We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Carbon Nanotubes and Graphene as Additives in 3D Printing

Steve F. A. Acquah, Branden E. Leonhardt,
Mesopotamia S. Nowotarski, James M. Magi,
Kaelynn A. Chambliss, Thaís E. S. Venzel,
Sagar D. Delekar and Lara A. Al-Hariri

Additional information is available at the end of the chapter

Abstract

3D printing is a revolutionary technology for the consumer and industrial markets. As the technology for 3D printing has expanded, the need for multi-materials that support fused deposition modeling and other forms of additive manufacturing is increasing. 3D printing filaments infused with carbon nanotubes and graphene are now commercially available, with the promise of producing conductive composites. This chapter explores some of the research, products, and challenges involved in bringing the next generation of functional printing materials to the consumer market.

Keywords: 3D printing, additive manufacturing, graphene, carbon nanotubes, carbon black

1. Introduction

Johannes Gutenberg catalyzed one of the first revolutions in education, with the development of the printing press, allowing the dissemination of information to take a more structured pathway. In the modern world, computers, smartphones, and the internet have all contributed to the advancements in science, technology, and engineering. 3D printing is another revolutionary technology for the consumer and industrial markets. Although the consumer market is still relatively young, the industrial sector has matured with its inception in the mid-1980s. The first 3D printer was created by Charles W. Hull of 3D Systems Corp. He published

patents detailing many of the concepts involved in 3D Printing, some of which are used today. Developments in the various forms of printing have resulted in the use of the umbrella term of additive manufacturing. At its core, 3D printing simply uses additives to create 3D structures produced from successive layers of additives, such as polymers, and is deposited onto a platform. There are many companies that develop affordable consumer 3D printers such as Makerbot and Flashforge (**Figure 1**).
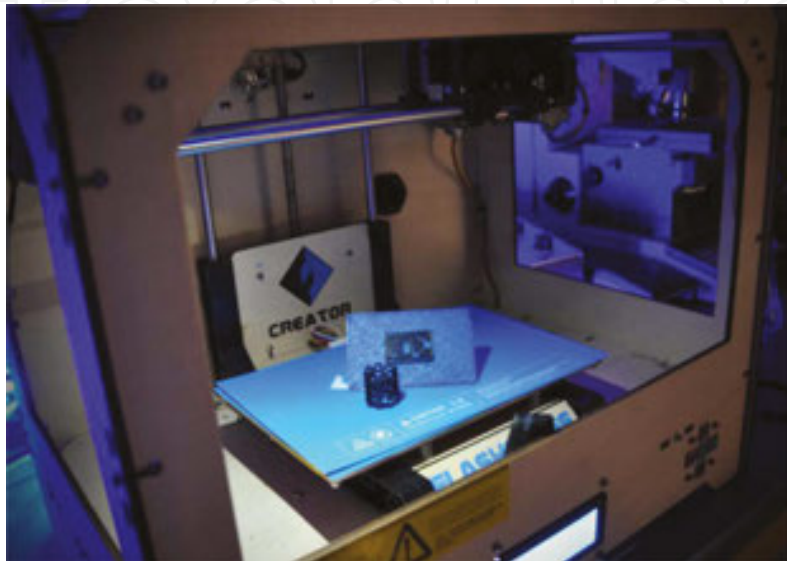

Figure 1. A Flashforge Creator 3D printer. This is a dual-extrusion printer with a build volume of 300 cubic inches.

The most recognizable form of 3D printing is thermoplastic extrusion, commonly known as fused deposition modelling (FDM) [1], where a filament (typically 1.75 mm) is unwound from a spool and fed into an extrusion assembly. The use of a motor-driven gear helps feed the filament into a temperature controlled melting chamber before the melted plastic is extruded through the tip of the nozzle. A fan is also used to help maintain the temperature as shown in **Figure 2**. The design of extruders continues to evolve, making printing more efficient by improvements in the regulating temperature across the extrusion assembly, and design modifications to reduce wear and blockages.

Polylactic acid (PLA), a sustainable biodegradable polymer, and acrylonitrile butadiene styrene (ABS), a strong terpolymer used in a range of manufactured products, are two of the most popular polymers used for FDM, and have formed the basis of the next generation of mixed material filaments for researchers. Other polymers used include polyvinyl alcohol (PVA), which is water soluble and biodegradable, and are support structures for 3D printing. Polyamides (nylons) are strong, abrasion resistant, and typically used for mechanical parts. All of these polymers have the potential for the inclusion of carbon nanostructured additives to extend their utility in multi-functional 3D printed composites.

There are many crowdfunded initiatives that are helping to further reduce the cost of entry level 3D printers and their accessories. Kickstarter, a world leading crowdfunding platform

has seen a large interest in 3D printers providing a unique opportunity for both early adopters and industry specialists to evaluate cutting edge technology. 'Form 1: An affordable, professional 3D printer' is an example of a successful Kickstarter initiative with 2068 backers who pledged a total of $2,945,885 to bring the project to life. The printer retails at $2799 from Formlabs. Another example of a successful Kickstarter initiative was Printrbot which raised $830,827 with 1808 backers, and sold units for $199.
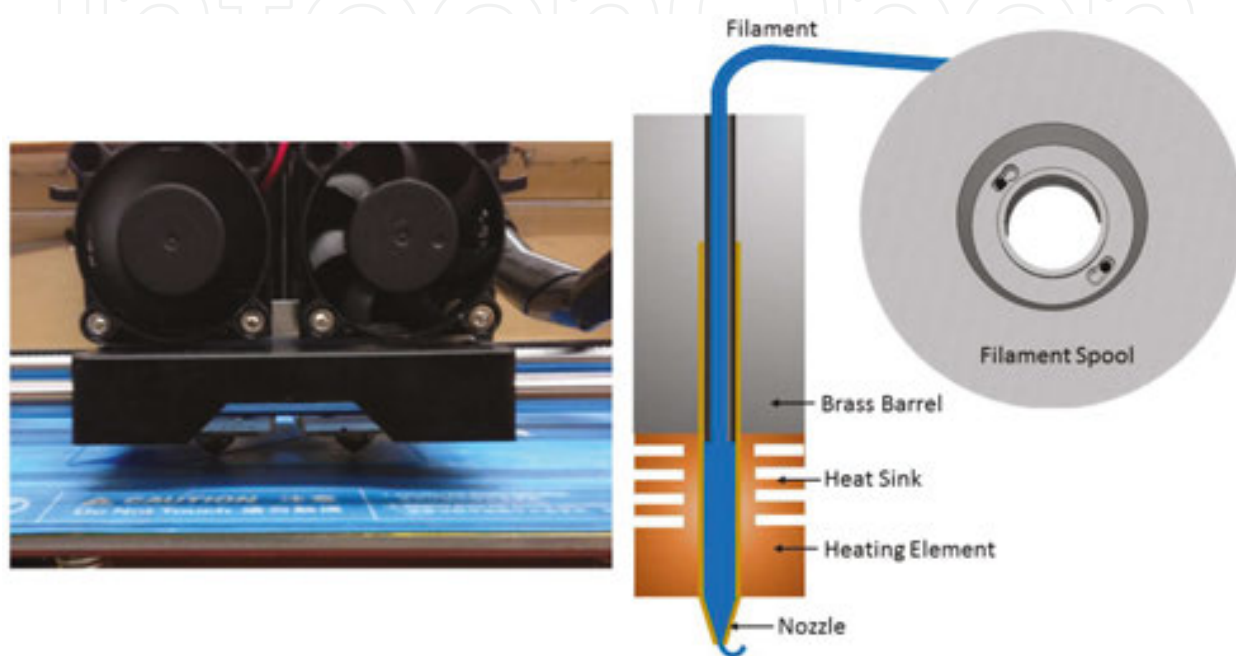

Figure 2. A picture of a dual extruder assembly from a FDM printer and a schematic of the extruder.

Selective laser sintering (SLS) is used to produce 3D components with a laser and powdered thermoplastics. During this process, a laser pulses onto a platform, creating a cross-section of the desired object on the powder. The laser is set to heat the powder just below its melting point causing it to fuse together. Fusing the powder in specific locations defined by the software creates the layers. An advantage of this method is the ability to process combinations of polymers and metals, and unused powder can be easily recycled. However, the particle size of the powder determines the precision of the print. This process has the potential for the incorporation of carbon nanotubes, but more research needs to be applied toward heat transfer processes [2].

Digital light processing (DLP) is another way of producing high resolution 3D objects. The process uses a vat of photopolymer with controlled exposure to the light from a DLP projector or an instrument using a digital micromirror device (DMD) [3]. The stage/build plate moves as the exposed liquid polymer hardens (**Figure 3**). Essentially, a 3D model on a computer is sliced into 2D cross-sectional layers to produce images that are sequentially sent to the DLP. The process continues until the 3D object is complete. Any remaining liquid photopolymer is then purged from the vat and the completed print removed.
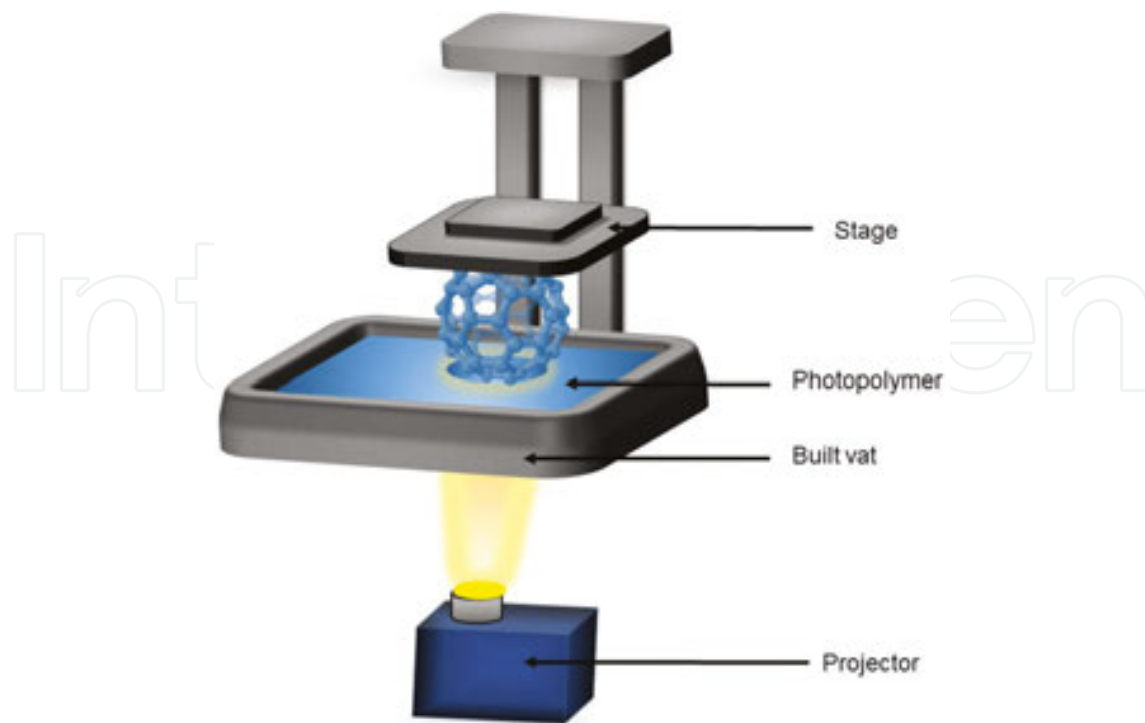
Figure 3. Diagram of a digital light processing printer.

Stereolithography is similar to DLP printing with the use of photopolymers, but differing with the laser based light source. Objects are produced by printed layers, one at a time, by the use of a laser beam on the surface of a vat of the liquid photopolymer. The polymer hardens over the areas where the laser strikes and a stage is moved down into the vat by one layer. Depending on the model of the printer, a recoater blade would move across the surface of the vat, helping to deposit the next layer of liquid polymer. This process is repeated until the print is completed and the printed object is raised from the vat and the liquid polymer drained. The printed object is then cleaned and cured in ultraviolet light to finish the processing. Stereolithography has been used with a range of materials including graphene oxide [4]. There are many potential applications that directly relate to the inclusion of carbon nanotubes and graphene as additives for 3D printing [5, 6] in a sector that is currently undergoing rapid growth. The 3D printing sector took over 20 years to reach $1 billion by 2009 and over the following three years it reached $2 billion. Analysis of the market suggests it may reach $10 billion by 2019 [7].

While there has been much praise for the 3D printing industry, there have also been some negative consequences on the environment and security. The process of thermal extrusion consumes a lot of electricity and the estimates of emission rates of ultra-fine particles were large for printing with PLA feedstock and even higher for printing with ABS thermoplastic feedstock [8]. Security has become an important issue after the fabrication of a 3D printed gun.

The US State Department is trying to implement a ban on the distribution of files for the 3D printing of guns; however, the nature of file distribution on the internet may make this almost

impossible to police. Initially only files for replacement gun parts were available, but a video soon demonstrated the successful operation of a printed gun.

2. Polymers in 3D printing

Additive manufacturing is developing to meet the demands for durable replacement parts, which need to conform to specific mechanical and design requirements. With thermal extrusion, new printing materials must have suitable rheological and thermal properties to be able to be extruded and solidify while maintaining the accuracy of successive layers. The use of polymers in additive manufacturing are governed by the glass transition temperature, melting point, heat capacity, melt viscosity at elevated temperatures, and the shear stress of the material. Understanding the relationship between the structural properties will aid in the development of advanced functional printing filaments and materials.

The glass transition temperature (Tg) is the temperature below which the polymer becomes brittle and hard like glass. The glass transition temperature is not the melting point, that is defined by the temperature at which crystalline or semi-crystalline polymers change from its crystal structure to its liquid form. Amorphous polymers have no sharp melting point due to their non-crystalline structure but they have a Tg temperature. Semi-crystalline polymers have both a Tg and melting temperature. Polymers that have a Tg below room temperature are elastic, while those with a Tg above room temperature tend to be rigid and brittle. The Tg is higher for polymers with stiff backbones and pendant groups that interact with nearby structures. Both of these features result in polymer chains requiring elevated temperatures to move. One example of a rigid backbone is a benzene ring as found in poly(p-phenylene) while a flexible backbone can be found with the CH_2-CH_2 bond in poly(ethylene) (**Figure 4**). A bulky branch may act as a plasticizer and lower the Tg by decreasing the packing of polymer chains. This can be seen with poly(methyl methacrylate) with a Tg = 100-120°C as compared to a Tg of 20°C for poly(butyl methacrylate), a difference of three additional carbons in the branch.

Poly(etheylene)   Poly(p-phenylene)   Poly(methyl methacrylate)   Poly(butyl methacrylate)
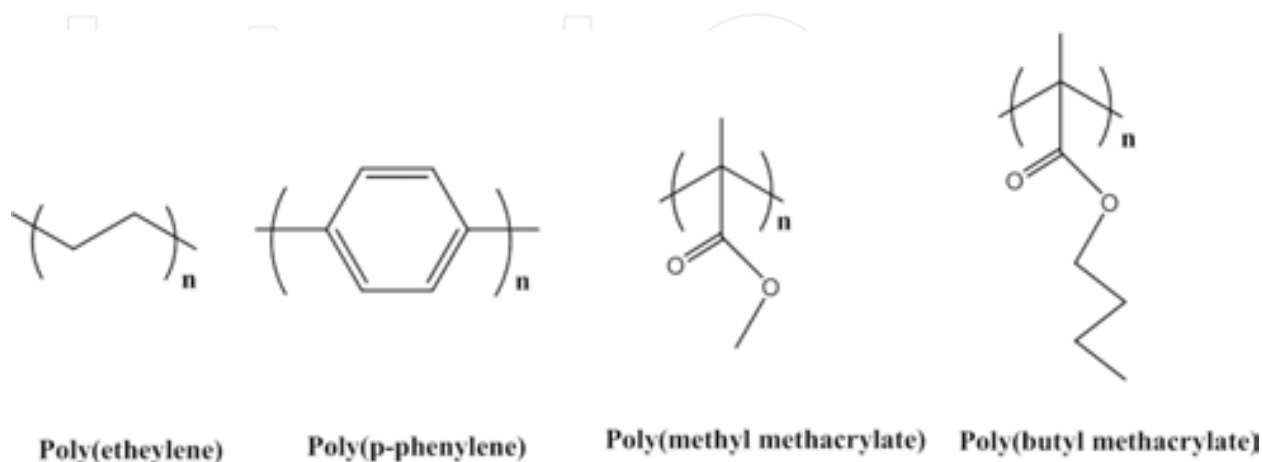
Figure 4. Structure of poly(ethylene), poly(p-phenylene), poly(methyl methacrylate) and poly(butyl methacrylate).

Amorphous polymers decrease in strength above the Tg and start to soften gradually while the viscosity changes.

The lower the Tg of the polymer, the faster it reaches the optimal viscosity for extrusion. Heat capacity also plays a role in homogeneity during the heating process. The Tg should be lower than the degradation temperature of the polymer, or in a temperature range where there are no chemical changes. The heat capacity of semi-crystalline polymers has a greater change compared to amorphous polymers. As a polymer is heated above its Tg, the viscosity will change based on the temperature and shear rate as it reaches the printing nozzle. The shear rate is higher at the printing nozzle (100–200 s^{-1}) compared to the other parts of the extrusion assembly.

The effect of viscosity is even more pronounced as the polymer is extruded from the nozzle as there is a possibility of radial flow. This phenomenon, typically known as swelling at the nozzle, can be quantified by calculating the ratio of the maximum diameter of the extruded material to the diameter of the nozzle. The addition of inelastic (ceramics) and carbon fillers to the polymer reduce swelling at the nozzle and results in an increase in the resolution of printing [9]. A sphere of polymer melt is then deposited on the substrate. The cross-sectional area of that sphere is proportional to the flow rate (q) of the polymer melt and inversely proportional to the velocity of the printing head, as shown in Eq. (**1**). The effect of the flow rate is shown in Eq. (**2**), where k is a constant depending on dimensions of the liquefier/melting chamber, ΔP is the change in pressure, and η is the viscosity of the polymer melt. The higher the viscosity, the lower the flow rate and cross-sectional area of the deposited sphere. A small cross-sectional area results in a higher resolution of the object or part printed.

$$A = \frac{q}{v_{printing\ head}} \tag{1}$$

$$q = \frac{\pi\ k\ \Delta P}{8\eta} \tag{2}$$

The interaction between the printed melt and the surface depends on the surface tension and roughness. The polymer melt should adhere to the substrate allowing it to be removed once the polymer solidifies. The next interaction is between the first deposited polymer layer and the next layer. This interaction will have a critical role in mechanical properties, structure, and success or failure of the object or parts. For bonding to occur at that level, the deposited polymer needs to reach or surpass its Tg. This can be achieved by the transfer of heat from the melt polymer to the deposited polymer layer.

2.1. Thermoplastic resurgence

Thermoplastic polymers like polyamide, polyolefin, polystyrene, polyester, and their co-polymers are favored in many applications from fabrics to packaging due to their excellent

mechanical properties, durability, relative ease of processing, and the possibility of recycling. A thermoplastic is a polymer that softens upon heating above a temperature range and then solidifies upon cooling; this process can be repeated several times. At the molecular level, the polymer chains are associated via intermolecular Van der Waals forces that are easily broken at elevated temperatures. In contrast, thermoset polymers harden upon heating and are no longer moldable, decomposing at high temperatures. For 3D printing, thermoplastic polymers are the best candidates since they melt and mold during the extrusion process, and this has caused a resurgence in the production of these polymers with a focus on sustainability for the 3D printing industry [10]. Thermoset polymers are only used with their corresponding monomers, with an initiator added, as the printed materials are cured by ultraviolet light or heat during post processing.

The most common materials used in 3D printing (FDM in specific) are amorphous thermo-plastic ter-acrylonitrile-butadiene-styrene (ABS), PLA (**Figure 5**), PVA, polycaprolactone (PCL), and nylon.

Figure 5. Commercially available PLA and ABS pellets.

ABS is a terpolymer that is made from acrylonitrile, 1-3-butadiene, and styrene (**Figure 6**). The ratio of each monomer in ABS can be selectively modified, based on the synthesis method used, to yield different grades of ABS with the required mechanical, thermal, and processing properties. The percentage of styrene can vary from 65–76% and acrylonitrile by 24–35%. ABS

is a light-weight, rubber-toughened thermoplastic, with low temperature toughness, and is stronger than polystyrene. It adopts the rubbery properties from polybutadiene, the toughness of acrylonitrile, while maintaining the reflective property of polystyrene, which can be enhanced using acetone. ABS is chemically resistant to water, aqueous acids, and alkali solutions but reacts/dissolves in carbon tetrachloride, concentrated nitric acid, concentrated sulfuric acid, esters, and acetone. For 3D printing, ABS can be produced in a variety of colors by adding pigments as raw ABS is translucent. Due to the reactive double bond in the polybutadiene region of the terpolymer, it may be oxidized in ultraviolet light, so indoor applications are preferred. Commercially available ABS filaments sold for 3D printing are extruded at 220–235°C, below the degradation temperature (400°C) at which it decomposes into its carcinogenic monomers. Due to its amorphous nature, ABS has no specific melting point and glass transition temperature, but it does have a range of 80 to 125°C. ABS, extrusion grade, has a tensile strength of 30–55 MPa and an elastic modulus of 897–2898 MPa.
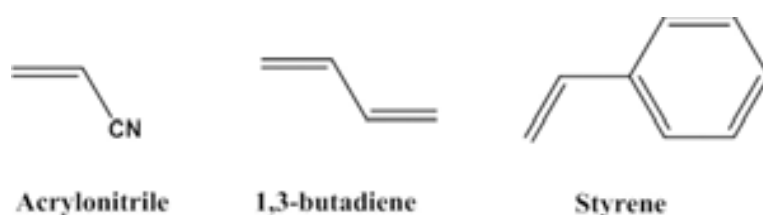

Figure 6. Monomers of ABS.

PLA (**Figure 7**) is a biodegradable and low toxicity polyester thermoplastic made from lactide or lactic acid monomers. Both can be derived from the fermentation of carbohydrates which is a renewable resource, so PLA is considered an ecofriendly thermoplastic. PLA can be produced in amorphous and crystalline form. The most common way to produce high molecular weight PLA is by the ring opening of lactide catalyzed by a metal. PLA produced by this method is a racemic mixture of both L and D PLA (stereocenter is labeled in **Figure 7**– red star). PLA is a hygroscopic thermoplastic; it can undergo degradation with elevated humidity and temperature. PLA has a glass transition temperature of 40–70°C and a melting point of 130–180°C. Various degrees of degradation at 210 and 240°C have been reported [11], and the rate of degradation was high at 240°C. Moisture has a strong effect on degradation at 210°C. PLA undergoes thermal degradation, scission of bonds, and results in weight loss which has an effect on mechanical and rheological properties [12, 13]. It is worth noting that the extent of degradation also depends on other factors ranging from molecular weight to particle size. Commercially available PLA filaments are printed at 180–220°C at which it can react with water, if present, and cause discoloration and degradation, which might affect the end product mechanically. Amorphous PLA is soluble in most organic solvents, while crystalline PLA is soluble at elevated temperatures. PLA has a high tensile strength of 48–52 MPa, a tensile modulus of 3500 MPa, and good heat salability but tends to be brittle.

PVA is a hydrophilic, water soluble, biodegradable thermoplastic polymer (**Figure 7**). PVA is synthesized by the hydrolysis or alcoholysis of poly(vinyl acetate) (PVAc) due to the instability of its vinyl alcohol monomer. It can be produced in two types: partially hydrolyzed or fully

hydrolyzed and can reach up to 99% hydrolysis. It has been used in the medical and industrial sectors, as PVA is biocompatible due to its low toxicity and minimal cell adhesion to its surface. The molecular weight of PVA depends on the molecular weight of the PVAc and can vary from 20,000–400,000 g/mol which affects the properties of PVA. When PVA has a molecular weight of 75,000–81,000 g/mol and is 98–99% hydrolyzed, it has a tensile strength of 17 MPa, and a tensile modulus of 1470 MPa [14]. PVA with a molecular weight of 146,000–186,000 g/mol when 98–99% hydrolyzed has a tensile strength of 51 MPa and tensile modulus of 443 MPa. PVA being soluble in water makes it suitable as support material for printing complex objects by forming a support structure. Initially, PVA rafts can be printed or dual extrusion printing techniques can be used to fill voids or intricate fine details during the print. The finished object can then be immersed in water to dissolve the PVA and leave the other extruded polymer in place. Rubber-elastomer filaments made of PVA with another polymer, sold under name of "Lay-felt", are commercially available to produce micro-porous objects as end products by immersing printed objects in water.

PCL (**Figure 7**) is polymerized from a caprolactone (a five member ring cyclic ester) monomer by ring opening catalyzed by stannous octoate. PCL is hydrophobic and soluble in chloroform, carbon tetrachloride, cyclohexanone, benzene, and toluene. PCL biodegrades in the presence of microorganisms. It has a low glass transition temperature of -60°C [15], which makes it less brittle than other polymers with glass transition temperatures above room temperature. It also has a low melting point of 59–64°C with the advantage of low processing temperatures especially when mixed with other materials to form composites.
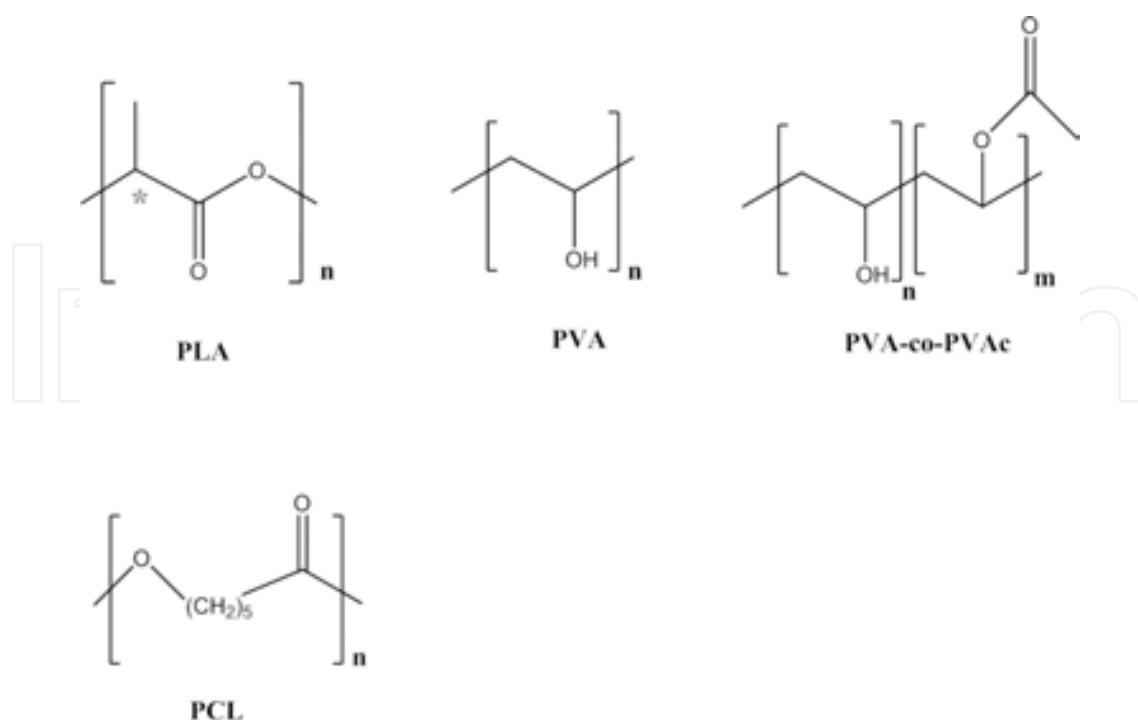

Figure 7. Structures of PLA, PVA, PVA-co-PVAc, and PCL.

3. Carbon nanotubes

Carbon nanotubes are known for their mechanical, electrical, and thermal properties, which initially makes them a suitable candidate to integrate into 3D printing polymers. MWCNTs have structural defects which provide suitable nucleation sites that allow for strong interactions with polymers [16] and for cross-linking and functionalization [17–19]. A homogeneous dispersion of carbon nanotubes in polymeric solutions are essential if they are to be used for enhanced CNT based filaments. The familiar problem of the aggregation of CNTs 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 (the transition between an insulating and conductive polymer) while maintaining the parameters for 3D printing.

The theoretical concentration of carbon nanotubes required to reach the electrical percolation threshold for a CNT/Polymer composite can be obtained, as a first step, by the use of the power law:

$$\sigma \propto (\varphi - \varphi_c)^{\alpha}$$

where σ is the electrical conductivity, φ is the MWCNT volume concentration in the nanocomposite, φ_c is the critical MWCNT volume concentration at electrical percolation, and α is a critical exponent [6]. A comprehensive table of percolation thresholds for CNTs in polymer matrices was assembled by Bauhofer et al. [20]. It was also noted by Bauhofer that there were conflicting results concerning the dependence of the percolation threshold on the aspect ratio. The excluded volume analysis conducted by Celzard et al. showed that the percolation threshold of a fiber suspension would decrease when the aspect ratio increased [21]. Research by Bai et al. demonstrated a decreasing set of values for the percolation threshold when the CNT length increased [22]; however, Martin et al. [23] found an increasing percolation threshold when the CNT length increased. This problem can be reconciled by considering the type of percolation thresholds. Bai et al. possibly obtained statistical thresholds while Martin et al. acquired kinetic percolation. This is important to know as theoretical analyses reported tend to ignore the movement of filler particles and only seem to predict the dependence of the statistical percolation threshold on the filler aspect ratio.

Ultrahigh molecular weight polyethylene (UHMWPE) has been processed with MWCNTs and extruded to produce filaments [24]. However, it is not feasible to produce UHMWPE filaments by conventional extrusion due to the high Weissenberg effects [25] that would likely affect the flux during extrusion both for filament production and 3D printing. An alternative would be to use the gel-spinning technique [26] in which the polymer is dissolved and spun. The addition of MWCNTs can be problematic as they tend to aggregate during the solvent evaporation stage, but the problems were addressed by using a range of techniques including sonication, melt mixing, and extrusion [24].

The compatibilization of a polymer is simply the addition of a material to immiscible blends of polymers resulting in an increase in stability. Compatibilized polyolefin rubber is an example of a composite that can be made conductive by the addition of carbon nanotubes [27] or graphene. The percolation threshold has been widely studied with carbon nanotube systems [28, 29]. The study of PC, ABS, and MWCNT composites confirmed that localization of MWCNTs changes from the ABS to the PC phase when the rubber content was reduced from 60 to 5% [30]. At low concentrations of rubber, MWCNTs localized in the PC phase resulting in an increase in conductivity and a low percolation threshold of around 0.5–1 wt% [28].

Ternary systems could be an important framework for developing advanced 3D printing materials. With the ternary mixture of PCL, PLA, and MWCNT, it has been shown that the localization of carboxylic functionalized nanotubes can be identified at the PCL phase and at the phase interface. When the MWCNTs are not functionalized, they can only be located at the PCL phase resulting in an elevated percolation threshold. Ternary composites exhibit conductivities that are 3–4 orders higher than binary composites when the MWCNT content reaches 1 wt% [31]. Pötschke et al. developed a method to mix MWCNTs into thermoplastic matrices of PC and polyamide-6 (PA6) by melt blending the PE based masterbatch with high MWCNT loading. This improved the CNT dispersion in PC and PA6 and also reduced the percolation threshold [32]. In general, there are many strategies that can be applied to the mixing of CNTs with polymers.

Postiglione et al. reported the assembly of conductive 3D structures using a PLA/MWCNT nanocomposite using liquid deposition modeling (LDM) with dichloromethane (DCM) [6]. They reported a percolation threshold concentration of 0.67% with a conductivity of 10 S/m, and the highest conductivity was obtained with 5 wt% MWCNT with 100 S/m. Postiglione found that at a composition of 35% PLA in DCM with 1 wt% MWCNT, the rheological effects prevent the extrusion through the 3D printer as a higher pressure from the extrusion assembly would be required. Nanocomposites made from 25 wt% of PLA in DCM with 1 wt% MWCNTs can be printed out at a lower shear stress with a higher shear rate ($1–50$ s^{-1}) when compared to 30 wt% PLA in DCM with 1 wt% MWCNTs (shear rates $5–11$ s^{-1}). Although the 25 wt% PLA/CNT mixture prints at a higher speed, a better resolution product was obtained using a 30 wt% PLA/CNT mixture at 10s^{-1} and a low speed of 0.1 mm s^{-1}.

Grafting of single wall carbon nanotubes SWCNTs to poly(L-lactic acid) has been investigated [33] but so far MWCNTs are dominant, possibly due to their increased metallic character. However, Vatani et al. reported the fabrication of a highly stretchable sensor by dispersing 1 wt% SWCNT (average diameter 1.5 nm, length 1–5 micrometer) in a matrix of a blend of two photocurable monomers (cyclic trimethylolpropane formal acrylate and acrylate ester) [34]. The monomers/SWCNT composite was printed using direct writing into a polyurethane substrate on which the monomers were photo cured. The wires sustained strain up to 90% elongation and resistivity change increased proportionally with the strain.

3.1. Delivering on the hype

It is well known that the advent of carbon nanotubes caused a flurry of interest with researchers over how these nanoscale tubes could change the way we live. While it is easy to lead research

by conjecture, once a plateau is reached, the refinement of the field begins. What we are seeing now is the development of stronger and highly efficient carbon nanotube based composites that, without the fanfare, are making their way into products.

An article in Chemical and Engineering News [35] highlighted the difficulty in working on the field of carbon nanotubes. Phaedon Avouris, a member of the American Academy of Arts and Sciences and an expert in the field of carbon nanotubes and graphene said when scientists work on new materials, there is a rush to characterize it, publish papers in prominent journals, and then move on to a different material, "We're left with a lot of unfinished work and unproven claims". Although a fundamental understanding of the research topic may be achieved, few people are determined to solve the problems that facilitate the transition to applications.

Production capacity of multi-walled tubes has peaked with Timesnano and Showa Denko, each producing over 2500 metric tons every year, but demand is still growing with conductive adhesives and fire retardant plastics leading the requests for applications [35]. In 2015, over 400 metric tons of multi-walled carbon nanotubes were used for conductive polymer composites with estimates reaching 1700 metric tons by the year 2020. It is possible that this may increase further as carbon nanotubes continue to transition into additive manufacturing.

Mihail Roco, the senior adviser for nanotechnology at the National Science Foundation (NSF) said that carbon nanotubes form a component of nanotechnology. "Components are essential in advancing nanoscience, but they're not the end goal in applications." The NSF intends to advance toward the goal of building nanotech systems that provide answers to problems in industry and other areas. Carbon nanotubes have steered researchers toward the development of prototypes, and will continue to promote innovation over the next decade. Roco also said, "Carbon nanotubes focused attention on understanding matter at the nanoscale, on making new tools, on performance, on how to create groups that could cross disciplines". This shows that beyond the hype, the legacy of carbon nanotubes for nanotechnology may prove to be an important milestone.

3.2. Commercial carbon nanotube materials for 3D printing

3DXTech is a company that provides filaments containing carbon nanotubes. Their 3DXNano™ ESD ABS filaments (containing MWCNTs) are available with diameters of 1.75 mm and 2.85 mm. The filament is tailored toward applications that require electrostatic discharge (ESD). The filament is produced using MG-94 Premium ABS and mixed with MWCNTs, and process/dispersion modifiers. 3DXTech state that the Tensile strength is 42 MPa in comparison to 41 MPa for the unfilled ABS. The surface resistance for '3DXNano™ ESD ABS' is 10^7-10^9 Ω. An extrusion temperature of 220–240°C with a FDM platform temperature of 100–110°C is also suggested.

Nanocyl are one of the worldwide leading experts in CNT based materials, producing research and industry grade carbon nanotubes. One of their product lines, PLASTICYL™, is a collection of carbon nanotubes thermoplastic concentrates for applications requiring electrical conductivity with good mechanical properties. The concentrates contain 10–20% of carbon nanotubes

and are available in a diverse range of thermoplastic resins, including PC, PP, PA, PET, HDPE, and others. Although these enhanced thermoplastics were not specifically aimed at the FDM sector, they have a formulation that makes them applicable, subject to the temperature range of the extruder. PLASTICYL™ can be used in many applications and a surface resistivity range of 1–10^{12} Ω, and the typical loading for static dissipative applications are around 2–3% of CNTs in the final compound. The conductivity can be tailored for a given loading of CNTs, depending on the compounding conditions, and the viscosity of the basic resin. Nanocyl optimizes the dispersion of CNTs in a wide range of thermoplastics with the PLASTICYL™ range (www.nanocyl.com).

F-Electric is a PLA-based filament produced by 'Functionalize' that incorporates carbon nanotubes. F-Electric is one of the best conductive 3D filaments available on the market with a 0.75 $\Omega\bullet$cm in volume resistivity. **Table 1** shows some of the commercially available carbon nanotube based materials.

Company	Product
3DXTech	3DXNano™ ESD ABS + Carbon Nanotube Filament
	3DXNano™ ESD PETG + Carbon Nanotube Filament
Functionalize F-Electric	Functionalize F-Electric filament (PLA & Carbon Nanotube)
Filabot	MWCNT1 Multi Walled Carbon Nanotube Pellets
Cheap Tubes Inc.	Carbon Nanotube Masterbatches CNT-ABS-10
Nanocyl	PLASTICYL™ ABS 1501*
	PLASTICYL™ HIPS 1001
	PLASTICYL™ PC 1501
	PLASTICYL™ PP 2001

Table 1. Companies that provide filaments and pellets containing carbon nanotubes.

3.3. Filament production

Consumer 3D printers are perfect for creating replacement parts and tools, and supporting learning from K-12 to higher education, but the process can produce a lot of waste from failed prints, supports, and rafts. Recycling these materials can be highly effective in reducing the costs of printing. Crowdfunded initiatives have been the main driving force in producing filament reclaimers with products such as the Filastruder (filastruder.com) and the Filabot (filabot.com) range of extruders and accessories. The process of reusing filaments is further complicated by the need to break down the waste so that it can be successfully channeled through a feed screw through to the melting chamber (surrounded by a heater) as shown in **Figure 8**. Extruded filaments can be collected on automated systems such as the Filabot Spooler, allowing the spool to be detached and connected to a 3D printer when completed.
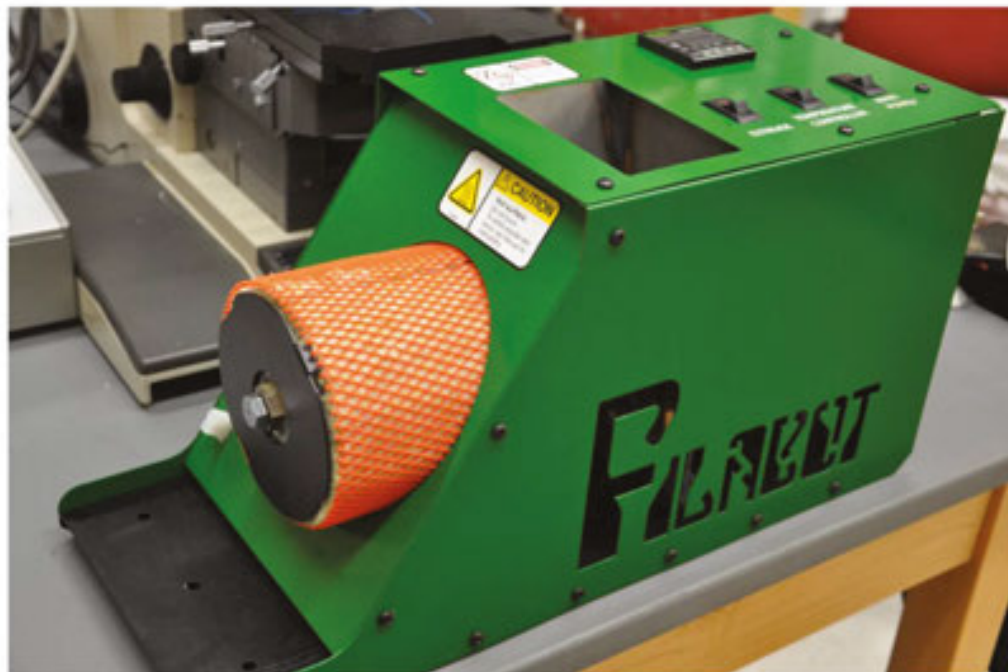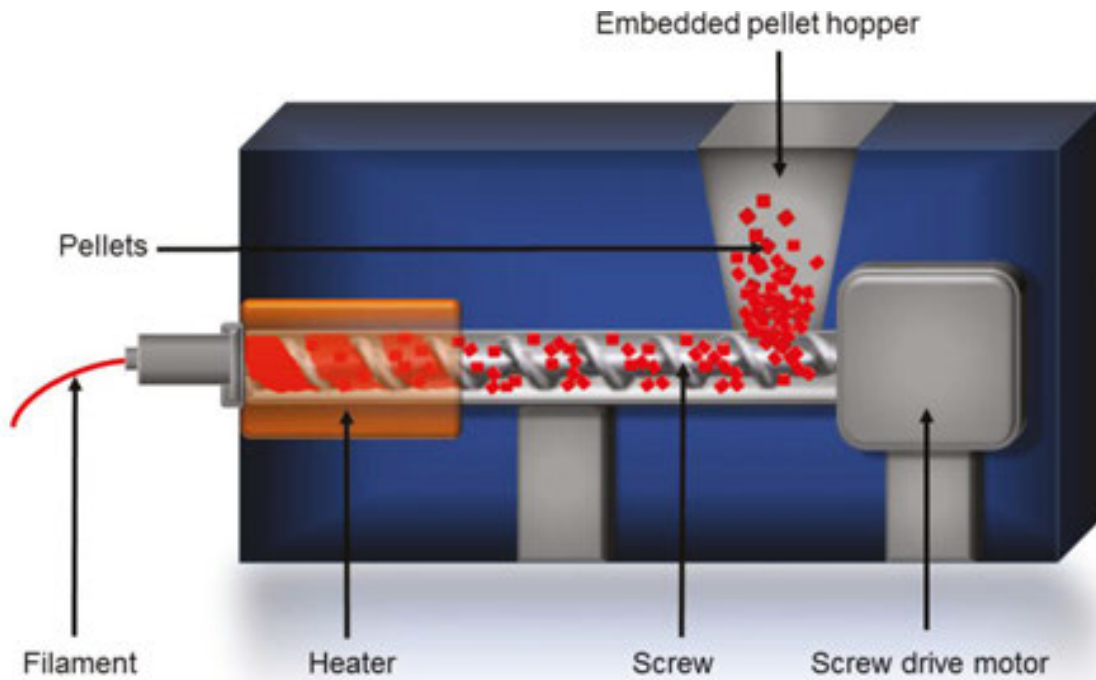
Figure 8. Diagram of a filament maker and a picture of the 'Filabot – Original' used for producing filaments by FDM.

Graphene exhibits a range of exceptional qualities including flexibility and conductivity. 3D printing filaments augmented with graphene have the potential to enhance the manufacturing process of strong conductive composites. There are many applications of these carbon

nanostructured additives in 3D printer filaments including sensors, trackpads, electromagnetic, and RF shielding.

4. Graphene

Graphene has been rising in popularity as a material that would revolutionize electronics; fortunately, graphene has safely passed the peak of overestimated expectations and is now settling on some novel applications. Graphene has many interesting properties such as low resistivity, excellent thermal conductivity, optical transparency, and high electron mobility.

There are only a select few companies that have produced graphene enhanced 3D printing materials, including Angstron Materials and Graphene 3D Labs (**Table 2**).

Company	Product
Black Magic 3D	Conductive Graphene Filament
	Conductive Thermoplastic Graphene/PLA Pellets
Filabot	Graphite Infused Filament—ABS Based
Angstron Materials	Graphene Enhanced Nanocomposites—PP, PC, ABS
Graphene 3D Lab	GRAPH-PLA (Graphene/PLA Pellets)

Table 2. Commercial graphene or graphite infused 3D printing materials.

4.1. Polymer integration

The use of graphene in 3D printing started with the Canadian company Grafoid, resulting in the product MesoGraf, which is produced from raw, unprocessed graphite ore in a one-step process. It is envisaged that the use of graphene in 3D printing will aid in conductivity and strength. Grafoid worked with Altamat to construct a facility to produce MesoGraf graphene-based powders and filaments for 3D printing, and Grafoid intends to supply a diverse catalog of MesoGraf-based powders and filaments to aid companies with additive manufacturing processes to produce their end-product prototypes and end-user products.

There are some limitations with current 3D printing technology, especially when attempting to produce filaments with advance functional materials such as metals, graphene and carbon nanotubes. Problems may be associated with the size of particles and temperature variations of the constituents within a polymer matrix.

Research is still ongoing into making FDM more applicable to producing advanced functional 3D printed materials in Dr. Acquah's research group at Florida State University. The research group is using a combination of graphene-enhanced and carbon nanotube-enhanced 3D printing materials to tailor the properties. Research is also focusing on modifying polymers with graphene [36]. Although graphene has also been referred to as a remarkable material, homogeneous mixtures of graphene and polymers are essential to exploit the unique proper-

ties [37]. Wei et al. [38] stated that the major problem confronted by graphene composites was that of phase separation between graphene sheets. They addressed the problem with the use of graphene oxide (GO) to substitute graphene as the additive. GO contains oxygenated functional groups on its basal planes, which may assist graphene's dispersion in polymer phases [38].
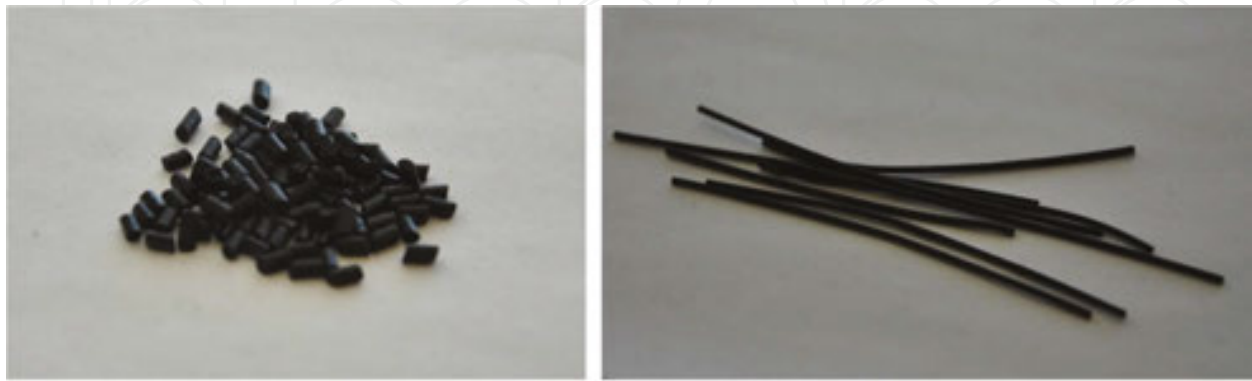

Figure 9. Graphene infused PLA pellets and 1.75 mm filaments.

Graphene 3D Labs is working on 3D printable batteries incorporating graphene, with the potential to surpass current commercially available batteries. They demonstrated a prototype battery in 2014 and the following year launched conductive graphene filaments for 3D printing. The filaments and pellets (**Figure 9**) contain highly conductive proprietary nanocarbon materials with PLA. Both the filaments and pellets extruded through a filament-producer are compatible with commercially available FDM printers. The volume resistivity is listed as 1 $\Omega \bullet$cm which provides an excellent starting point for 3D printed circuitry and capacitive touch sensors.

Research by Seung Kwon Seol of the Korea Electrotechnology Research Institute has demonstrated a process that is capable of 3D printing pure graphene nanostructures [39]. This achievement marked the first time graphene has been printed by itself without being used as the additive. The research available in the journal 'Advanced Materials' shows potential for expansion once the challenges such as reducing the size of the extruded material and increasing the yield are addressed.

5. Carbon structured additives

Carbon Nanotubes and Graphene are some of the popular choices as additives for 3D printing, but carbon black (CB) and carbon fibres are unique carbon structured additives that have an extensive history in manufacturing, tailoring the properties of composites for electronic applications, and structural reinforcement respectively.

5.1. Carbon black

CB is soot-like in its appearance but differs from soot at the molecular level. CB is produced from the incomplete combustion of heavy petroleum products such as coal tar. As such, it is readily available and inexpensive. It is considered one of the most popular conductive additives because of its low cost and chemical stability [40].

A conductive thermoplastic composite called 'carbomorph' which can be extruded through a consumer 3D printer has been produced [15]. In this work, Leigh et al. reported on the 3D printing of a piezo-resistive sensor from a composite of PCL with 15 wt% of CB as filler. Leigh stated that the transition from insulating to non-insulating behavior for composites with conductive filler is generally observed when the volume concentration of filler reaches a threshold of around 25% [41]. However, their decision to use 15 wt% CB was based on optimization, considering the thermal and rheological parameters required for successful printing. The thermoplastic polymer selected for the composite was the polymorph PCL. Bending the sensor resulted in a change of resistivity of 4%. The conductivity of the printed filament made from the PCL/CB composite was 11.1 S/m, which falls within the range of semi-conductors.

Resistance was tested using 5 mm cubes of carbomorph by two-probe measurements with the two opposite cube faces (painted with silver conductive paint). The resistivity of the composite, in-plane with the layers, was 0.09 ± 0.01 ohm m^{-1} and perpendicular to the layers, the resistivity was 0.12 ± 0.01 ohm m^{-1}. This is a significant observation as the reduction in the resistivity of 25% from the perpendicular to parallel orientation is a feature that needs to be considered for the next generation of functional composites. The plane of the layers of the printed filaments provides an unperturbed conductive pathway between the electrodes, while perpendicular to the layers, the conductive pathway depends upon the connection between successive layers.
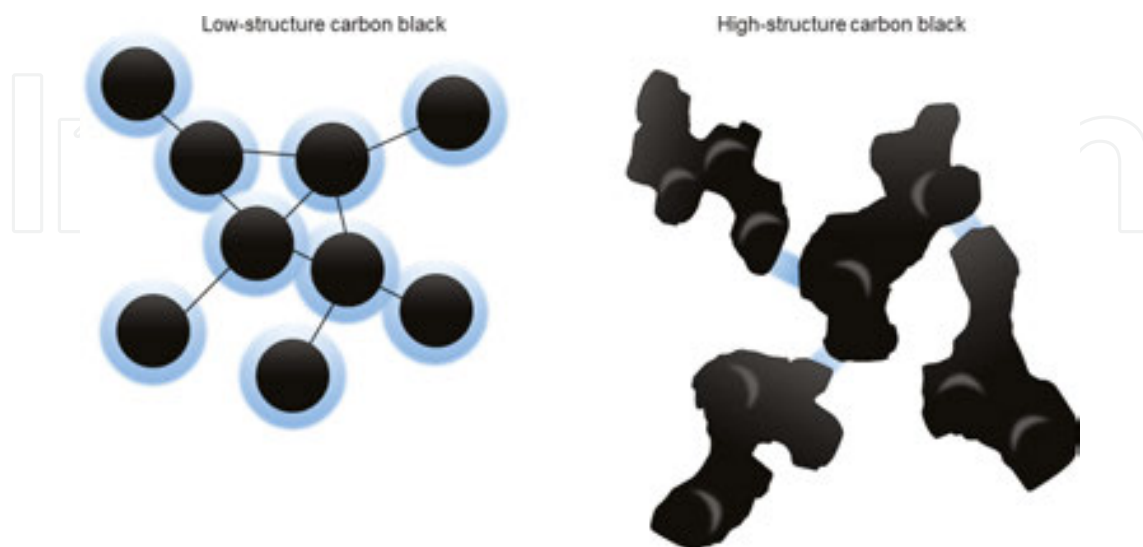

Figure 10. Low-structure and high-structure carbon black. Figure adapted from Balberg [42].

Work by Balberg into the electrical phenomena in CB-polymer composites looked at the difficulties in establishing the percolation threshold for the incorporation of CB into polymers [42]. While he noted that previous studies in his reviews had explained the electrical data within the confines of inter-particle tunneling conduction [43] and/or that of classical percolation theory, the observations were far more convoluted. He noted that for different types of CB, the same volume percent of the CB phase in the composite produces different values for the resistivity [44, 45]. By investigating the characteristics, Balberg stated that the values of the (apparent) percolation threshold and the (apparent) percolation critical resistivity-exponent depended strongly on the particular type of CB. The particles could be treated in terms of how spherical-like they look, with more spherical CB particles termed 'low-structure' CB, in comparison to 'high-structure' CB. **Figure 10** shows the closely packed network of spheres representing the low structure in a polymer composite with nearest-neighbor tunneling. The black spherical structures are the CB particles, and the blue shells represent the tunneling distance. The nearest-neighbor connections (black lines) indicate the dominant conducting elements that result in percolation-like behavior. **Figure 10** also shows a high-structure CB polymer composite. The distances between the nearest inter-particle surfaces have a narrow, non-diverging distribution of the tunneling-resistor values in the network.

PLA filaments with CB as an additive are commercially available (**Figure 11**). Proto-pasta offers filaments that have a volume resistivity of 15 $\Omega\bullet$cm, resulting in 3D prints that are 30 $\Omega\bullet$cm perpendicular to the layers, and 115 $\Omega\bullet$cm through the layers.

Figure 11. Conductive PLA 1.75 mm filament containing carbon black.

5.2. Carbon fiber

As a stalwart of modern engineering, carbon fibers are an important part of reinforcement in composite materials. Properties such as low weight, high tensile strength, and low thermal expansion are some of the advantages of incorporating these fibers in composites. One of the known limitations of FDM is the low transfer of strength in the printed composites, but the use of carbon fibers in 3D printing is an important step toward creating high strength composites. Ning et al. reported printing out parts from an ABS/carbon fiber composite with different percentages by weight. The highest tensile strength reported for a 5 wt% composite of carbon fibers in ABS, printed using FDM was 42 MPa [46]. The tensile strength dropped as the percentage of carbon fiber increased to 10 wt%. The ductilities of all composites were less than the pure ABS. The 7.5 wt% carbon fiber composite had the largest value for the Young's modulus. The reduction in the tensile strength and ductility of composites exceeding 10 wt% was due to the higher porosity of those composites.

A new start-up, MarkForged Inc., has been working on improving the integration of carbon fibers. The company has developed a new printer which uses two separate print-heads. The first head dispenses a polymer such as nylon or PLA, while the other dispenses a carbon fiber tow which is a coated thermoplastic. As the carbon fiber can be introduced during any part of the print process, composites can be produced without reinforced sections. MarkForged reported that tests demonstrated that the parts produced were stronger than 6061-T6 aluminum.

Carbon fiber filaments are also offered by Proto-pasta with fibers mixed with PLA. Proto-pasta states that the abrasive nature of the filament may cause the extrusion nozzle to fail prematurely.

6. Discussion

Additive manufacturing is a multi-disciplinary field that encompasses many aspects of chemistry, physics, and engineering in a manner not so dissimilar from its nanoscale counterpart, in the field of nanotechnology. The two areas of development that steer advances are the composition of the next generation of filaments, pellets, and resins for printing; and the equipment used for filament production. One of the most important examples of the level of advancement in both areas is the 3D printing of bio-inspired materials. Kang et al. recently produced life-sized body parts and tissues with living cells acting as the printing materials. The parts were stable enough to be used as viable replacements that could be tailored to individual needs rather than generic replacements [47].

One of the limitations of consumer thermoplastic extrusion is the temperature range of the extruder assembly. While entry level printers were designed to work with ABS and PLA filaments, this meant that the nozzle temperatures were only required to reach 230–240°C. The latest generation of extruders such as the E3D V6 hotend are capable of high temperature extrusion up to 300°C and 400°C when the thermistor is exchanged for a thermocouple. These

temperatures are essential for multi-material filaments that may require elevated temperatures, and polycarbonate and nylon based filaments. The high temperatures would also create additional problems with mixed materials. Polymers may degrade at higher temperatures and the carbon nanostructured additives may cause unfavourable results during extrusion. Stratasys offer a proprietary product called Digital Materials which are a range of several hundred combinations of PolyJet base resins. The Objet260 Connex 3D printing platforms use the PolyJet resin and are capable of depositing three materials with a layer thickness of 16 μm. The build resolution is 600 dpi on both the X-axis and Y-axis, and 1600 dpi on the Z-axis.

The difficulty in producing mixed material filaments with carbon nanostructures, and the additional problems associated with the rheology and flux during FDM extrusion may be addressed by a move toward other additive manufacturing techniques such as the PolyJet system. Carbon nanotubes, graphene, and CB have been explored as additives for SLS [48–50]. The main issue again is creating a homogeneous distribution of the carbon nanostructures, but this can be achieved by simple mixing techniques. Paggi et al. reported on the process for the optimization of PA12/MWCNT nanocomposites by SLS [48]. They described a procedure for dispersing the MWCNT powder initially in chloroform using ultrasonic techniques for one hour. They added the polyamide powder to the suspension and continued mixing on a magnetic stir plate for 50 min to homogenize the solution. After a filtration process with a cellulose filter, the mixture was washed with acetone and placed in an oven at 80°C for four hours. Rotary blades were then used to homogenize the final powder. A CO_2 laser (10 watts) with a beam diameter of 250 μm was used to fuse the powder. Pulsed mode was used to operate the laser at 5 kHz and the average layer thickness produced was 200 μm.

The worldwide market for 3D printing, including the services sector, will likely increase at a compound annual growth rate (CAGR) of 32.2% from 2014 to 2019 [51]. Some additive manufacturing processes show good potential for growth from 2014 to 2019. The 3D stereolithography sector is estimated to rise to $1.8 billion with a CAGR of 27.5%. PolyJet technology will rise to a modest $334 million, but with a CAGR of 40.7%. FDM will almost reach $1 billion with a CAGR of 30%, and SLS is expected to reach $504 million with a CAGR of 32.3%, so development into additives for these industries will continue to be strong. The industry segment focusing on services including design and development, manufacturing, and equipment repair will contribute to 53% of revenues. BCC Research also estimates that 'services' will reach $7.8 billion in 2019 with a CAGR of 31.4% from 2014 to 2019 [51].

The major advantage in this market is the high level of diversification in the technology and applications. Advances in the design and function of 3D printers have catalysed the development of multi-material filaments and printing techniques that overcome some of the limitations of the durability of printed composites. 3D printing may also have a pronounced effect on more traditional manufacturing processes, affecting many aspects from the design and development of materials to the cost savings through the rapid production of custom parts. For consumers, it is the potential to be able to print replacement parts for household appliances.

7. Summary

Polymer composites with conductive fillers have the potential to be used in many areas from engineering to consumer product development, with tunable properties that include elasticity, durability, water wettability (hydrophobic/hydrophilic), and conductance.

The use of metal fillers in polymer composites have been reported [52], and although the ability to print with conductive filler such as a metal is a clear advantage, the difficulty resides in the processability of the composite which may affect the quality and resolution of the 3D object. To reach a workable conductivity, the percentage weight of filler may need to increase, which causes an increase in the density and viscosity of the composite. The addition of the filler affects the rheological properties of the polymer. Metallic fillers are usually susceptible to oxidation, and most of the conductive fillers used are in a 5–120 μm diameter range, which can be a challenge by itself causing blockages at the nozzle-opening of most types of FDM printers, which typically have a nozzle diameter of 400 μm.

Carbon nanotubes as an additive for 3D printing are relatively new but an essential step toward the production of mixed-materials 3D printing. Much of the work in this area has focused on producing homogenous mixtures with PLA and ABS, with the goal of reducing the percolation threshold for conductivity. Polyhydroxylated fullerenes may also be an important bridge toward creating homogenous mixtures in polymers [53].

Graphene has been incorporated into filaments for FDM by a small but growing number of commercial entities. Its incorporation into filaments and pellets has been marketed primarily for their electron transport properties, as an improvement over CB based filaments.

Author details

Steve F. A. Acquah[1*], Branden E. Leonhardt[1], Mesopotamia S. Nowotarski[1], James M. Magi[1], Kaelynn A. Chambliss[1], Thaís E. S. Venzel[1], Sagar D. Delekar[1] and Lara A. Al-Hariri[2]

*Address all correspondence to: sacquah@chem.fsu.edu

1 Department of Chemistry & Biochemistry, Florida State University, Tallahassee, FL, USA

2 Department of Chemistry, University of Massachusetts Amherst, Amherst, MA, USA

References

[1] Gross BC, Erkal JL, Lockwood SY, Chen CP, Spence DM. Evaluation of 3D printing and its potential impact on biotechnology and the chemical sciences. Anal Chem. 2014;86(7): 3240–53.

[2]   Bai JM, Goodridge RD, Yuan SQ, Zhou K, Chua CK, Wei J. Thermal influence of CNT on the polyamide 12 nanocomposite for selective laser sintering. Molecules. 2015;20(10):19041–50.

[3]   Shallan AI, Smejkal P, Corban M, Guijt RM, Breadmore MC. Cost-effective three-dimensional printing of visibly transparent microchips within minutes. Anal Chem. 2014;86(6):3124–30.

[4]   Lin D, Jin S, Zhang F, Wang C, Wang Y, Zhou C, et al. 3D stereolithography printing of graphene oxide reinforced complex architectures. Nanotechnology. 2015;26(43): 434003.

[5]   Lawes S, Riese A, Sun Q, Cheng NC, Sun XL. Printing nanostructured carbon for energy storage and conversion applications. Carbon. 2015;92:150–76.

[6]   Postiglione G, Natale G, Griffini G, Levi M, Turri S. Conductive 3D microstructures by direct 3D printing of polymer/carbon nanotube nanocomposites via liquid deposition modeling. Composites A Appl Sci Manufact. 2015;76:110–4.

[7]   McWilliams A. Advanced materials for 3D printing: Technologies and global markets. BCC Res. 2014 .

[8]   Stephens B, Azimi P, El Orch Z, Ramos T. Ultrafine particle emissions from desktop 3D printers. Atmos Environ. 2013;79:334–9.

[9]   Turner BN, Strong R, Gold SA. A review of melt extrusion additive manufacturing processes: I. Process design and modeling. Rapid Prototyp J. 2014;20(3):192–204.

[10] Gebler M, Uiterkamp A, Visser C. A global sustainability perspective on 3D printing technologies (vol 74, p. 158, 2014). Energy Policy. 2015;85:511.

[11] Garlotta D. A literature review of poly(lactic acid). J Polym Environ. 2001;9(2):63–84.

[12] Al-Itry R, Lamnawar K, Maazouz A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. Polym Degrad Stabil. 2012;97(10):1898–914.

[13] Pelegrini K, Donazzolo I, Brambilla V, Grisa AMC, Piazza D, Zattera AJ, et al. Degra-dation of PLA and PLA in composites with triacetin and buriti fiber after 600 days in a simulated marine environment. J Appl Polym Sci. 2016;133(15):43290.

[14] Tan BK, Ching YC, Poh SC, Abdullah LC, Gan SN. A review of natural fiber reinforced poly(vinyl alcohol) based composites: Application and opportunity. Polymers. 2015;7(11):2205–22.

[15] Leigh SJ, Bradley RJ, Purssell CP, Billson DR, Hutchins DA. A simple, low-cost conductive composite material for 3D printing of electronic sensors. PLoS One. 2012 ; 7(11).

[16] McCarthy B, Coleman JN, Curran SA, Dalton AB, Davey AP, Konya Z, et al. Observation of site selective binding in a polymer nanotube composite. J Mater Sci Lett. 2000;19(24):2239–41.

[17] Gao YL, Zhai QJ, Barrett R, Dalal NS, Kroto HW, Acquah SFA. Piezoelectric enhanced cross-linked multi-walled carbon nanotube paper. Carbon. 2013;64:544–7.

[18] Steven E, Saleh WR, Lebedev V, Acquah SFA, Laukhin V, Alamo RG, et al. Carbon nanotubes on a spider silk scaffold. Nat Commun. 2013 ;4.

[19] Ventura DN, Stone RA, Chen KS, Hariri HH, Riddle KA, Fellers TJ, et al. Assembly of cross-linked multi-walled carbon nanotube mats. Carbon. 2010;48(4):987–94.

[20] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. Compos Sci Technol. 2009;69(10):1486–98.

[21] Celzard A, McRae E, Deleuze C, Dufort M, Furdin G, Marêché JF. Critical concentration in percolating systems containing a high-aspect-ratio filler. Phys Rev B. 1996;53(10): 6209–14.

[22] Bai JB, Allaoui A. Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites —experimental investigation. Compos A Appl Sci Manufact. 2003;34(8):689–94.

[23] Martin CA, Sandler JKW, Shaffer MSP, Schwarz MK, Bauhofer W, Schulte K, et al. Formation of percolating networks in multi-wall carbon-nanotube–epoxy composites. Compos Sci Technol. 2004;64(15):2309–16.

[24] Mahfuz H, Khan MR, Leventouri T, Liarokapis E. Investigation of MWCNT reinforcement on the strain hardening behavior of ultrahigh molecular weight polyethylene. J Nanotechnol. 2011;2011:9.

[25] Smook J, Pennings AJ. Suspension spinning of ultrahigh molecular-weight polyethylene. Polym Bull. 1983;10(7–8):291–7.

[26] Pakhomov PM, Golikova AY, Khizhnyak SD, Shavyrina MA, Galitsin VP, Gribanov SA, et al. The structure of high-strength ultrahigh-molecular-weight polyethylene fibres fabricated by the gel-spinning method. Fibre Chem. 2006;38(3):200–6.

[27] Daver F, Baez E, Shanks RA, Brandt M. Conductive polyolefin-rubber nanocomposites with carbon nanotubes. Compos A Appl Sci Manufact. 2016;80:13–20.

[28] Besco S, Modesti M, Lorenzetti A, Donadi S, McNally T. Effect of modified clay on the morphology and electric properties of PC/ABS-MWCNT composites. J Appl Polym Sci. 2012;124(5):3617–25.

[29] Ji MZ, Deng H, Yan DX, Li XY, Duan LY, Fu Q. Selective localization of multi-walled carbon nanotubes in thermoplastic elastomer blends: An effective method for tunable resistivity-strain sensing behavior. Compos Sci Technol. 2014;92:16–26.

[30] Sun Y, Guo Z-X, Yu J. Effect of ABS rubber content on the localization of MWCNTs in PC/ABS blends and electrical resistivity of the composites. Macromol Mater Eng. 2010;295(3):263–8.

[31] Wu D, Zhang Y, Zhang M, Yu W. Selective localization of multiwalled carbon nanotubes in poly(ε-caprolactone)/polylactide blend. Biomacromolecules. 2009;10(2):417–24.

[32] Pötschke P, Pegel S, Claes M, Bonduel D. A novel strategy to incorporate carbon nanotubes into thermoplastic matrices. Macromol Rapid Commun. 2008;29(3):244–51.

[33] Olalde B, Aizpurua JM, Garcia A, Bustero I, Obieta I, Jurado MJ. Single-walled carbon nanotubes and multiwalled carbon nanotubes functionalized with poly(L-lactic acid): a comparative study. J Phys Chem C. 2008;112(29):10663–7.

[34] Vatani M, Lu Y, Lee K-S, Kim H-C, Choi J-W. Direct-write stretchable sensors using single-walled carbon nanotube/polymer matrix. J Electr Packag. 2013;135(1):011009.

[35] Davenport M. Twists and shouts: A nanotube story. Chem Eng News. 2015;93(23):10–5.

[36] Barletta M, Puopolo M, Tagliaferri V, Vesco S. Graphene-modified poly(lactic acid) for packaging: Material formulation, processing and performance. J Appl Polym Sci. 2016 ; 133(2).

[37] Huang X, Qi XY, Boey F, Zhang H. Graphene-based composites. Chem Soc Rev. 2012;41(2):666–86.

[38] Wei XJ, Li D, Jiang W, Gu ZM, Wang XJ, Zhang ZX, et al. 3D printable graphene composite. Sci Rep. 2015 ;5.

[39] Kim JH, Chang WS, Kim D, Yang JR, Han JT, Lee GW, et al. 3D printing of reduced graphene oxide nanowires. Adv Mater. 2015;27(1):157–61.

[40] Soares BG, Touchaleaume F, Calheiros LF, Barra GMO. Effect of double percolation on the electrical properties and electromagnetic interference shielding effectiveness of carbon-black-loaded polystyrene/ethylene vinyl acetate copolymer blends. J Appl Polym Sci. 2016 ;133(7).

[41] Reboul JP, Moussalli G. About some DC conduction processes in carbon-black filled polymers. Int J Polym Mater. 1976;5(1–2):133–46.f

[42] Balberg I. A comprehensive picture of the electrical phenomena in carbon black–polymer composites. Carbon. 2002;40(2):139–43.

[43] Balberg I. Tunneling and nonuniversal conductivity in composite-materials. Phys Rev Lett. 1987;59(12):1305–8.

[44] Rubin Z, Sunshine SA, Heaney MB, Bloom I, Balberg I. Critical behavior of the electrical transport properties in a tunneling-percolation system. Phys Rev B. 1999;59(19):12196–9.

[45] Sichel EK, Gittleman JI, Sheng P. Transport properties of the composite-material carbon-poly(vinyl chloride). Phys Rev B. 1978;18(10):5712–6.

[46] Ning F, Cong W, Qiu J, Wei J, Wang S. Additive manufacturing of carbon fiber reinforced thermoplastic composites using fused deposition modeling. Compos B Eng. 2015;80:369–78.

[47] Kang H-W, Lee SJ, Ko IK, Kengla C, Yoo JJ, Atala A. A 3D bioprinting system to produce human-scale tissue constructs with structural integrity. Nat Biotech. 2016;34(3):312–9.

[48] Paggi RA, Beal VE, Salmoria GV. Process optimization for PA12/MWCNT nanocomposite manufacturing by selective laser sintering. Int J Adv Manuf Technol. 2013;66(9–12):1977–85.

[49] Athreya SR, Kalaitzidou K, Das S. Microstructure, thermomechanical properties, and electrical conductivity of carbon black-filled nylon-12 nanocomposites prepared by selective laser sintering. Polym Eng Sci. 2012;52(1):12–20.

[50] Makuch A, Trzaska M, Skalski K, Bajkowski M. PA-G composite powder for innovative additive techniques. Compos Theory Pract. 2015;15(3):152–7.

[51] Varotto A. Global markets for 3D printing. BCC Res. 2015. Report No.: IAS102A.

[52] Liu H, Webster TJ. Enhanced biological and mechanical properties of well-dispersed nanophase ceramics in polymer composites: From 2D to 3D printed structures. Mater Sci Eng C. 2011;31(2):77–89.

[53] Penkova AV, Acquah SFA, Dmitrenko ME, Sokolova MP, Mikhailova ME, Polyakov ES, et al. Improvement of pervaporation PVA membranes by the controlled incorporation of fullerenol nanoparticles. Mater Des. 2016;96:416–23.