A review of recently developed polymer composite materials for fused deposition modeling 3D printing

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Abstract
Additive Manufacturing (AM) is a rapidly evolving technology due to its numerous advantages over traditional manufacturing processes. AM processable materials are limited and have poor mechanical performance, restraining the technology’s potential for functional part manufacturing. Although FDM is the most popular and growing technique, the inferiority of the material limits its application to prototyping. Nanocomposite material improves the thermal, mechanical, and electrical performance of FDM objects. Mostly polymer nanocomposites are feasible to process and several researchers have reported enhanced performance with polymer nanocomposites. Carbon nanotubes, graphene nanoplatelets, nano clay, and carbon fiber are primary reinforcements to thermoplastics. The current state of the art relevant to advances in nanocomposites for the FDM process, as well as the influence of nanofillers on mechanical properties of the build object are reviewed in this paper.

Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| AM            | Additive manufacturing |
| 3D            | Three dimensional |
| FDM           | Fused deposition modeling |
| SLA           | Stereolithography apparatus |
| SLS           | Selective laser sintering |
| EBM           | Electron beam melting |
| SLM           | Selective laser melting |
| LOM           | Laminated object manufacturing |
| Sic           | Silicon carbide |
| ZrO2          | Zirconium oxide |
| ABS           | Acrylonitrile butadiene styrene |
| PA            | Polyamide or nylon |
| PLA           | Polylactic acid |
| PBT           | Polybutylene terephthalate |
| PEI           | Polyetherimide |
| PEEK          | Polyether ether ketone |
| HDPE          | High density polyethylene |
| PP            | Polypropylene |
| TPU           | Thermoplastic polyurethane |
| PHA           | Polyhydroxy alkanoate |
1. Introduction

Additive Manufacturing (AM), more commonly known as 3D printing, is a new, fast-growing, most versatile, revolutionary technique and cluster of developing technologies through layer-by-layer addition on a single cross-section at a time, which fabricate complex structures and intricate components with minimal material waste, design freedom, and bulk customization [1–5]. When compared to conventional manufacturing technology, AM has garnered more interest from the manufacturing industry and academic communities. Various techniques of AM, such as fused deposition modelling (FDM) [6], stereolithography apparatus (SLA) [7], continuous liquid interface production [8], digital light processing [9], selective laser sintering (SLS) [10, 11], electron beam melting (EBM) [12, 13], selective laser melting (SLM) [14], laminated object manufacturing (LOM) [15, 16], and inkjet printing, are currently being developed. SLA and LOM have been utilized successfully to fabricate items from Sic [17] and ZrO2 [18]. Inkjet printing has extended applications to bio-printing which has recently drawn curiosity, it’s possible because of user-friendliness [19]. SLS has been employed in the processing of polymers [19]/polymer composites [20, 21], most notably PA12 [22–24], and carbon fiber reinforced PA12 [25]. The scarcity of processable materials hampered the development of SLS. In comparison to SLS, EBM and SLM have been used in a broader range of material systems, including alloys of titanium [26], copper matrix composites [27], and various metal powders [28, 29]. However, both the EBM and SLM equipment, as well as the powder ingredients, were prohibitively expensive.

Scott Crump invented an FDM 3D printer in the late 1980s, and Stratasys industrialized it in 1990 [30]. In the FDM method, the material is initially fed in the form of filament to the extrusion chamber, where it is heated and transformed to liquid form before being printed on the build platform using nozzles as shown in figure 1. Because of its ease of use, low cost, and environmental friendliness, FDM is now widely used in product development, prototyping, and manufacturing processes in a wide range of industries, including household appliances, automobiles [31], toys, architecture, medical appliances, aircraft, and aerospace. The limited mechanical characteristics of the 3D printed objects are one of the key constraints of FDM [32–34]. Such as the mechanical strength of FDM printed goods is typically lower than that of injection molded ones, due to weak regions between the layers [35]. Another barrier is the restricted availability of commercial filaments, which
limits the use of the FDM technique to produce complicated functional goods. FDM 3D printers often employ thermoplastics such as polyetherimide, ABS [36, 37], polycarbonate [38], polymethylmethacrylate, polybutylene terephthalate [39] polycaprolactone [5], nylon [30, 40], polypropylene [41], polylactic acid (PLA) [42], and their composites [43]. In order to improve mechanical characteristics inclusion of filler to the thermoplastic matrix is most common and effective. When the diameter of the filler particles is of the order of nanometre (~100 nm), the composite material is classified as nanocomposite [44, 45]. Mechanical, thermal, and physical characteristics of nanocomposite improved with the strong molecular interaction between polymer resin and nanofiller [46, 47]. Nanofillers can be of various forms such as particles, sheets, or fibers, these are carbon fiber, nano clay, carbon nanotube, graphene nanoplatelets, glass fiber, etc. At the moment, thermoplastic materials are the only options for the FDM technique. Nonetheless, the nanocomposite development allows for the expansion of the range of materials that can be processed, as long as the new material can be extruded in a filament form with required characteristics such as stiffness and flexibility [31].

Masood et al [30] first induced iron (Fe) particles in the nylon matrix to develop a novel composite for FDM for application in direct rapid tooling and injection molding tool inserts. Nikzad et al [48] used Fe and copper as the reinforcements for ABS which reported the high potential for direct application in rapid prototyping and functional part development. Similar results were also obtained by Singh et al [44] with Nylon and aluminum oxide composite for FDM. The flexibility of filament and mechanical performance improved significantly with the metallic fillers. Nanocomposite filament of ABS/titanium dioxide shows minor deterioration of ABS but has almost identical mechanical properties as ABS [45].

Polymer composites with discontinuous fibers also reported comparative performance than ceramics and metals [49]. Zhong et al [46] developed short glass fiber reinforced ABS composite and observed increased strength but decreased flexibility, which was enhanced by the inclusion of a stabilizer and a compatibilizer. ABS composite containing vapor grown carbon fiber (VGCF) [49, 50], carbon fiber [33, 51], exhibited good mechanical, thermal, and electrical characteristics, and with the increase of fiber length tensile properties increased. Short CF reinforced PP enhanced the flexural modulus and flexural strength by 400% and 150% respectively [52]. PLA with CF also improved the interfacial bonding strength and optimized printing parameters resulted in increased strength, tensile modulus, and flexural strength [53–55]. Plymill et al [56] developed an improved and sustainable feedstock material for FDM through reinforcement of PLA with graphene and MWCNT with 47% and 41% respective increase in tensile strength. Dul et al [57] also reported homogeneous and uniform dispersion for ABS/CNT nanocomposite with no evidence of agglomeration and porosity for various orientations, along with enhanced mechanical and thermal properties. Graphene also acts positive filler for conductive polymers and successfully developed filaments of GNP reinforced PA 12 [52], ABS [36], PLA [58] with better mechanical, thermal, and electrical properties. The incorporation of graphene/CNT hybrid biﬁlar into ABS was also used to improve the characteristics of FDM products [59]. Toyota first
confirmed the possibility of producing nanocomposite materials using nylon 6 and nano clay in the 1980s and reported the strength surged by more than 50% [60, 61]. The thermal characteristics of an ABS/montmorillonite nanocomposite were investigated by Wang et al [62]. They discovered that the intercalated-exfoliated structure was formed and that only 5% of the OMMT increased the thermal stability of ABS. Furthermore, Yeh et al [63] investigated the tensile strength of ABS/organoclay nanocomposites and observed that by adding only 3 wt. % organoclay, the tensile strength can be increased by 15%. This literature discusses similar development of advanced polymer nanocomposite materials, their processing difficulties, and the influence of nano filler on the performance of the 3D part, particularly mechanical performance. The objective of this review is to summarize all the polymer nanocomposites developed for the FDM technique.

2. Polymer/Carbon nanotube (CNT) nanocomposites

CNT is one of the best reinforcements for polymer material and this causes enhanced properties of the high-performance polymer [64–69]. CNT arises when the graphene sheet is rolled to generate a cylinder with half-spherical capped ends. In 1991 Iijima et al [70] invented MWCNT through the arc-discharge evaporation technique which consists of a co-axial array of CNT. SWCNT attracts each other to develop a rope kind of structure. CNT has good potential for research and industry applications because of preferably good mechanical, thermal and electrical properties, low density, low melt flow viscosity, and high aspect ratio [71–74]. Ajayan et al [75] developed nanocomposite by CNT reinforcement first time in the’90s. Nanocomposite enhances the mechanical, thermal, and electrical properties including thermal and electrical conductivity, tensile strength, toughness, and tensile modulus, etc [76–81]. Above the percolation threshold of nano filler, conductive path developed by filler particles [82]. Covalent carbon–carbon bond in the case of polymer highly improves strength and stiffness but proper dispersion is a concern because large surfaces of CNT can cause agglomeration [83–85].

2.1. ABS/CNT nanocomposite

MWCNT reinforced ABS nanocomposite up to 8 wt. % of filler, melt compounded, and extruded through twin screw extruder by Dorigato et al [81] for FDM printer to investigate mechanical, thermal, and electrical performance. Melt flow index (MFI) values have a sudden drop after 1 wt. % of MWCNT and there are difficulties in processing nanocomposites having higher MWCNT content than 4 wt. % due to very low MFI values, as shown in figure 2(d). Also, stiffness, yield stress, and elastic modulus increase, and fracture strain decrease due to the reduction of the cross-section of specimens because of the presence of voids. The thermal diffusivity of ABS with 6 wt. % MWCNT having horizontal concentric orientation was 55% higher than neat ABS printed by FDM. Various build orientations are shown in figures 2(a)–(c).

Afterward, Dul et al [57] verified nanofiller network formation causes a rapid decrement in MFI and increment in pressure and torque during the filament extrusion. Nanocomposite has no voids, no change in glass transition temperature, also dispersion was uniform and homogeneous for all the build orientations. The maximum increase in elastic modulus for 6 wt. % of CNT and there was a reduction at 8 wt. % of CNT (19%
The density has a linear increase with the CNT loading. Overall proven, CNT addition increases both tensile modulus, yield strength, thermal stability, and decreases creep compliance of all samples. Sezer et al. [86] reinforced MWCNT, in which nozzle clogging and brittle filament are the two major issues, among them nozzle clogging was due to MWCNT agglomeration [figure 3] due to this loading restricted up to 10 wt.%. The ultimate tensile strength for the [0°, 90°] raster pattern first decreases up to 40 MPa at 1 wt. % and then a predominant increase to 58 MPa at 7 wt.% loading, which is a 288% increase compared to neat ABS. The initial decrease was may be due to improper interfacial adhesion with the polymer. UTS for raster angle [−45°, 45°] remains almost unchanged for the MWCNT loadings of 1 wt. % and 3 wt. % compared to FDM printed blank ABS. [0°, 90°] layers showed an insignificant increase in young’s modulus at 1 wt%, but significant and linear increase with other loadings and for 10 wt.% 688% increases compared to blank ABS. The same trend is followed by [−45°, 45°] layers for young’s modulus but with lower values.

Figure 3. SEM of 10 wt. % MWCNT fractured tensile test specimen. Reprinted from [86], Copyright 2019, with permission from Elsevier.

Plymill et al. [56] developed the biodegradable and biocompatible PLA nanocomposite based on the GNP and MWCNT reinforcements. SEM micrographs reported almost similar fracture mechanisms in the cases, which meant that a new fracture mechanism was not developed due to the filler addition, also no clumping indicated homogeneous dispersion of filler. Generating filaments were visible distinctly, also a significant gap among them. Tensile test results have shown the maximum increase in mechanical properties with 0.2 wt. % GNP was 47% in UTS and 17% in elastic modulus as compared to neat PLA. MWCNT based samples have a maximum increase at 0.1 wt.% loading which was 41% in UTS and 26% in elastic modulus. The impact strength has the same trend as tensile strength and no significant improvement in crystallinity and thermal properties.

Ali et al. [88] reported minor agglomerates at 0.5 wt. % and 1 wt. % was the due to limit of melt compounding to achieve higher dispersion. Tensile strength and modulus of outcome product decrease with increasing layer thickness because the contact area of trans-raster bonding decreased [83]. A reduction of 50% in young’s modulus with the decrement in infill density from 80% to 40% while the trend was nonlinear with infill density. Honeycomb structure combines the load transfer characteristics of both [−45°, 45°] and [0°, 90°] infill patterns by having path elements being both angled and parallel to the loading axis which resulted to achieve tensile properties in between the two patterns mentioned above [0°, 90°] raster has a better elastic modulus and tensile
strength than \([-45^\circ, 45^\circ]\). Also, the honeycomb infill pattern can be an alternative to \([0^\circ, 90^\circ]\) to enhance the tensile properties.

### 2.3. Polybutylene terephthalate (PBT)/CNT nanocomposite

Gnanasekaran et al. [84] used non-conventional polymer PBT with fillers CNT and GNP for FDM to achieve mechanically robust and highly functional material. Results reported better mechanical and conductive properties of 3D printed PBT/CNT nanocomposite as compared to neat PBT. Along with this aesthetics and elastic behavior were also better. CNT and GNP have added in a very small volume fraction hence the effect of optimized printing parameters was insignificant. Successfully developed a new nanocomposite for the FDM printer to enhance the potential and material options for generating functional objects at a cheaper cost. Also demonstrated printing through multiple printing heads to print more than one filament material at the same instant.

### 2.4. Polyetherimide (PEI)/CNT nanocomposite

Kaynan et al. [85] indicated neat PEI has a smooth surface and sharp cracks are clearly visible which are due to uninterrupted breakage of filament. Rougher filament surface was visualized in the case of 5 and 7 wt. % CNT loadings. Overall homogeneous dispersion and good adhesion confirm the high compatibility of CNT with the PEI matrix. Tensile strength of neat PEI and 5 wt. % CNT PEI were almost the same, but significant decrease in elongation at break. Modulus, brittleness, and stiffness (55% increase) also increased significantly because of efficient interfacial strength, dispersion, and alignment of CNT. At higher temperatures, CNT amount has a significant effect such as weight loss of neat PEI, 5 and 7 wt. % CNTs reinforced PEI were 45%, 37%, and 36%, respectively at 800°C which shows CNT addition improves thermal stability as compared to neat PEI due to the physical barrier of CNT in the matrix.

### 2.5. Polyether ether ketone (PEEK)/CNT nanocomposite

Berretta et al. [89] observed that the UTS of modified FDM prints has a minor increase for 1 wt. % CNT but a substantial decrease for 5 wt. % CNT, which can be attributed to the addition of CNT causing the formation of porosity zones. The UTS of filament, single layer FDM to FDM printed tensile bar showed a declining trend, indicating that each step of processing reduces the tensile characteristics, similar results were achieved previously by Wu et al. [90] on pristine PEEK and ABS materials. The shear strength of PEEK and 1 wt. % CNT/PEEK is nearly the same, however, there is a decrease at 5 wt.% loading, which could be due to differences in surface properties between 1 wt.% and 5 wt.% during the melting process. Since 5 wt.% CNT is a significant proportion that contributes to the polymer’s increased viscosity, several studies have noted processing issues with 5% CNT [81]. Figure 4 shows the TEM images of 5% CNT filaments which indicates good dispersion of CNT in the PEEK but the outcomes on the FDM printed samples were opposite as tensile performance at this loading was worst as compared to other. This indicates that the performance of the final printed sample cannot be predicted by TEM images of filaments and printing parameters. Also, indicate AM process has a great influence on the properties of the final object.

Other researchers also worked on nanocomposite development for the FDM process that is collectively discussed and effect on the performance briefly mentioned in table 1.

### 3. Polymer/nano clay (NC) nanocomposite

Polymer-layered silicate nanocomposites enhance mechanical properties such as dynamic mechanical analysis [98], tensile [99], and flexural properties [100] compared to the pristine polymer. Montmorillonite (MMT) is a smectite clay with an octahedral alumina sheet sandwiched between two tetrahedral silicate sheets, forming a layer with a thickness of approx. 1 nm that is piled up by Vander wall forces as shown in figure 5. Alkyl Ammonium substitutes sodium as interlayer cations, increasing basal spacing and decreasing the inorganic host’s surface energy, promoting polymer wetting and improving interfacial interaction [100, 101]. NC is the most preferred reinforcement because of its ease of availability, cheaper cost, higher aspect ratio, cation exchangeability and can be surface treated with different surfactants [102]. The fire retardancy sector has the prime applications of clay-reinforced nanocomposites [103]. Sufficient increase in tensile strength, elastic modulus, and heat deflection temperature reported by many studies which drastically enhanced the domain of applications [104, 105].

#### 3.1. High density polyethylene (HDPE)/nano clay (NC) nanocomposite

Beeetty et al. [105] developed HDPE/NC nanocomposite, found a continuous reduction in MFI values and continuous increases in the density of filaments and prints with the filler addition, indicating dense and non-
porous prints. SEM micrographs post tensile fracture reported plastic deformation in neat HDPE print, however, nanocomposites print have brittle failure. Increase in elastic modulus for 5 wt. % NC print was 41.14%, demonstrated increased stiffness. UTS of the same was highest (16.9 MPa) and 22.46% higher as compared to neat HDPE print, the cause might be the large surface area of NC available for load distribution. UTS of prints was higher compared to their respective loaded filaments, indicating processing parameters and the process itself has a positive impact on the UTS. The experiment has shown good potential to replace some of the functional products manufactured by injection molding and compression molding.

3.2. ABS/nano clay nanocomposite

Weng et al [106] melt intercalated ABS with organically modified montmorillonite (OMMT) nano clay with twin-screw extruder and filaments of diameter 1.75 mm ± 0.1 mm preparation through a single screw extruder having three configurations of 1 wt. % (ABS1), 3 wt. % (ABS3) and 5wt. % (ABS 5) of OMMT. FDM print and injection molded samples of ABS 5 enhanced tensile strength by 43% and 28.9% respectively. OMMT filler improved mechanical properties such as tensile modulus (38.48% for ABS 5), flexural strength (33.33% for ABS 5), flexural modulus, and dynamic mechanical storage modulus. Also increase in linear shrinkage ratio, thermal stability, and decrease in elongation at break, caused by resistance to mobility due to filler addition. Tensile strength with strain plot shown in figure 6a, also tensile strength and modulus with concentration is shown in figure 6b.

Francis et al [107] showed a continuous increase of tensile and yield strength from 5 wt. % to 10 wt. % OMMT, but after that, there was a decrease, and elongation at break continuously reduces. Tensile, and yield strength were maximum for 10 wt. % and minimum for 15 wt. %. FDM printed 10 wt. % specimens reported 24.6% enhancement in compressive strength and 6.5% in hardness compared to neat ABS. There were two kinds of voids in nanocomposite print, one due to FDM however the next due to the entrapped gases evolved during filament preparation, but overall porosity was very less compared to neat ABS.

In further investigation Francis [108] emphasized on very low content, particularly .05%, .10% and .15wt. % NC, this restraint is caused by the brittleness of filament and difficulty in FDM printing. Optimized results reported by 0.10 wt. % filament sample hence fabricated, for this print UTS increased by 14.8%, but for hybrid parts, UTS was equal for longitudinal and boundary reinforced specimen, but less than ABS and for transverse reinforcement negative impact resulted. Elastic modulus increase for longitudinal, boundary, and transverse reinforcement was 147.8%, 94.8%, and 70% respectively over neat ABS. Compressive strength increased by 24%
Table 1. Summary of CNT reinforced polymer nanocomposites for FDM.

| S. no. | Matrix polymer | Nano-filler | Concentration [wt. %] | Effect on the performance / Remark | References |
|--------|----------------|-------------|------------------------|------------------------------------|------------|
| 1.     | PLA            | MWCNT       | 0.1 to 0.5             | 41% increase in UTS and 26% increase in elastic modulus with 0.1 wt.% MWCNT. The impact strength has the same trend as tensile strength. Insignificant thermal improvements. | [56]       |
| 2.     | ABS            | CNT         | 1 to 8                 | Enhanced yield strength and elastic modulus. Good electrical conductivity. Optimum wt.% suggested as 6 wt.%. | [57]       |
| 3.     | ABS            | CNT         | 6                      | 25% increase in elastic modulus. Slight increase in strength. | [59]       |
| 4.     | ABS            | CNT         | 1 to 8                 | Thermal diffusivity with 6 wt.% MWCNT increased by 55%. MFI resulted to be a resistance for higher filler addition. | [81]       |
| 5.     | ABS            | MWCNT       | 1 to 10                | Tensile strength increased by 288% with only 7 wt.% loadings. Ductile to brittle change of structure. | [86]       |
| 6.     | PLA            | MWCNT       | 0.1 to 1               | Increasing layer thickness decreases tensile strength and elastic modulus. Honeycomb pattern showed improved tensile performance. | [88]       |
| 7.     | PBT            | CNT         | —                      | Enhanced mechanical, conductive, and aesthetic properties. | [84]       |
| 8.     | PEI            | CNT         | Up to 7                | Significantly enhanced surface conductivity, 55% increase in stiffness and 35% reduced elongation at break. | [85]       |
| 9.     | PEEK           | CNT         | 1, 5                   | Porous zones due to CNT caused reduced tensile strength at higher loading. Uniform dispersion of CNT achieved. | [89]       |
| 10.    | UHMWPE         | MWCNT       | 2                      | Filaments have 62% and 114% respective increases in tensile strength and modulus. Strain hardening of filament causes a 15% increase in crystallinity. Solution spinning methodology was suggested to produce nanocomposite filament. | [91]       |
| 11.    | ABS            | MWCNT       | 15                     | Pure ABS filament coated with MWCNT increases 51% tensile strength and nanocomposite filament increases tensile strength by 25%. | [92]       |
| 12.    | ULTEM          | CNT         | 4.7                    | Improved mechanical properties and also electrical conductivity. Tensile strength increased by 25%. | [93]       |
| 13.    | ABS            | MWCNT       | 1                      | Significant increase in tensile strength, tensile modulus, and flexural modulus with very low concentration. Improved anisotropy. | [94]       |
| 14.    | TPU            | MWCNT       | 1 to 3                 | Good suitability for highly sensitive liquid sensors. Raster pattern change from linear to angled also enhances the sensitivity. Improved sensor sensitivity while decreasing infill density and MWCNT content. | [95]       |
| 15.    | ABS            | MWCNT       | 0.5 to 1               | 1 wt.% causes enhanced mechanical properties in tension and also electrical conductivity. Below that concentration mechanical performance deteriorates but electrical conductivity was still good. | [96]       |
| 16.    | ABS            | CNT         | 0.5 to 3               | 16% increase in elastic modulus with 3 wt.% MWCNT. | [97]       |
for ABS/NC compared to neat ABS but hybrid parts have shown very little increment, also elongation at break was minimum for hybrid parts.

3.3. Polylactic acid (PLA)/nano clay nanocomposite
Coppola et al [109] found intercalated/exfoliated morphology of filaments and nanocomposites of PLA/OMMT Closite 30B through x-ray diffraction, also no change in glass transition temperature of filaments with filler addition. The nucleating effect of nano clay was seen in the cold crystallization temperature as, it was lower for neat PLA than nanocomposite filament, which could be an indicator of an increase in crystallization temperature. Storage modulus also indicated better thermal stability of nanocomposite filament than neat PLA filament. Filament and print have similar morphology and the elastic modulus of printed nanocomposite was 15% higher than virgin PLA. Later, Coppola et al [110] showed the strong dependency of properties of the printed specimen on the nozzle temperature. Nozzle temperature 15 °C higher than the melting temperature caused higher elastic modulus of the printed nanocomposite.

3.4. Polypropylene (PP)/nano clay nanocomposite
Aumnate et al [111] introduced a novel filament of PP/Nano clay nanocomposite for FDM 3D printing. First-ever successful filament preparation by melt intercalation using a twin-screw extruder and also printed. The masterbatch method is used for the composite concentration. High shrinkage and warpage during printing which occurs due to semi-crystalline characteristics of PP are prevented by enhancing mechanical performance. PP/organoclay nanocomposites prepared in this study have mixed intercalated/exfoliated microstructure. A brief analysis of all the nanocomposites based on nanoclay for FDM is shown in table 2.
| S. no. | Matrix polymer | Nano-filler | Concentration [wt. %] | Effect on the performance/Remark | References |
|--------|----------------|-------------|------------------------|---------------------------------|------------|
| 1.     | HDPE           | NC          | 0.5, 1, 2, and 5       | UTS and elastic modulus increase by 41.14% and 22.46% for 5 wt.% content. Enhanced filament stiffness. | [105]      |
| 2.     | ABS            | OMMT        | 1, 3 and 5             | Tensile strength and elastic modulus increased by 43% and 200% respectively. | [106]      |
| 3.     | ABS            | OMMT        | 5, 10 and 15           | UTS increases from 5 wt.% to 10 wt.% after that it decreases. Elongation at break decreases continuously. | [107]      |
| 4.     | ABS            | NC          | 0.05, 0.10 and 0.5     | Reduction in voids. Average increments as 14.5% in tensile strength, 21% in modulus, 24% in compressive strength. | [108]      |
| 5.     | PLA            | OMMT        | 4                      | 15% increase in elastic modulus. Improved morphology and thermal stability of filaments. Better shape stability. | [109]      |
| 6.     | PP             | NC          | 3                      | Successful preparation of filament by the twin-screw extruder. | [111]      |
| 7.     | ABS            | OMMT        | 1, 3 and 5             | Filament modification approach for \textit{in situ} polymerization enhanced 10.8% tensile strength, 64% permittivity, and also thermal stability. | [112]      |
| 8.     | ABS            | OMMT        | —                      | Enhanced mechanical performance. Indicated good potential for microwave and radio frequency applications. 8.75% increase in elastic modulus. | [113]      |
| 9.     | ABS            | MMT         | 1                      | Improved mechanical properties. Flexural and tensile strength increases by 17.1% and 25.8% respectively. | [114]      |
4. Polymer/Carbon fiber (CF) composite

Carbon fiber stimulates polymer to accomplish good thermal and mechanical performances along with other benefits such as low cost and density, high aspect ratio, homogeneous dispersion ability \[115, 116\]. The thermoplastic matrix binds and protect the fibers and transfer the load to the fibers which support the load \[117–119\]. The melt mixing method of composite preparation is preferred due to its industrial-friendly nature and simplicity \[120, 121\]. High fiber loading, heat treatment, and surface treatment solely improve the mechanical characteristics of CF composites \[122, 123\]. Applications of CFRP are in the fuselage of Airbus A350 aircraft, automobile parts, wind turbine blades, and endoscopic surgery. As a result of their outstanding characteristics, CFRP has the potential to be an alternative to steel and thermosetting polymers \[124\]. Researchers are interested in developing new fabrication processes for CFRP, and additive manufacturing is one of such approaches.

4.1. ABS/CF composite

Shofner et al \[49\] developed vapor-grown carbon fiber (VGCF) composite through high shear rate Banbury mixing to achieve homogeneous and uniform dispersion without breaking of the fiber. The SEM before compounding shows tangled mass of VGCF and the SEM images of extruded filament indicate homogeneous dispersion, well-aligned fibers along the longitudinal direction, and also ABS surrounds the individual fibers and each fiber is isolated from others. Tensile strength of 10 wt.% VGCF print was 29% higher than the virgin polymer. Composite has average tensile strength and modulus, 37.4 MPa and 0.79 GPa respectively which were 39% and 60% higher than neat ABS specimen, also average 86% decrease in elongation at break.

Later, Shofner et al \[124\] employed the extrusion freeform fabrication (EFF) processing method for the ABS/VGCF composite which is a solid freeform fabrication (SFF) technique. ABS polymer having higher butadiene than the regular ABS, have higher toughness and pellets of VGCF was used, also compounding and extrusion process was similar to Shofner et al \[49\]. Isotropic fiber orientation, enhanced tensile strength, and elastic modulus were observed before the EFF processing. After EFF processing, composite had the same tensile strength and elastic modulus as virgin ABS, due to incomplete interlayer fusion and interlayer voids, despite the improved fiber orientation.

Tekinalp et al \[33\] found the FDM processing of short carbon fiber (0.2–0.4 mm) reinforced composite filaments improved mechanical performance, but also generated significant problems and compared the results with a compression molding (CM). Nozzle clogging was observed for some layers of 40 wt. %, below that content it was insignificant. Pristine ABS prints have higher tensile strength than CM sample (figure 7a), although found large gaps between beads but FDM enhance the molecular orientation which increased the tensile properties, this was earlier also reported in \[125\]. Tensile strength and modulus increased with the fiber content, fiber length, and orientation as also depicted in figure 7.

Ning et al \[51\] found tensile strength and elastic modulus increase initially, reaches a maximum, and then decrease and then again increase with the concentration of CF. Yield strength and toughness decrease with CF other than at 5 wt.% where an insignificant rise was observed then again it decreases to 10 wt.% then it starts to increase. Young’s modulus and tensile strength were higher for large fiber length and toughness, ductility higher for smaller fiber length, and also no significant influence of fiber length on yield strength. At 10 wt.% carbon
fiber, SEM micrographs in Figure 8 show fibers pulled out of the matrix, indicating increased porosity and weak interfacial bonding at higher concentrations.

4.2. Polypropylene (PP)/CF composite
Spoerk et al [52] found short CF content of 10 vol. % containing a stabilizer, a commercial compatibilizer with PP grafted with maleic anhydride has strong fiber-matrix adhesion, uniform filler dispersion, errorless filament extrusion, and printability. In the most optimistic orientation of fibers, modulus and flexural strength enhancement compared to PP was more than 400% and 150%, respectively. And for the most pessimistic orientation increase was 60% and 20% respectively. 10 vol.% CF content causes a 100% and 400% increase in filament yield stress and young’s modulus respectively and yield strain decrease to 50%.

4.3. Polyamide (PA)/CF composite
Liao et al [126] found for the FDM process CF preferentially aligned along the printing direction caused improved tensile, flexural properties without sacrificing impact strength and also increasing thermal conductivity. For FDM processed 10 wt.% CF anisotropic high-performance PA 12 composite specimen tensile and flexural strength increased by 102.2% and 251.1% respectively. The elongation at break has a sharp decrease from 192.1% to 8.1% due to an increase of defect density, indicating the change of nature from ductile to brittle. Impact strength decreases with the addition of CF, reaches a minimum at 2 wt.% CF then begins to increase, crosses the value of neat polymer at 10 wt.%. The initial decrease could be due to the stress concentration generated by CF at the end of the fiber. Further research on this can provide a composite with excellent properties and expand the applications of FDM.

Badini et al [127] examined the mechanical characteristics of PA6/CF composite with the modification of fiber orientation for FDM printing. Strength and stiffness in the fiber alignment direction were maximum and these properties were 60% lower in the perpendicular orientation indicating anisotropic mechanical nature. The inclusion of CF caused a decrease in ductility. Young modulus and tensile strength along the fiber direction were 9,906 MPa and 97.7 GPa, also these parameters increase with the increase in the strain rate.

4.4. PLA/CF composite
Tian et al [53] investigated the influence of temperature of liquefier, hatch spacing, and layer thickness on the flexural strength and flexural modulus of FDM prints of PLA/CF composite, also results are shown in Figure 9. The temperature of liquefier ranges from 200 °C–230 °C causes impregnation of polymer into the fiber bundle due to which flexural strength and modulus increase. An increase in hatch spacing from 0.4 mm to 1.8 mm, decreases the flexural strength from 335 MPa to 130 MPa, and also flexural modulus was reduced from 30 GPa to 6.26 GPa. An increase in layer thickness causes a sudden decrease in flexural strength, the maximum achieved flexural strength was 240 MPa for 0.3 mm layer thickness. After optimizing the three printing parameters with a fiber content of 27 wt.% maximum flexural strength of 335 MPa and flexural modulus of 30 GPa for FDM print was obtained.

Li et al [54] reported that the CF preprocessed with a PLA sizing agent will cause an increase in interfacial bonding strength between resin and fiber. As Yu et al [128] reported weak interfacial bonding, to fix this surface modification of carbon fiber bundle is performed which results in an increase in tensile and flexural strength of a composite by 13.8% and 164% than the untreated CF reinforced specimens. Compared to PLA, the storage...
modulus of modified carbon fiber reinforced samples and original fiber reinforced samples is higher about 166% and 351%, respectively.

Ferreira et al. [55] established that increase in tensile strength with the increase in CF content will be up to a limit, beyond that increase in CF content causes a reduction in the tensile strength to the value of pure thermoplastics. Uniform microstructure of FDM printed specimen with more than twice (2.2 times) tensile modulus and 1.16 times in-plane modulus of rigidity compared to pure PLA obtained. There is no significant effect on the tensile strength of the print with CF incorporation also ultimate load is mostly carried by matrix only, which indicates weak matrix fiber load transfer because of poor adhesion as earlier reported in [128]. Enhanced brittle nature obtained with CF addition as also depicted in [129]. Carbon fiber reinforced composites with an effect on various properties are summarized in table 3.

5. Polymer/Graphene nanocomposite

Recent studies have focused on graphene because of its unique characteristics. Graphene nanoplatelets are ultrathin particles made up of several graphene sheets placed together in a short stack [36]. Graphene nanoplatelets (GNPs) have a platelet morphology with a thickness ranging from 3 to 100 nm, are thought to be good reinforcing fillers for polymer-based composites due to their superior mechanical, thermal, and electrical properties, and also have the potential to large-scale manufacture at a low cost [137]. Physical techniques of synthesizing graphene-based nanocomposite can diminish their aspect ratio, lowering their reinforcing ability [138]. Exfoliation of graphene before the production of nanocomposite is also advantageous for improved performance [139].

5.1. ABS/GNP nanocomposite

Dul et al. [36] investigated FDM filament of ABS/GNP nanocomposite compounded through solvent-free melt compounding method. MFI decreases with GNP addition caused an increase in viscosity hence 4wt% GNP is taken as optimal content. Filler addition increases the elastic modulus while decreasing tensile strength and strain at break as shown in figure 10. Elastic modulus of horizontally oriented sample is less than CM because compaction pressure is applied only in CM, not applied in extrusion and FDM process.
Table 3. Summary of carbon fiber reinforced polymer composites for FDM.

| S. No. | Matrix polymer | Filler | Concentration [wt. %] | Effect on the performance / Remark | References |
|--------|----------------|--------|------------------------|-----------------------------------|------------|
| 1.     | PLA            | CF     | 10, 20, 30, 40         | Increase in tensile strength, elastic modulus, toughness was 80%, 200%, and 220%. | [33]       |
| 2.     | ABS            | VGCF   | Up to 10               | Increased tensile strength, modulus, and stiffness. Reduced elongation at break | [49]       |
| 3.     | ABS            | CF     | 3.5, 7.5, 10, 15       | 22.5% and 30.5% enhanced tensile strength and modulus respectively. 10 wt.% is the optimum concentration. | [51]       |
| 4.     | PLA            | Continuous CF | 27 | Temperature of liquefier improved flexural properties but hatch spacing and layer thickness deteriorate them. | [53]       |
| 5.     | PLA            | Short CF | 15 | 2.2 times increase in tensile modulus. Tensile strength decreases for both 0° and 90° print orientation. | [55]       |
| 6.     | PA 12          | CF     | 2, 4, 6, 8, 10         | Thermal conductivity, tensile strength, and flexural strength improved. Initially, stress concentration decreases impact strength. | [126]      |
| 7.     | PLA            | Continuous CF | 5 | Designed modified extruder for FDM printer. Enhance tensile (35%) and flexural strength (108%). Delamination was the cause of failure. | [130]      |
| 8.     | PLA            | Continuous CF | — | Novel methodology developed for FDM fabrication. CF showed better mechanical properties than jute fibers. | [131]      |
| 9.     | Nylon          | Continuous CF | 41 vol.% | Tensile and flexural strength of CF was better than GF reinforcement but hardness is better for GF. | [132]      |
| 10.    | Nylon          | CF     | —                      | CF increased 6.3 times tensile strength than pure nylon. Tensile strength sequence obtained as. Carbon fibre > Glass fibre > Kevlar fibre. | [133]      |
| 11.    | Nylon          | CF     | —                      | Dimensional accuracy and mechanical performance were investigated. Anisotropic mechanical properties. | [134]      |
| 12.    | PEEK           | CF     | 5                      | Good applicability for bone grafting. Tensile strength, tensile modulus, bending strength, bending modulus, and compressive modulus increase by 6.94, 13.52, and 25% respectively. | [135]      |
| 13.    | Nylon          | Short CF | — | Continuous CF has shown better tensile strength and stiffness than short CF. Continuous CF has limited control over the placement and causes porosity with intricate structure. | [136]      |
5.2. PA/GNP nanocomposite

Zhu et al. [140] found uniform dispersion of lower GNP contents but non-uniform dispersion even for the lower GNP content for larger size GNP particles. GNP content decreases the elongation at break and UTS but increases the elastic modulus and best mechanical performance for 0° raster angle. Elastic modulus and thermal conductivity for print were 7% and 51.4% higher, respectively with 0° orientation than CM specimen. There was a decrease in crystallinity of PA 12 with GNP which indicates better thermal conductivity, better accuracy, and better thermal stability. These results verified that the GNP incorporation can enhance the thermal conductivity of FDM print over CM which could further enhance the heat management.

Xi et al. [141] developed PA6/graphene composite for FDM through melt blending process and orthogonal tests were performed to evaluate the fabrication process. Nozzle temperature 245 °C, printing speed 27 mm s\(^{-1}\), the diameter of the nozzle 0.4 mm, and layer thickness 0.20 mm were the optimum process parameters. The graphene concentration, nozzle temperature, printing speed, and platform temperature are listed in decreasing order of influence on mechanical performance. FDM components with 0.05 wt.% graphene concentration resulted in the most high-grade mechanical performance.

5.3. PLA/GNP nanocomposite

Prashantha et al. [58] observed homogenous dispersion of GNP, good interlayer adhesion 3D printed part, GNP are well disseminated in the PLA matrix even at 10 wt.% content. GNP was able to build an interconnected filler network across the PLA matrix during 3D printing as it has a high population density and aspect ratio. The mechanical and thermomechanical properties of virgin PLA were improved and ductility degraded by the inclusion of GNPs. This paper described how FDM technology can be used to create a multifunctional biodegradable PLA matrix that is packed with conducting graphene nanoplatelets. These first findings suggest that PLA/GNP nanocomposite is a highly promising novel 3D printable biomaterial that merits further functional research, including tissue engineering, bioelectronics, and biosensors.

6. Other polymer composites

6.1. HDPE/Cenospheres composite

Patil et al. [142] utilized the most extensively used virgin high-density polyethylene (HDPE) polymer matrix granules and lightweight eco-friendly fly ash cenospheres as reinforcement with no surface treatment for FDM filament. MFI decreases with cenosphere content by 39.29, 60.54, and 70.51% for 20, 40, and 60 vol% respectively, the same trend documented in earlier literature [143, 144]. Cenospheres content increases the voids, developing them as good energy-absorbing material, also porosity observed only in foam filaments. Printed specimens have 78.86% higher tensile modulus and two-time fracture strength than injection molded ones. Flexural modulus has an increasing trend with cenosphere content and highest for 60 vol % composition that is 1.56 times higher than neat HDPE.

6.2. Polymer/Carbon Black composite

Zhang et al. [145] focused on the conductive ABS/ Carbon black composite FDM parts with variable structural features. The resistivity of printed samples of the composite was significantly higher(46.55% higher in the...
horizontal direction of the cube) than that of filaments. Resistivity in the horizontal direction is affected by an air gap and layer thickness while in the vertical direction it is affected by an air gap and raster width. The internal structure and resistivity of 3D printed objects are also influenced by process parameters.

Li and Sun et al [146] developed PA66/carbon powder (CP) composite filaments and the effect of printing parameters on the thermal deformation degree of the composite was investigated. There was an improvement in stiffness and a drop in thermal deformation with the incorporation of CP. The decrease in warpage and thermal deformation displacement of FDM print was 49.7% and 11.4% with 20 wt. % addition of CP compared to pure PA66. Also, the best performance was obtained with a 240 °C nozzle and 90 °C hot bed temperature.

### 6.3. Nylon/ Kevlar fiber composite

Dong et al [147] developed a Nylon/Kevlar fiber composite for FDM that enhanced the elastic modulus and tensile strength of the print up to 27 GPa and 333 MPa respectively for continuous fiber, also these increments were very poor in short fibers. The elastic modulus for the fiber perpendicular to the tensile force is only 0.84 GPa. The interlayer bonding between nylon and fiber was poor, and the elastic modulus was not particularly impacted by the position of the fiber, although it was preferred to have 5 layers of nylon on the surface of the component. Optimization of process parameters can be done by analyzing the bonding and flexural strength. The new procedure should be planned to more flexibly control the toolpath of the kevlar fiber so that the fiber orientation can be adjusted according to the principal stress.

### 6.4. ABS/micro-diamond composite

Waheed et al [148] developed a modified 3D printer in which steel gears are replaced by titanium gears to process micro-diamond reinforced filament to achieve high thermal conductivity. The composite was thermally conductive and electrically insulating as per the need of the electronics industry. Multiple extrusions are required to obtain homogeneous and uniform filaments having 37.5 and 60 wt. % synthetic micro diamonds reinforced ABS. A five-fold increase in thermal conductivity and an improvement of 32% in hydrophilicity compared to pure ABS. Elastic modulus improved from 1050 to 1490 MPa (41.9%) for 60 wt.% micro-diamond compared to pure ABS.

### 6.5. Polypropylene (PP)/Glass fiber composite

Carneiro et al[149] found adhesion between nearby filaments in the FDM part, obtained with varied printing orientations, however, the samples were stiffer in the filament direction, as expected. The mechanical characteristics were unaffected by layer thickness but the degree of infill has a notable and linear impact. When compared to samples produced by compression molding, the mechanical performance of printed samples suffers a 20%–30% loss, depending on the printing parameter values employed.

### 6.6. Polyamide blends

Jia and He et al[150] added maleic anhydride grafted poly (ethylene 1-octene) (POE-g-MAH) with PA6 to enhance toughness and avoid critical warpage for the FDM processing. The amorphous POE-g-MAH has good compatibility with PA6 and many short-chain branches, which caused a decrease in warpage. POE-g-MAH and poly styrene (PS) into PA6 resulted in reduced shrinkage stress due to the hindrance in regular molecular arrangement during cooling. As the PS weight increases the warpage degree of ternary blend decreases, which reduces to 1.06% with 20 wt.% loading. The flexural, impact, and tensile strength of PA6/POE-g-MAH/PS was improved to 24.1 ± 0.7 MPa, 31.5 ± 1.3 MPa, and 33.5 ± 1.2 kJ m−2, respectively. Overall, this study developed new scope to reduce the FDM processing issues for various applications.

Peng and He et al[151] blended PA6/polypropylene (PP) and maleic anhydride-grafted poly(ethylene-octene) (POE-g-MAH) employed as a modifier and compatibilizer. PA6/POE-g-MAH/PP alloy prints with 30 wt.% of PA6 and weight ratio of PP and POE-g-MAH of 1:5:1 has high mechanical performance and dimensional stability. The shape memory effect was most noticeable in 30% of PA6 FDM prints with 45° /−45° infill pattern, 100% infill density, and 175 °C deformation temperature. Polymer blend fabricated complex parts with thermally activated shape memory performance which is good for 4D printing and advanced applications.

### 6.7. Functionally gradient composites

Wang et al[152] fabricated thermoplastic functionally gradient composite parts (TFGCP) through multicomponent FDM printing and investigated thermal conductive properties. In this experiment polycaprolactone (PCL) was the matrix and aluminum nitride (AlN), boron nitride (BN) powders were the reinforcements to develop a functionally gradient composite. Notched impact strength increases with the small addition of AlN-30 and reaches highest at 20 wt.%. BN increases the brittleness and impact strength decreases suddenly after 40 wt.% loading. The thermal conductivity increases to 1.543 W/mk from 0.233 W/mk with 70
Table 4. Graphene and other reinforced polymer composites for FDM.

| S. no. | Matrix polymer | filler          | Concentration [wt. %] | Effect on the performance/Remark | References |
|--------|----------------|-----------------|------------------------|----------------------------------|------------|
| 1.     | ABS            | GNP             | 2,4,8                  | Improved elastic modulus and deteriorated tensile strength and strain at break. | [36]       |
| 2.     | Nylon          | Fe              | 30,40                  | Flexible feedstock filaments for producing functional parts and direct tooling on FDM machines. | [39]       |
| 3.     | PA 12          | GNP             | 2,4,6,8,10             | Improved elastic modulus and degraded UTS and strain at break. Lower crystallinity and enhanced thermal stability. | [40]       |
| 4.     | ABS            | Micro diamonds  | 37.5,60                | 60 wt. % of micro-diamond increased 41.9% elastic modulus compared to neat ABS. | [48]       |
| 5.     | PP             | GF              | 30                     | Mechanical performance was much better than neat PP. | [49]       |
| 6.     | TPU/PLA        | Graphene oxide  | TPU:PLA—7:3 GO—5:2,5  | Elastic modulus and tensile strength increase by 75.5% and 69.2%, respectively. Aided cell growth | [54]       |
| 7.     | Polyvinylidene fluoride | Zirconium tungstate | 1 to 10               | Good printability with low coefficient of thermal expansion and improved dimensional tolerances. | [55]       |
| 8.     | ABS            | Graphene oxide  | .02 to .06             | Tensile strength and stiffness increase. Maximum improved performance at .06 wt.%. 55% increase in toughness and strain at break was 29%. | [56]       |
| 9.     | HDPE           | Card board dust | 20 to 75%              | Diminshed plastic deformation. Increase damping capacity. Cheap structure. | [57]       |
Table 5. Mechanical and electrical characteristics variation with the fillers.

| Sample                     | Filler content | Tensile strength [Change%] | Elastic modulus [Change%] | Strain at break [Change%] | Electrical conductivity S/cm | References |
|----------------------------|----------------|-----------------------------|---------------------------|---------------------------|-------------------------------|------------|
| ABS/MWCNT                  | 7 wt.%         | +288%                       | —                         | —                         | —                             | [86]       |
| ABS/MWCNT                  | 10 wt.%        | —                           | +668%                     | −30%                      | 2.32 × 10−4                  | [86]       |
| PLA/MWCNT                  | 0.1 wt.%       | +41%                        | +26%                      | —                         | —                             | [56]       |
| PLA/Graphene               | 0.2 wt.%       | +47%                        | +17%                      | —                         | —                             | [56]       |
| ABS/GNP                    | 6 wt.%         | −1%                         | +38%                      | —                         | 1.9 × 10−15                  | [59]       |
| ABS/CNT                    | 6 wt.%         | +5%                         | +19%                      | —                         | 6.8 × 10−6                   | [59]       |
| ABS/GNP + CNT              | 6 wt.%         | −4%                         | +38%                      | —                         | 2.0 × 10−2                   | [59]       |
| PLA/r-GO                   | 6 wt.%         | +74%                        | +36%                      | —                         | 4.7 × 10−0                   | [158]      |
| PHA/f-MWCNT                | 1 wt.%         | +102%                       | +33%                      | —                         | 1.0 × 10−7                   | [159]      |
| PLA/GNP + CNT              | 12 wt.%        | —                           | −20%                      | —                         | —                             | [87]       |
| PLA/GNP + CNT              | 6 wt.%         | −21%                        | +46%                      | —                         | 2.2 × 10−3                   | [160]      |
| PEEK/GNP + CNT             | 7 wt.%         | −+2%                        | −+11%                     | —                         | −1.0 × 10−6                  | [161]      |
| ABS/CNT                    | 6 wt.%         | +8.5%                       | +22.37%                   | −85%                      | —                             | [108]      |
| ABS/MWCNT                  | 6 wt.%         | +11.23%                     | +23.54%                   | −15%                      | —                             | [81]       |
| ABS/Short carbon fiber     | 5 wt.%         | +22.5%                      | —                         | —                         | —                             | [51]       |
| ABS/Short carbon fiber     | 7.5 wt.%       | —                           | +30.5%                    | —                         | —                             | [51]       |
| ABS/Graphene               | 4 wt.%         | −7.5%                       | +52%                      | −28.6%                    | —                             | [36]       |
| ABS/VGCF                   | 10 wt.%        | +39%                        | +61.2%                    | —                         | —                             | [49]       |
| PP/GF                      | 30 wt.%        | +40%                        | +30%                      | —                         | —                             | [149]      |
| PP/GF                      | 30 wt.%        | +65%                        | +700%                     | —                         | —                             | [162]      |
| PLA/Tricalcium phosphate   | 2.5 wt.%       | +25%                        | +14.8%                    | —                         | —                             | [42]       |
| HDPE/Cenospheres           | 60 vol%        | −33.65%                     | +71.5%                    | −89%                      | —                             | [142]      |
| PLA/Short carbon fiber     | 15 wt.%        | −4.3%                       | +113%                     | —                         | —                             | [55]       |
| Polyamide 12/CF            | 10 wt.%        | +102.2%                     | +265.8%                   | −97.78%                   | —                             | [126]      |
| PLA/CF                     | 5 wt.%         | +22.5%                      | +30.5%                    | —                         | —                             | [51]       |
| ABS/Short carbon fiber     | 40 wt.%        | +115%                       | +700%                     | —                         | —                             | [33]       |
| ABS/OMMT                   | 5 wt.%         | +43%                        | +200%                     | —                         | —                             | [106]      |
| HDPE/NC                    | 5 wt.%         | +22.5%                      | +8.6%                     | −37.69%                   | —                             | [105]      |

* Relative percentage variation concerning the neat polymeric matrix.

wt.% AlN addition compared to pure PCL. Thermal conductivity of 50 wt.% BN was 2.463 W/mk and the thermal conductivity plot for BN was above the AlN plot. This research also found that the thermal conductivity depends on the orientation of fiber loading.

Zhang et al [153] analyzed functionally gradient composite (FGC) with variable gradients of fillers to develop the correlation between the structure and characteristics. Mechanical properties were analyzed as integral and found affected by loading direction. PCL composites have higher interlaminar shear strength and lower storage modulus as compared to pure polymer. Tensile strength increases with the upward gradient of filler, achieve peak, and then decrease. Tensile strength increases by 32.8% (PCL/AlN-30) and 39.1% (PCL/BN-30) compared to pure PCL. Overall, this study has built a foundation for potential applications in various domains for FGCs processed through FDM.

Other researchers have also attempted to develop composites for FDM filament with several modifications, these are mentioned in table 4. Comparative variation of diverse properties with various fillers and matrix was also illustrated in table 5.

7. Discussion and recommendations

Melt flow index restricts the increment in filler content insertion because this provokes an increase in viscosity of the material results difficulty in extrusion of filament. MFI and aspired performance are the fundamental determinants to optimize the percentage of filler content. Melt compounding with a higher shear rate through a twin-screw extruder reduces the agglomeration and achieves a homogeneous, uniform, and nonporous
structure of nanocomposite. Incorporation of any nanofiller will cause enhanced brittle nature due to which strain at break decrease in all nanocomposites.

ABS/MWCNT nanocomposite exhibits a maximum accretion in tensile strength of 288% with 7 wt. % filler and that is in elastic modulus was 788% with 10 wt.% filler, beyond 10 wt.% growth rate was slower. MWCNT causes an addition in density, thermal stability, aesthetics, and shrinkage in creep compliance, with extremely low loading insignificant advancement in thermal characteristics. Raster angle \([0^\circ, 90^\circ]\) has much better mechanical properties than \([-45^\circ, 45^\circ]\), also horizontal concentric orientation has better mechanical performance than vertical concentric orientation, registering mechanical anisotropy. Honeycomb pattern obtained to be an alternative of \([0^\circ, 90^\circ]\) raster to improve tensile properties, also bi-fillers contribute to deteriorating the performance of FDM part.NC provides a large surface area for load distribution, hence UTS improves with the filler inclusion, and the maximum increase in tensile strength and elastic modulus was 43% and 200%, respectively. Electrical conductivity increase was also encouraging as it improves 700% by CNT inclusion to ABS.NC composite FDM prints were dense, non-porous, and improved linear shrinkage ratio and thermal stability. Because of the FDM procedure and the entrapped gases, there are relatively few voids. The elastic modulus of hybrid reinforced components increases most for longitudinal reinforcement, then for boundary reinforcement, and least for transverse reinforcement. Nozzle temperature is recommended to be higher than the melting temperature to obtain attractive performance and the clogging was predominant after 40 wt.% inclusion of CF below that content it was insignificant. Fiber content, fiber length, and improved orientation result in enhanced tensile strength and modulus, still, out-of-plane performance was not good. Flexural performance increases with a rise in temperature of liquefier and decreases with an increase in hatch spacing and layer thickness. GNP aids to the elastic modulus improvement more than tensile strength. Thermal conductivity can increase more than CM specimen with GNP addition. Cenospheres reinforcement can develop lightweight high-performance materials for FDM.

8. Conclusions

This research paper, addressed the various polymer nanocomposite material recently developed and processed through fused deposition modeling. FDM method has already some restrictions for the polymers, and the processing of nanocomposites adds a few more major obstructions. Some of the key problems are nanoparticle agglomeration, an appropriate loading ratio, process parameter optimization, mechanical anisotropy, and accomplishing exfoliation. Trivial literature has been implemented to optimize the process parameters of nanocomposites processing through FDM. Nanocomposites of various conventional and non-conventional important thermoplastics were reported promising results in terms of improved characteristics which include mechanical, thermal, and electrical. Numerous additional exercises were also attempted such as filament alteration, twin nozzle extrusion, and post-processing techniques to ease the processing and advance performance. Even though most of the mechanical characteristics improve such as tensile, flexural, and shear properties but some decreases such as ductile nature, melt flow index, etc Heat management and electrical performance of the nanocomposites can upgrade as the demand in the application.

Nanocomposites have broadened the scope of FDM application in the fabrication of functional parts. An expansion in the number of compatible materials for the FDM technique will prompt the manufacturer’s ability to exhibit multifunctional products to nurture in the market. Overall, this review explored the novel polymer nanocomposite materials to expand the scope of materials for FDM and this range must magnify for prospective research.

9. Future research potential

This review article gathered information on innovative polymer nanocomposites for FDM, with an emphasis on mechanical performance. The author recognized certain analysis opportunities where researchers could concentrate their endeavors.

- Although most prior research has concentrated on quantifying the tensile features of FDM composites. Non-tensile attributes and failure/failure dynamics experiments are considered for the development of FDM components.
- Furthermore, understanding the interactions amid FDM methodology, component shape, and mechanical performance is required to enhance the mechanical performance of FDM parts.
• Moreover, FDM components have terrible out-of-plane/anisotropic performance because of weak interlayer bonding, exploratory research should be dedicated to improving characteristics in the perpendicular direction.

• Along with this, post-processing techniques, such as thermal treatment, surface finish, deliberate removal of supporting materials, etc can also contribute to multifunctional product manufacturing through FDM.

• Another issue is that no test standards have been developed for any of the AM processes; research should be directed in this regard as well to suit the performance better than traditional techniques.

• Strategically focused research should to performed with MWCNT reinforced polymers to explore the enormous potential to achieve improved mechanical properties.

• Processing conditions can be optimized through simulation and a modified printer can be developed so that the difficulties during fabrication of nanocomposites such as nozzle clogging can be minimized and enhanced performance can easily be achieved.

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