the customers using simple software resulting in an ideal fit. Vankova et al.[165] fabricated personal protective mask with PLA by using FDM printer Prusa i3 MK3. The compact structure of these PLA protective masks can be deemed a satisfactory safeguard against particles, including microorganisms and viruses. Embossed nanofiber membranes (ENMs) with 3D patterns were developed by Eunjoo Koh et al. for usage in air mask filtration[166] by using polyester (PET) and ABS polymers at room temperature. The 3D-printed ENM exhibited good mechanical and chemical durableness. Although FDM is currently evolving as an alternative for conventional production procedures in air filtration, use of polymer bio nanocomposites have not yet been thoroughly introduced as a potential substitute for the polymers that are used in FDM.

Bio-based materials applications in the sustainable packaging industry have seen tremendous expansion as a result of current consumer market trends toward greener packaging and waste reduction.[167] Bio-based sustainable packaging materials should ideally be made from renewable resources or by-products of agricultural or food processing, which are gaining traction in business and academics and do not compete with primary food production. Currently, the food containers are made of synthetic polymers like polyolefins, the bags are made of low-density polyethylene and polypropylene. To improve the mechanical, antioxidant, and antimicrobial properties the micro or nanoparticles like Cu, Ag, Zn, and Ti nanostructures are reinforced in the polymers.[44] Biswas et al.[123] fabricated a biodegradable polymer film using silicon/carbon nanoparticles (SCNP) synthesized from rice husk through pyrolysis. These hybrid nanoparticles are mixed with polymer pellets and the films were prepared by 3D printing. With the inclusion of SCNP, the thermal stability and tensile properties were improved. Biswas et al.[168] developed a composite film by 3D printing with Ag assisted bio-based silica-carbon nanoparticles (SCAg-NPs) as filler and polymer solution as matrix material. The silica/carbon nanoparticles are derived from rice husk powder. With the reinforcement of SCAg-NPs thermal stability has been improved. However, there is moderate improvement in tensile properties.

3D printing is still in its infancy and has numerous hurdles, particularly in terms of industrial upscaling. Industry is very interested in incorporating AM into their operations, and AM has already made the transition from prototype to production. NASA and Piper aircraft are two foremost companies in the aerospace sector that employ FDM to print manufacturing tools, functional prototypes, concept models, and some multifaceted lightweight parts.[50] The Airbus A350 XWB is a great example which consists of more than 1000 3D-printed parts. FDM 3D printing is used by BMW, Volkswagen, and Ford to generate a variety of items such as jigs and fixtures, tooling, and prototypes.[169] Team Penske is one of America's most popular pro car racing teams that uses FDM carbon fiber/Nylon 12 composites to print prototypes and end use parts for their IndyCar and NASCAR race cars.[170] However, the FDM 3D-printed parts that were used in the abovementioned applications were strictly polymer composites. The applications of polymer bio nanocomposites have not yet been industrialized due to the limitations imposed on printing by the filler induced polymers.

5 | FUTURE TREND

Bio-based polymer nanocomposites derived from the biological resources, such as starch, biomass (cellulose, lignin, hemicellulose etc.), agricultural waste (rice husk, wood flour, sugarcane bagasse etc.) are the most plentiful bio-based feedstocks for FDM. These composite feedstock filaments have been developed in laboratories to date, but they can be commercialized in the near future with few tweaks. Because the FDM is constrained by viable materials, further research can be carried out to discover functional materials by reinforcing different bio fillers of nanosize which aids in expanding the spectrum of functional materials. Bio-based nanocomposites can be used as the ultimate objective of the FDM process to create functional, cost-effective, and customizable items.

One of the most important factors influencing the quality of printed products is the processing parameters. For producing high quality functional products additional investigation is needed on understanding the behavior and compatibility difficulties between nanoparticles and matrix materials by establishing theoretical models. Although efforts are being made in the FDM of polymer bio nanocomposites, there is still a lot of work to be done such as in improving thermal and mechanical properties, before bio-based nano polymers can reach their applicability in full potential. On account of the fact that this review is presented in the material point of view, the advancements are suggested based on the applicability of polymer bio nanocomposites in futuristic solutions.

Most of the industries including aerospace, automotive, and biomedical have adapted FDM-printed parts of polymer composites to substitute the traditionally produced parts. Owing to the successful solutions in eliminating the limitations of the polymers in the recent years, the commercial polymeric feedstock filaments are used for these industrial applications. Although the laboratory scale customized filaments with bio-based fillers exhibited superior properties compared to the commercial filaments, the challenges introduced with the printing of filler materials hinders them from being widely used in the industrial sectors. However, introducing nanofillers can minimize the limitations of these materials. Hence, much more study is needed in the abovementioned sectors using FDM printing of bio-based polymer nanocomposites which enhances the functionality of the printed parts.

6 | CONCLUSIONS

The paper provides a synopsis of research efforts that were performed for the manifestation of novel materials for the FDM. The evolution of the novel supplies that are viable with FDM will enable to expand its scope for multifarious applications. It is well known that over the last two decades, the research activity associated with the production of bio-based materials has increased progressively to reduce environmental issues. Most of the research has been carried out to enhance the properties of the FDM-printed parts by inventing composite materials. As a result of this review, it was determined that bio-based polymer nanocomposite materials can be employed as a feedstock for FDM in two different methods. They are as follows: (1) bio-based polymers such as PLA, PHA, and PCL reinforced with metal, ceramic, and carbon nanoparticles as fillers; (2) reinforcement of bio-based materials such as lignin, cellulose, CNC from plum seed shells, carbon from coconut shell powder as fillers in polymers. Specifically, bio-based nanofillers play an important role in customizing the mechanical and thermal properties of filaments and printed parts through FDM. The reinforcement of the fillers at low percentages has been beneficial essentially for the stiffness and strength of bio-based nanocomposite filaments and also for the FDM-printed specimens. However, higher loading may lead to void formation which results in inferior mechanical abilities. Although numerous efforts were made to overcome the challenge of presence of voids, there has not been much progress in developing bio-based polymer nanocomposites. In addition to the void formation, the bio-based filler induced polymers suffer other challenges related to the processing of the material. Furthermore, the variables in processing parameters are unlimited and hence the quality of the products is thoroughly checked for morphology and distribution of the filaments as well as the printed parts. Nevertheless, using nanofillers can reduce some of the limitations that are related to the particle size while extruding the filament and can improve the thermomechanical properties of the printed products. However, there is a definite need for future investigation of polymer bio-based nanocomposites to understand the interrelation between material and the machine parameters to successfully modernize the pertinence of FDM.

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CONFLICT OF INTEREST

The authors do not have any conflicts of interest.

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