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3D-Printed Conductive Filaments Based on Carbon Nanostructures Embedded in a Polymer Matrix:

A Review

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ABSTRACT

Conductive and magnetic filaments are revolutionizing three-dimensional printing (3DP) to a new level. This review study presents the current state of the art on the subject, summarizing recent high impact studies about main advances regarding the application of 3DP filaments based on carbon nanostructures such as graphene, carbon fibers, nanotubes, and conductive carbon black embedded in a polymer matrix, by reviewing its main characteristics and showing the main producers and also the products available on the market. The availability of inexpensive, reliable, and electrically conductive material will be indispensable for the fabrication of circuits and sensors before the full potential of 3DP for customized products incorporating electrical elements can be fully explored.

KEYWORDS

Additive Manufacturing, Carbon Nanostructures, Conductive Filaments, Magnetic Filaments, Polymer Nanocomposites

INTRODUCTION

3DP is revolutionizing the world, computer designed objects fabricated using 3D-printers can be more complex than conventionally machined parts, such emergent manufacturing technology promises to boost the fabrication of highly sophisticated parts directly from computer-aided designs. Now it is possible to 3DP lightweight structures with high dimensional accuracy at lower cost for customized geometries (Chua & Leong 2016). Over the past few years, the intrinsic limitations of neat polymers, metals, and ceramics have propelled toward better alternative composite materials to enhance mechanical and other essential properties; nowadays 3DP research follows a similar direction from neat to composite material (Velu et al., 2019).

3DP filaments infused with carbon nanotubes such as graphene are now commercially available, with the promise to produce conductive and magnetic composites (Al-Hariri et al., 2016; Kwok et al., 2017).

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3DP utilizes different techniques for the manufacturing of prototypes, the main techniques include: inkjet printing (IJP); fused deposition modeling (FDM); fabrication with fused filament (FFF); powder-bed fusion (PBD); micro-stereolithography (MSL); dynamic optical projection stereolithography (DOPsL); direct-write assembly (DW); selective laser sintering (SLS); solvent-cast 3DP (SC-3DP); conformal 3DP (C-3DP); two-photon polymerization (TPP); UV-3DP; and stereolithography (SLA); among others (Farahani et al., 2016; Tian et al., 2016).

3DP of polymer nanocomposites (PNCs) with a relatively low amount of layered silicate fillers or conductive nanofillers, such as carbon nanotubes, graphene and metal particles are used to build objects with multifunctional properties having good electrical and thermal conductivity, mechanical strength, and stiffness at relative low cost (Postiglione et al., 2015; Francis & Jain 2016).

In conductive PNCs, the electrical conductivity is governed by electrical percolation, which requires a minimum filler content (volume fraction) to convert an insulating polymer matrix into a conductive composite (Alig et al., 2007). This minimum volume fraction of nanofillers, referred as percolation threshold, strongly depends on factors like, shape and size distribution of the nanofillers (Otten & Van Der Schoot 2009; Gnanasekaran et al., 2014), attractive interactions (Vigolog et al., 2005), and processing methods such as dispersion and agglomeration of nanofillers (Gnanasekaran et al., 2016).

Several studies have been reported on 3DP of conductive PNCs, based on conventionally used 3D printing polymers like poly lactic acid (PLA) and acrylonitrile butadiene styrene (ABS) (Tian et al., 2016; Guo et al., 2015; Rymansaib et al., 2016; Wei et al., 2015). However, the development of new conductive PNC materials for a desktop 3D printer is highly desirable to achieve better printability, mechanical properties and electrical conductivity (Gnanasekaran et al., 2017).

Inside this context, this review study present recent advances towards the application of 3DP technology using conductive and magnetic filaments based on carbon nanostructures embedded in polymer matrix, by showing its main characteristics and also summarizes the producer companies and products available in the market.

STATE-OF-THE-ART

Carbon Nanotubes (CNT)

CNT are known for their optimal mechanical, electrical and thermal properties, which makes them a suitable candidate to integrate 3DP polymers. Multiwall Carbon Nanotubes (MWCNTs) have structural defects which provide suitable nucleation sites allowing strong interactions with polymers (McCarthy et al., 2000) and for cross-linking and functionalization (Gao et al., 2013; Ventura et al., 2010).

A homogeneous dispersion CNT´s in polymeric solutions is essential for enhanced CNT based filaments. The familiar problem of CNTs aggregation can be detrimental to FDM, possibly causing blockages at the nozzle and flux instability while printing, so research has focused on determining the concentration of CNTs that would surpass the percolation threshold while maintaining the parameters for 3D printing (Al-Hariri et al., 2016).

Continuous CNT yarn filaments can be employed as an inherently multifunctional feedstock for 3DP, since it becomes possible to use a single material to impart multiple functionalities in components and take advantage of the tailor-ability offered by FFF over other conventional fabrication techniques (Gardner et al., 2016).

There is the possibility to tap into the electrical properties of CNTs in order to fabricate conductive composites using a standard commercial 3D-printer (Gonzalez et al., 2017). Lee et al. (2018) investigated the 3DP of nano-conductive MWCNTs scaffolds for nerve regeneration, by incorporating MWCNTs with PEGDA thereby enhancing electrical properties as well as nanofeatures on the surface of the scaffold. An SLA 3DP was employed to fabricate a well-dispersed MWCNT-hydrogel composite neural scaffold with a tunable porous structure. 3DP allowed the easy fabrication of complex 3D scaffolds with extremely intricate micro-architectures and controlled porosity.

Eshkalak et al. (2017) present a review on IJP of CNT composites for smart applications. IJP is emerging as an attractive technology for wide variety of industrial and scientific applications due to its mildness, simplicity, low-cost and scalability of production. It can perform as a carrier medium for number of filler materials and recently CNT ink has been utilized in inkjet printing. Outstanding characteristics of CNT´s and their reasonable price, has made this technology a good choice for various electronic applications such as sensors, transparent electrodes, flexible and printable electronics. One way of obtaining highly conductive patterns such as electric circuits is through the incorporation of conductive organic and metallic particles and also polymers into carbon nanotubes.

Graphene (Gr)

Since globalization has taken place, carbon (in different forms) has been considered a fundamental material in most of the three-dimensional (3D) / four-dimensional (4D) printing applications (Singh et al., 2018; Horst et al., 2018). Graphene is a highly expensive engineering material with remarkable mechanical/metallurgical/thermal/ and electrical properties. Some studies reported the production of low-cost Gr-reinforced polymer matrix-based feedstock filament for FDM applications (Singh & Kumar, 2018).

Graphene has risen in popularity as a material that would revolutionize electronics; fortunately, Gr has safely passed the peak of overestimated expectations and is now settling on some novel applications, due its interesting properties such as low resistivity, excellent thermal conductivity, optical transparency, and high electron mobility. Gr exhibits a range of exceptional qualities including flexibility and conductivity. 3DP filaments augmented with Gr have the potential to enhance the manufacturing process of strong conductive composites. There are many applications of these carbon nanostructured additives in 3DP filaments including sensors, trackpads, electromagnetic, and RF shielding (Al-Hariri et al., 2016).

3D-Gr-based architectures such as Gr-based hydrogels, aerogels, foams, and sponges have attracted huge attention owing to the combination of the structural interconnectivities and the outstanding properties of Gr offering interesting structures with low density, high porosity, large surface area, stable mechanical properties, fast mass and optimal electron transport. Being extensively studied for a wide range of applications including capacitors, batteries, sensors, catalysts, etc. (Yang et al., 2015).

Over the last decade, a great deal of research has been devoted to the design and development of Gr-based polymer nanocomposites characterized by a prescribed arrangement of the graphene-based nanosheets into spatially segregated 3D architectures. The formation of a continuous filler network obtained by confining the nanosheets into a constrained volume of the polymeric matrix is particularly attractive from a technological point of view. Indeed, the realization of segregated 3D-Gr-based architectures allows to properly tailor the overall performances of the resulting polymer nanocomposites, providing significant improvements in terms of structural and functional features (Salzano et al., 2018).

Cardoso et al. (2018) investigated potential applications of low-cost fused deposition modeling 3D-printers to fabricate multiuse 3D-printed electrochemical cells for flow or batch measurements as well as the 3DP of electrochemical sensing platforms. The authors successfully 3DP electrochemical cells and sensors using acrylonitrile butadiene styrene (ABS) and conductive graphene-doped polylactic acid (G-PLA) filaments.

Huang et al. (2019) studied a graphene-based elastomer for sensors with tunable and high sensitivity was fabricated by using three-dimensional printing, in which a printable ink was developed by homogenizing graphene and polydimethylsiloxane (PDMS). To make the elastomer tunable and highly sensitive, different microstructures Gr-PDMS can be formed. The controllable design and scalable fabrication of the advanced functional material suggests that tunable strain sensors and wearable devices have great potential for different applications, which is a finding that can be referenced by future studies on 3D-Gr based sensors.

The manufacturing 3D-Gr monolith with high mechanical and electrical performance has become an urgent issue in view of their potential applications in energy and electronics fields. Due to the structure rigidity and poor liquid-phase processing capability of graphene sheets, it is challenging to fabricate 3D-Gr monolith with high mechanical performance, including strength, toughness and resiliency. Ma et al. (2019) demonstrate a strategy to fabricate high-performance; shape-designable 3D-Gr monolith through a 3DP method based on large-sized graphene oxide (LGO) fluid ink. The resulting monolith exhibits low density (12.8 mg/cm^3), high electrical conductivity (41.1 S/m), high specific strength (10.7×10^3 N·m/Kg) and compressibility (up to 80% compressive strain). Such a 3DP technique enables to achieve complicated monolith structures and broadens the application range of graphene.

Mohan et al. (2018) demonstrate the development of novel highly conductive 3D-printable hybrid polymer-graphene composites. The key factors identified have included the polarity of the primary polymer, the level of homogeneity of the dispersion of the conductive filler materials and the crystallinity of the resulting composite which in this case is increased by the addition of sucrose. Optimizing for these factors the production method has been able to manufacture samples with an electrical conductivity of up to 14.2 S.cm^{-1} at filler loading of 10 wt. % graphene and 10 wt. % conductive polymer in the base polymethyl methacrylate matrix. These have been investigated for application in 3DP as an alternative to wiring or expensive printable conductive inks, and successful samples have been produced with an electrical conductivity of 11.3 S.cm^{-1}.

Huang et al. (2018) demonstrated a novel strategy to prepare printable graphene ink is reported first, and three-dimensional scaffolds with high content (50 wt %) and aligned graphene are achieved by three-dimensional printing. From results adequate shear thinning and rheology behavior are required for printable graphene ink to flow through the nozzle smoothly and self-support during the printing process. The scaffolds with different contents and printing parameters exhibit good resolution and good bonding between layers. The alignment of graphene sheets along the direction of flowing can be observed due to the shear stress in the nozzle. When the temperature rises up to 450 °C, electrical conductivities along transvers and longitudinal directions of 50 wt % are enhanced to 479.2 and 425.6 S/m, which are 6.7 and 8.4 times higher than that at room temperature, respectively. The alignment can contribute to the electrical anisotropy of three-dimensional graphene scaffolds. The electrical resistance variations under compression and electrical anisotropy demonstrate the potential application of the graphene scaffolds in electrical device, sensor, especially combined with 3DP.

Azhari et al. (2017) introduce a powder-bed technique for the fabrication of crack-free, mm-thick graphene-based electrodes, with high surface area that can be printed in complex shapes. While this technology has the potential to be used in many applications including energy storage, conversion, and sensing. In his work, they demonstrate their use as high performance supercapacitors. From results, devices fabricated using thermally exfoliated graphene oxide powder had gravimetric and areal capacitance of ~260 F g^{-1} and ~700 mF cm^{-2}, respectively at 5 mV s^{-1} in 1 M H_2SO_4 electrolyte. The supercapacitors retained 80% of their capacity over 1000 cycles. This technique provides a promising route for the fabrication and commercialization of thick, porous graphene-based devices.

Carbon Black (CB)

Dawoud et al. (2018) studied the strain sensing behavior of 3D-printed of CB filled with ABS (CB-ABS). Experimental work revealed that internal stresses can be detected based on monitoring the change in resistance as a response to strain. The functionalized composite can be used as a strain sensor as for health monitoring purposes, to give an example.

Jayanth & Senthil (2019) also studied CB-ABS filaments for the 3DP of low-cost concave capacitive sensor used to measure the void fraction of two-phase flow. The variation in capacitance values of 3DP sensor was found to be less when compared to a copper sensor, but still measurable, the capacitance value increases with an increase in width and thickness of the 3DP CB-ABS sensor.

Flowers et al. (2017) described the use of dual-material fused filament fabrication for 3DP of electronic components and circuits with conductive thermoplastic filaments. The resistivity of traces printed from conductive thermoplastic filaments made with carbon-black, graphene, and copper as conductive fillers was found to be 12, 0.78, and 0.014 Ω cm, respectively, enabling the creation of resistors with values spanning 3 orders of magnitude. The carbon black and graphene filaments were brittle and fractured easily, but the copper-based filament could be bent at least 500 times with little change in its resistance. Impedance measurements made on the thermoplastic filaments demonstrate that the copper-based filament had an impedance similar to a copper PCB trace at frequencies greater than 1 MHz. Dual 3DP material was used to fabricate a variety of inductors and capacitors with properties that could be predictably tuned by modifying either the geometry of the components, or the materials used to fabricate the components. These resistors, capacitors, and inductors were combined to create a fully 3D-printed high-pass filter with properties comparable to its conventional counterparts. The relatively low impedance of the copper-based filament enabled its use for 3DP of a receiver coil for wireless power transfer. The potential of using FFF to create complex circuits composed of either embedded or fully-printed electronic components is showed.

Carbon Fibers (CF)

Li et al. (2016) investigated the continuous CF´s reinforced with PLA (CF-PLA). The experimental results demonstrated that the tensile strength and flexural strengths of modified carbon fiber reinforced composites were 13.8% and 164% higher than original carbon fiber reinforced samples.

Zhu et al. (2018) developed a novel method to fabricate carbon fiber reinforced SiC (CF/SiC) composites by combining 3DP and liquid silicon infiltration process. Green parts are firstly fabricated through 3DP from a starting phenolic resin coated carbon fiber composite powder; then the green parts are subjected to vacuum resin infiltration and pyrolysis successively to generate carbon fiber/carbon (CF/C) preforms; finally, the Cf/C preforms are infiltrated with liquid silicon to obtain CF/SiC composites. From results, the 3DP processing parameters show significant effects on the physical properties of the green parts and also the resultant CF/C preforms, consequently greatly affecting the microstructures and mechanical performances of the final CF/SiC composites. The overall linear shrinkage of the CF/SiC composites is less than 3%, and the maximum density, flexural strength and fracture toughness are 2.83 ± 0.03 g/cm3, 249 ± 17.0 MPa and 3.48 ± 0.24 MPa m1/2, respectively. It demonstrates the capability of making near net-shape Cf/SiC composite parts with complex structures.

Conductive silicon rubbers (CSRs) are potential candidates for strain sensor application owing to their specific electrical response and superior mechanical flexibility. Huang et al. (2018) studied carbon fiber-filled CSRs printed by an extrusion device. Thixotropic agent was added to modify mobility and viscosity of the liquid CSR. It was found that the CSR with 5 wt% thixotropic agent addition exhibited better shape-retention. Fibers in matrix were observed to be oriented in the printing direction resulting in an anisotropic electrical and mechanical behavior. The printed CSRs showed better electrical and mechanical properties along the orientation direction of fibers. In particular, the volume resistivity at the orientation direction was 6.8 times lower than that at perpendicular direction. Higher tensile strength, larger elongation at break, and higher Young’s modulus were found along the orientation direction when the printed CSRs were stretched, where a large number of fibers were pulled out and visible holes remained at the fractured surface. Electrical responses of the CSRs under various loadings, including stretching, compressing, bending, twisting and cyclic folding, were closely related with deformations of the CSRs. Sandwich strain sensors were finally fabricated to verify a practical application as motion sensor of the printed CSRs.

Hao et al. (2018) studied a continuous carbon-fiber reinforced thermosetting composites prepared using 3DP followed by characterization of their mechanical properties. First, a 3DP platform was fabricated to prepare the composites based on FDM. Then, the composites lamina and grids were manufactured using an FDM-based platform, and then the mechanical properties of the composite lamina were characterized. The results showed that the mechanical performance of the 3D-printed thermosetting composites was superior to that of similar 3D-printed thermoplastic composites and 3D-printed short carbon fiber reinforced composites.

Yao et al. (2017) presented a technique for both structural reinforcement and self-monitoring of thermoplastic parts manufactured by FDM. Continuous carbon fiber tows were embedded into FDM printed structures during the printing process, and the strength and piezoresistive behavior of the printed structures were evaluated. The specimens reinforced with Cf showed a strength increase of 70% and flexural strength increase of 18.7% compared to non-reinforced specimens. In addition, the slope of fractional change in electric resistance with strain became a good indicator of strain measurement within the elastic region and damage detection in the yield region. Furthermore, lightweight and print duration reductions were achieved by decreasing the fill density while maintaining the structural strength, where up to 26.01% weight reduction and 11.41% print time reductions were achieved without decreasing the tensile strength.

Caminero et al. (2018) investigated the impact damage resistance of 3D-printed continuous fiber reinforced thermoplastic composites using fused deposition modeling. It was observed that the effect of layer thickness of nylon samples on the impact performance was different for flat and on-edge samples. Impact strength increases as layer thickness increases in flat samples but, conversely, it decreases in on-edge samples, depicting a more brittle fracture. In addition, the results show that impact strength increases as fiber volume content increases in most cases. Glass fiber reinforced samples exhibits the highest impact strength and carbon fiber reinforced samples the lowest one and similar to nylon performance. Furthermore, on-edge reinforced samples exhibit higher values of impact strength than flat reinforced samples. The impact strength exhibited by 3D-printed composites is significantly higher than the usual 3D-printed thermoplastics and, in some cases, even better than common pre-preg. materials.

The increasing need for prototyping and customization of fiber reinforced polymer composite parts is prompting innovations in new manufacturing processes to realize short manufacturing cycle time and low production cost, which is challenging to accomplish using conventional molding process. Goh et al. (2018) made a comparison of fracture behaviors between 3D-printed carbon and glass fiber reinforced composites is performed. The FFF technique was employed to fabricate continuous carbon and glass FRTP composites and its microstructural characteristics and the resulting tensile, flexural, and quasi-static indentation characteristics of the printed composites were examined.

Blok et al. (2018) investigated the 3DP of fiber reinforced thermoplastic composites. Carbon fibers were embedded into a thermoplastic matrix to increase strength and stiffness. From results, the printing of continuous carbon fibers using the MarkOne printer gives significant increases in performance over unreinforced thermoplastics, with mechanical properties in the same order of magnitude of typical unidirectional epoxy matrix composites. The method, however, is limited in design freedom as the brittle continuous carbon fibers cannot be deposited freely through small steering radii and sharp angles. Filaments with embedded short carbon microfibers (~100 μm) show better print capabilities and are suitable for use with standard printing methods, but only offer a slight increase in mechanical properties over the pure thermoplastic properties. It is hypothesized that increasing the fiber length in short fiber filament is expected to lead to increased mechanical properties, potentially approaching those of continuous fiber composites, whilst keeping the high degree of design freedom of the FFF process.

Tian et al. (2016) investigated a novel 3DP based fabrication process of Continuous Fiber Reinforced Thermoplastic Composites (CFRTPCs). Continuous CF-PLA filament were utilized as reinforcing phase and matrix, respectively, and simultaneously fed into the FDM process realizing the integrated preparation and forming of CFRTPCs. Interfaces and performance of printed composites were systematically studied by analyzing the influencing of process parameters on the temperature and pressure in the process. Forming mechanism of multiple interfaces was proposed and utilized to explain the correlations between process and performance. The fiber content of the printed specimens can be easily controlled by changing the process parameters. When the fiber content reached 27%, flexural strength of 335 MPa and modulus of 30 GPa were obtained for the printed composite specimens. Composite components fabricated demonstrated the process feasibility, potential applications could be found in the field of aviation and aerospace.

Other Polymer Nanocomposites (PNCs)

Dickson et al. (2017) evaluated the performance of continuous carbon, Kevlar and glass fiber reinforced composites manufactured using FDM technique. It was demonstrated that among the fibers investigated, those fabricated using carbon fiber yielded the largest increase in mechanical strength per fiber volume. Its tensile strength values were up to 6.3 times higher than those obtained with the non-reinforced nylon polymer. As the carbon and glass fiber volume fraction increased so too did the level of air inclusion in the composite matrix, which impacted on mechanical performance. As a result, a maximum efficiency in tensile strength was observed in glass specimen as fiber content approached 22.5%, with higher fiber contents (up to 33%), yielding only minor increases in strength.

Kwok et al. (2017) described the fabrication, characterization, stress testing, and application of a low-cost thermoplastic conductive composite that has been processed into filament form for 3DP.

Sanatgar et al. (2017) investigated a novel printing process for deposition of polymers on synthetic fabrics to introduce more flexible, resource-efficient and cost-effective textile functionalization processes than conventional printing process like screen and inkjet printing. The polymers were printed in different series of experimental design: nylon on polyamide 66 (PA66) fabrics, polylactic acid (PLA) on PA66 fabric, PLA on PLA fabric, and finally nanosize carbon black/PLA (CB/PLA) and multi-wall carbon nanotubes/PLA (CNT/PLA) nanocomposites on PLA fabrics. Tekinalp et al. (2014) researched short fiber (0.2–0.4 mm) reinforced acrylonitrile–butadiene–styrene composites as a feedstock for 3D-printing in terms of their processability, microstructure and mechanical performance. The additive components were compared with traditional compression molded composites.

Sweeney et al. (2017) studied the welding of 3D-printed carbon nanotube–polymer composites by locally induced microwave heating. A key obstacle facing 3D-printed plastic parts in engineering applications is the weak weld between successive filament traces, which often leads to delamination and mechanical failure. The results showed after printing, microwave irradiation is shown to improve the weld fracture strength by 275%.

Hu et al. (2018) analyzed the 3DP of graphene-aluminum nanocomposites. From results, the Vickers hardness and nano-indentation tests showed that the hardness of the composites was greatly enhanced. Compared with pure aluminum counterpart, the Vickers hardness of the best composite sample achieves a 75.3% increase. The experimental results suggest the efficacy of laser 3DP technology to fabricate Gr-Al composites.

Kim et al. (2017) evaluated the 3DP of multiaxial force sensors using carbon nanotube (CNT)/thermoplastic polyurethane (TPU) nanocomposite filaments. Due its customizability, rapid manufacturing, and economic feasibility, this manufacturing approach allows direct fabrication of multiaxial sensors without additional assembly or integration processes.

Kim et al. (2018) studied the effect of FDM 3DP on three phase dielectric nanocomposites using poly(vinylidene) fluoride (PVDF), $BaTiO_3$ (BT), and multiwall carbon nanotubes (CNTs). PVDF polymer and BT ceramics are piezo-, pyro- and di-electric materials extensively used for sensor and energy storage/harvesting applications due to their unique characteristic of dipole polarization. To increase dielectric property, CNTs have been recently utilized for uniform dispersion of BT nanoparticles, ultrahigh polarization density, and local micro-capacitor among matrix. It was proved that 3DP process provides homogeneous dispersion of nanoparticles, alleviating agglomeration of nanoparticles and reducing micro-crack/voids in matrix which can potentially enhance their dielectric property than traditional methods.

Mu et al. (2017) DLP of conductive complex structures. A DLP based 3DP technique was explored to manufacture electrically conductive objects of polymer nanocomposites. The concentrations of MWCNT as well as the printing parameters were investigated to yield optimal conductivity and printing quality. Results showed that 0.3 wt% loading of MWCNT in the resin matrix can provide the maximum electrical conductivity of 0.027S/m under the resin viscosity limit that allows high printing quality. With electric conductivity, the printed MWCNT nanocomposites can be used as smart materials and structures with strain sensitivity and shape memory effect. The printed conductive complex structures as hollow capacitive sensor, electrically activated shape memory composites, stretchable circuits, shows the versatility of DLP 3DP for conductive complex structures. In addition, mechanical tests showed that the addition of MWCNT could slightly increase the modulus and ultimate tensile stress while decreasing slightly the ultimate stretch, indicating that the new functionality is not obtained at the price of sacrificing mechanical properties.

He et al. (2016) demonstrated that printing a conductive ink formulated by blending 3D porous Gr-CNT assembly with ionic liquid (IL) on two-dimensional 2D graphene paper, leading to a freestanding GP supported graphene–CNT–IL nanocomposite (graphene–CNT–IL/GP). The incorporation of highly conductive CNTs into graphene assembly effectively increases its surface area and improves its electrical and mechanical properties. The graphene–CNT–IL/GP, as freestanding and flexible substrates, allows for efficient loading of PtAu alloy nanoparticles by means of ultrasonic-electrochemical deposition. Owing to the synergistic effect of PtAu alloy nanoparticles, 3D porous graphene–CNT scaffold, IL binder and 2D flexible GP substrate, the resultant lightweight nanohybrid paper electrode exhibits excellent sensing performances in nonenzymatic electrochemical detection of glucose in terms of sensitivity, selectivity, reproducibility and mechanical properties.

Zhong et al. (2017) studied the extrusion based on 3DP of graphene oxide (GO)/geopolymer (GOGP) nanocomposite. The addition of GO in geopolymeric aqueous mixture (alumiosilicate and alkaline-source particles) dramatically changes its rheology properties, and enable the 3DP that cannot be realized solely by geopolymer. The 3DPGOGP structures exhibited high mechanical properties with compressive strength higher than 30 MPa, and electrical conductivity of 102 S/m was achieved after annealing, which is among the highest conductive ceramic nanocomposites.

Commercial Filaments Available for 3DP

Table 1 presents a list of the main commercial producers of 3DP filaments based on carbon nanostructures embedded in polymer matrix:

3DP is a layer-by-layer process having the ability to fabricate sensors and circuits by depositing conductive and magnetic filaments to build electronic components via digital control. 3DP is revolutionizing the world; mainly because computer designed objects fabricated using 3D printers can be more complex than conventional machined parts. This niche of technology seems to be a transformative tool with more flexibility for 3DP, since conductive and magnetic filaments present a new chapter in 3DP having gained current vast interest as it offers significant advantages over the traditional materials. Advances in technologies related to carbon nanostructures embedded in polymer matrix will lead to design novel 3DP materials with specific advantages. 3DP potentially offers a high degree of freedom for the customization of practical products that incorporate electrical components. The availability of inexpensive, reliable, electrically conductive material will be indispensable in the fabrication of circuits and sensors before the full potential of 3DP for customized products incorporating electrical elements can be fully explored.

CONCLUSION

This review study summarizes the current state of the art concerning the 3DP of conductive and magnetic filaments based on carbon nanostructures aiming the potential application of these materials. Currently there is a wide range of commercially available filaments and this number will increase by

Table 1. 3DP filaments based on polymer nanocomposites

Company	Product	Material	Extruder Temp (C°)	Platform Temp (C°)
3DXTech	Carbon X	PEEK, Ultem, PC, Nylon, PETG, ABS, PLA	380°- 410°C 360 - 390°C 280 - 310°C 240 - 270°C 230-260°C 220-240°C 190-220°C.	130 - 150 ° C 140 - 160°C 110-120°C 80 - 100°C 70 a 90 ° C 100-110°C 23 - 60°C
Functionalize	F-Electric	PLA	215-230 ° C	X<70°C
Filabot	MWCNT1 Graphite Infused Filament	Nanotube Pellets ABS Based	160-180°C 225-235°C	80-100°C 100-110°C
BlackMagic3D	Conductive Thermoplastic Graphene G6-Impact	PlA PELLETS HIPS-Carbon	210-230°C 210-230°C	60-80°C 60-80°C
Angstron Materials	Graphene Enhanced Nanocomposites	PP, PC, ABS	not available	not available
Cheap Tubes Inc	Carbon nanotube Master batches Conductive nanotubes Composite Industrial Grade Multi Walled	CNT-PA6-15, CNT-PC-10, CNT-ABS-10, CNT-PP-20, CNT-PP-15, Carbon nanotubes	not available	not available
Nanocyl	Plasticyl MWCNTS	PA1501, PA1502, PA1503, HDPE1501, POM1001, TPU1001, PP2001, PC1501, ABS1501, EVA2001, LDPE2001, PEEK1001, HIPS1001, PTB1501, SEBS1001, PETG1001	not available	not available
Zyvex Technologies	ZNT (Zyvex nanotube technology) Epovex Adhesive	Polymer modified carbon nanotube additive Carbon nanotube-enhanced two-part epoxy adhesives	not available	not available
Vartega	Vartega Recycled Carbon Fiber	ABS, PA6, PA66, PBT, PC, PE, PEI, PEEK, PEK, POM, PP, PPS, PSU, PU	not available	not available
Advanc3D	AdWire Premium	PLA	not available	not available
Avante Technology	FilaOne Grey	FilaOne	205 – 210°C	
Stratasys	FDM PC	Nylon ABS	not available	not available

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Table 1. Continued

Company	Product	Material	Extruder Temp (C°)	Platform Temp (C°)
Innofil3D	Innoflex 40, 45, 60	Thermoplastic Copolyester Elastomer (TPC)	230-250°C not available	0-30°C not available
Formfutura	CarbonFil	PETG	230 - 265°C	0 - 60° C
Ziro	Carbon Fiber Filament Conductive Filament	PLA ABS	210-240°C 210-250°C	do not need 100-110°C
Proto-pasta	Electrically Conductive Carbon Fiber	PLA HTPLA, PLA	210-250°C 210-230°C	do not need do not need
Matterhackers	NylonX PRO Series Carbon ColorFabb XT-CF20 Carbon Fiber Reinforced	Nylon PETG PLA PLA PLA	250-265°C 240- 260°C 185-205°C 240-260°C 190-210°C	60-65°C 60-70°C do not need 70-90°C do not need
Yasin3D	Spool Conductiv Carbon Fiber Light Weight Carbon	ABS ABS, PLA ABS	200-260	do not need
Hawkvine	Carbon Fiber	PLA, ABS, PETG, Nylon	210-240°C 210-240°C	50°C 50°C
Haydale	Graphene-enhanced	PLA	200-210°C	58°C
Atomic Filament	Carbon Fiber Extreme Carbon Fiber Ultra	PLA, PETG ABS	190-230°C 240-265°C 235-255°C	not available
Sunlu	Super Sept Conductive high strength	ABS PLA, ABS PLA	190-220°C 190-220-°C 210-240°C	not available
Icefilaments	CARBON	PET	not available	not available
Dezhijian	High Rigidity Conductive ABS Carbon fiber	ABS ABS PETG	230-270°C 230-260°C 230-250°C	do not need 100-120°C 80-100°C
3D Printer Pro	Carbon fiber	ABS	220-260°C	not available
Graphene 3D Lab	Graphene	PLA, ABS	not available	not available

the coming years following the evolution of the theme. There is enormous scope for the application of this promising technology in designing various components and products, its future will rely on its prospective to provide 3DP systems capable of manufacturing sensors and electronics. Conductive and magnetic filaments are revolutionizing the 3DP technology to a new level.

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