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Fabrication of Polylactide/Carbon Nanopowder Filament using Melt Extrusion and Filament Characterization for 3D Printing

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In this study, less expensive mesoporous nano carbon (NC) infused in polylactide (PLA) thermoplastic filaments were fabricated to improve the electrical properties and maintaining sufficient strength for 3D printing. Solution blending was used for PLA-NC nanocomposite fabrication and melt extrusion was employed to make cylindrical filaments. Mechanical and electrical properties of 1–20 wt.% of NC-filaments were investigated and significant improvement of conductivity (3.76 S/m) and sufficient yield strength (35 MPa) were obtained. SEM images exhibited uniform dispersion of NC in polymer matrix and DSC results showed no significant changes in the glass transition temperature (Tg) for all the compositions. Perspective uses of this filament are for fabrication of electrical wires in 3D printed robots, drones, prosthetics, orthotics and others.

Keywords: Mesoporous carbon nanoparticles; conductive filament; 3D printing; thermoplastic composite; polylactide (PLA); robotics.

1. Introduction

3D printing is an additive manufacturing process that allows fabrication of objects directly from computer aided design (CAD) models and nowadays, it is becoming popular for the realization of physical models utilizing several materials such as polymer, metals, composites, etc. In 3D printing, parts are fabricated by bottom-up approach, forming one layer over another through computer control. The method of forming this layer depends upon the type of 3D printing. In a fused deposition modeling (FDM) technique, materials are added layer by layer by melting thermoplastics at an elevated temperature. FDM is the most widely used 3D printing technique due to its low operation cost, simplicity, almost no loss of material and easy operation. Complex shapes can be fabricated very easily by 3D printing, therefore, it is becoming a dominant choice for fabrication of humanoid robots,[1–4] prosthetics,[5–7] orthotics[8] and others.[9,10]

FDM process requires thermoplastic filament materials, printer head with heater and trajectories

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of the model being processed. Filaments are prepared by several methods and one of them is melt extrusion. In melt extrusion, a raw material, usually a polymer or a polymer blend, is melted by heat and forced to pass through an orifice by pressure, thus, creating a desired cross section. Most of the filaments used in 3D printing are fabricated by melt extrusion, using circular orifice, thus, making long cylindrical filaments.

Nanomaterials are often infused in a thermoplastic polymer as an additive because of their unique properties, which allow them to make functional and modified properties in their composite filament forms. Typical size of nanomaterials ranges from 1 nm to 100 nm in dimension. Materials at nanometer scale have unique properties compared to their millimeter and micrometer sized counterparts. Commonly used additive nanoparticles can be divided into three categories: (a) Metal nanoparticles such as gold, silver, zinc, copper nanoparticles.[11] (b) Ceramic and silicate nanoparticles, which include Nano Si, SiO_2, TiO_2.[12] (c) Carbon based nanomaterials such as nano carbon (NC) particles, carbon nanotube (CNT) and carbon nanofiber (CNF).[13] Single walled carbon nanotube (SWCNT) and multi walled carbon nanotube (MWCNT) are commonly used as additives in polymer composites. Mesoporous Nano Carbon known as NC is nano-sized porous carbon particle having diameter less than 500 nm. NC is widely used as a cheap substitute for CNT since 5 g of NC costs \$137 whereas 5 g CNT costs \$876 (Sigma-Aldrich current price as of Dec 31, 2016).

Several researches are being made in nanocomposites to improve their properties by adding nano materials. Sun *et al.*[14] studied the dispersion of nickel nanostrands (NiNS) in different polymer matrix and reported uniform dispersion of NiNS in thermoplastic polymer matrix. The study implemented solution mixing to form nanocomposites fabrication, and the composite showed good electrical conductivity of 10^{-3} S/m. Bhati *et al.*[15] showed enhancement of electrical conductivity of poly (3,4-ethylene dioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) as high as 33 S/m through the treatment of acids. Nanocomposites can also be fabricated by chemical functionalization of either polymer[16] or additive.[17] In another study by Jiang *et al.,*[18] polylactide (PLA) nanocomposites were prepared with nano-sized precipitated calcium carbonate (NPCC) and organically modified montmorillonite (MMT). They used melt extrusion for preparation of nanocomposite. Breuer and Sundararaj[13] reviewed several host polymer materials such as polypropylene (PP), nylon, polystyrene (PS), polycarbonate (PC), poly methyl methacrylate (PMMA) and polyamide (PA), and filler materials such as vapor grown carbon fiber (VGCF), SWNT and MWNT, and reported the electrical conductivity obtained from these materials with reference to the percolation threshold of the filler materials. CNT nanocomposites with different thermoplastics fabricated by melt extrusion,[19–21] direct melt mixing,[22–24] and special methods[25] have also been reported by several scholars in recent years.

Review works have been presented that emphasize the benefits and challenges of nanomaterials in the FDM. Ivanova *et al.*[26] summarized some available nanocomposites and their use in additive manufacturing including metal, CNT, carbon fiber, silicate and other semi-conductor filled nanocomposites. This study also described inherent challenges of merging additive manufacturing with nanocomposite. Most of the researches done in 3D printing of nanocomposites were focused on improving mechanical properties of the printed part. In general, only few studies are available that focus on improving the electrical and mechanical properties of filament by using nanocomposite polymer. We are interested in investigating multifunctional materials that can be used for structural, electrical and thermal applications, particularly focusing on the former two properties. In recent years, researchers are focusing on incorporating functional nanocomposite filaments in low cost 3D printers. Corcione *et al.*[27] demonstrated the possibility of using a 3D printed nanocomposite as a bone substitute. They used PLA-nanohydroxyapatite (PLA-nanoHA) composite filament fabricated by dual melt extrusion for 3D printing of molar tooth. Leigh *et al.*[28] reported a nanocomposite made by solution mixing of carbon black (CB) filler in polycaprolactone (PCL), called "carbomorph". They used this composite for 3D printing electronic sensors and conductive circuit printing. In another very recent study, Yu *et al.*[29] showed printing CNT and graphene fillers in the nanocomposite of PLA made by repeated melt blending. In a recent paper, our group[30] reported similar filament of PLA-NC fabricated by casting the solution in a rubber tube and slicing the tube after drying, which is a slightly different fabrication process that is discussed in this paper. Rubber tube casting method is useful for mixing different fillers uniformly in host polymer material in liquid state; however, it has limitation such as small filament length and lower mechanical properties. This worked reported 4 times more conductive filament with significant improvement in mechanical strength. Table 1 summarizes the achievements obtained by using various filler materials in a host material along with the material processing methods used in each case.

In this paper, composite filaments were made by using PLA and NC by melt extrusion process. PLA was used as the host substrate polymer since it is being used in many commonly used 3D printers, which can be easily replaced by other polymer like ABS, PC, and HDPE, etc. NC/PLA composite was first prepared and then used for filament fabrication. Detailed fabrication procedure is discussed in the experiment section of this paper. Mechanical,

Table 1. A glimpse of nanocomposite and fabrication methods from prior research reports.

Host material	Nano filler	Processing method	Property improved	Reference
PP	Organic modified mmt (o-mmt)	Chemical process were used	Mechanical (Young's modulus 660 MPa to 1040 MPa at 5% filler, yield strength from 29 to 31 at 2% filler) properties were improved	16
Styrene-b-(ethylene-co-butylene)-b-styrene (SEBS)	f-SWCNT	Solvent casting	2.7 times increase in modulus and 1.3 times increase in breaking stress	17
PLA	Montmorillonite (MMT), NPCC	Melt extrusion	Strain at break, tensile strength and Young's Modulus were improved	18
ABS	Carbon Nanotube, CNT	Mixed then melted with mechanical stirring and then injection molding	21.3% improvement in sound transmission loss and 18.5% improvement in stiffness	13
Polymorph thermoplastic	Carbon Black CB	Solution blending method	No property other than conductivity was discussed	28
PE	CNT	Dried material were extruded using mini-twin screw extruder at 70°C for 10 hr	Slight increase in yield strength but decrease in ultimate strength and strain. Also resistivity, thermal properties, strong modulus, complex viscosity, loss modulus were reported	21
PP	CNT	Special pan-milling for powder preparation than melt mixed in twin roll masticator	Mechanical Properties (tensile strength unchanged, yield strength 21 MPa to 27 MPa, Young's modulus 837 MPa to 1140 MPa, Strain from 716 to 791) were improved	25
PA6+ABS	pMWCNT/ fMWCNT	Using twin screw micro compounder	Electrical, rheological properties (Strong Modulus, complex viscosity, etc.) were reported	19
PA+ABS	CNT/Carbon black (CB)	Two step extrusion using co-rotating twin extruder	Mechanical, electrical, viscoelastic properties were reported	20
HDPE	MWCNT	Direct melt mixing	Mechanical properties (stiffness, peak load, work to failure) were improved	23
PLA	Nanohydro-xyapatite (HA)	Dual melt extrusion	Improvement in mechanical properties	27
PLA	Graphene/CNT	Dual melt extrusion	10^{17} times improvement in electrical conductivity compared to pure PLA and in certain cases improve mechanical properties	29
PLA	NC	Casting the solution in a rubber tube and slicing the tube after drying	Improved electrical properties	30

electrical and thermal properties of prepared filaments were examined using material characterization as well as the dispersion of NC in polymer matrix was investigated by scanning electron microscopy (SEM).

2. Experiment

2.1. *Materials*

Polylactic Acid (*PLA*): PLA fiber used in this study was supplied by MakerBot Corporation, USA. It was 1.75 mm in diameter icicle blue color roll. PLA was cut in small pieces of about 2–3 cm by scissor. *Nano Carbon* (*NC*): Mesoporous carbon, generally known as NC, was supplied by Sigma-Aldrich Corporation, USA. NC had < 500 nm particle size and $> 99.95\%$ trace metals basis. NC had specific surface area of 50–100 m^2/g and pore density of 0.25 cm^3/g.
Dichloromethane solvent (*DCM*): DCM was obtained from Sigma-Aldrich and it was used as a solvent for dissolving PLA.

2.2. *Nanocomposite preparation*

As mentioned before, solution mixing was used for composite fabrication. Measured weight of PLA was added into DCM (1:5 w/v ratio) in an air tight glass bottle and heated at 80°C on IKA C-MAG HS4 heating plate with magnetic stirring. Once PLA was completely dissolved, NC at different concentration was added into the solution and stirred about 30 min uniformly for good dispersion. When NC dispersed uniformly, the solution was poured into aluminum dishes and kept overnight for drying in ventilated fume hood. The composite in liquid form before drying is shown in Fig. 1. The prepared composite was labeled as PLAx%NC, where x is the percent weight of NC added in PLA-DCM solution. This also represents the weight ratio of NC to PLA in the composite filament.

2.3. *Melt extrusion*

Melt extrusion of the prepared composite samples was done using single screw extruder 'Filastruder', purchased from filastruder Snellville, Georgia. It had a 20.3 cm (8 inch) long 22.2 mm (7/8 inch) in diameter screw. The Screw shaft was coupled to 12 V motor by a belt which was connected to a power supply. The prepared composites were cut into small pieces of 2-3 mm and fed into the hopper of the extrusion apparatus. Extrusion was done at 180°C temperature through an orifice that had a diameter of 1.75 mm. It is known that most commonly used filament materials are of diameter 1.75 mm and this is one of the reasons for selecting the orifice size of the nozzle. After a few experiments, it was found that a minimum of 10 g of composite was required for complete formation of filament extruded out of the nozzle, and all extrusions were done with 10 g sample as shown in Fig. 1.

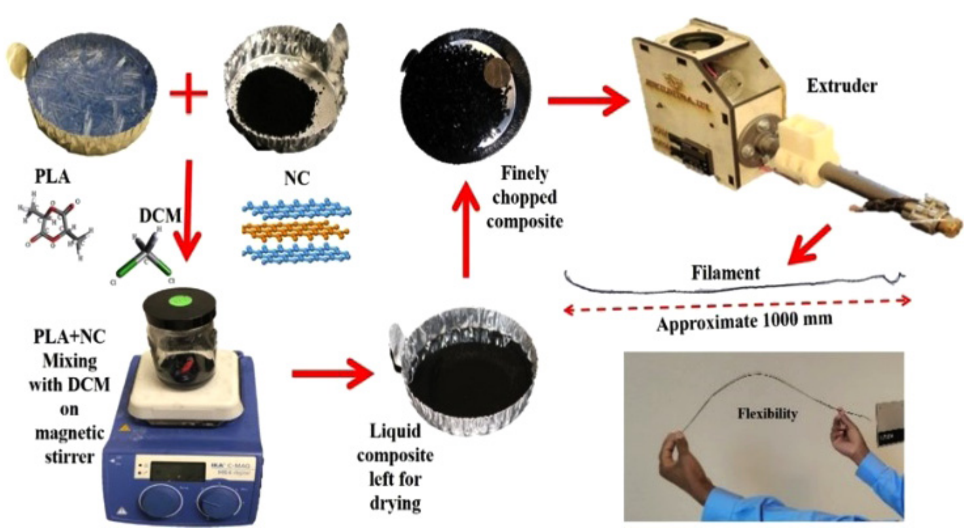


Fig. 1. Layout of filament fabrication process of nanocomposite by melt extrusion: mixing of PLA with DCM (1:5 w/v ratio) in airtight glass bottle, heated at 80°C and stirred magnetically. Once PLA was completely dissolved in DCM, NC was added, and stirred for uniform dispersion. The composite solution was dried in ventilated fume hood, cut into small pieces and fed into hopper for extrusion.

2.4. *Filament characterization*

The fabricated filaments were tested using standard material characterization, including electrical conductivity, tensile test, scanning electron microscopy and thermo-mechanical test.

Electrical conductivity
Electrical conductivity of the prepared samples was calculated by an indirect method. First, resistance between two points was measured using a multimeter (EXTECH MG300 Multimeter) considering the distance between the points and the area of the fabricated filament. The resistivity of the sample was then determined using the standard equation. The conductivity was then calculated by taking inverse of the resistivity. The resistance of a material can be determined from the following relationship:

$$\sigma = \frac{1}{\rho} = \frac{l}{RA}, \tag{1}$$

where σ is conductivity, ρ is resistivity, R is resistance, A is cross-sectional area and l is length of the sample.

Tensile testing
The prepared filaments were tested on INSTRON 5969 electromechanical universal testing machine to understand filament's mechanical behavior when an axial load is applied to it. The tensile load was applied on the sample and the elongation was recorded using Blue Hill software. Three samples ($N = 3$) for each composite were tested. The data obtained from the testing were used to plot load versus elongation for different NC% filaments.

The tensile stress, strain and modulus of the filament material can be determined from the following relationship:

$$\sigma_T = \frac{F}{A} = \frac{4F}{\pi D^2} = E\varepsilon, \tag{2}$$

where σ_T is tensile stress, F is the applied force, A is cross-sectional area and D is diameter, E is the modulus of the sample ε and is the strain.

Scanning Electron Microscopy (SEM)
To understand the dispersion of NC in the polymer matrix, SEM images of the prepared filament were taken. The SEM imaging was done using Zeiss-LEO Model 1530 Variable Pressure Field Effect Scanning Electron Microscope at NanoTech Institute, The University of Texas at Dallas (UTD). The SEM images were captured without any preprocessing of the sample surface.

Thermomechanical analysis
Thermomechanical properties of the prepared samples were measured using differential scanning calorimetry (DSC). TA instrument Q2000 differential scanning calorimeter was used for all measurements. Heating-cooling-heating cycle was used for taking DSC measurement. Midpoint of first transition stage in second heating cycle was recorded as glass transition temperature (T_g) while the peak temperate at melting transition in first heating cycle was taken as melting temperate (T_m), 15°C/min rate of heating and cooling was used for all the measurements.

3. Result and Discussion

3.1. *Electrical conductivity*

As mentioned before, the conductivity of fabricated filaments was calculated by an indirect method. Resistance was measured at multiple small sections and converted into conductivity using Eq. (1). The average value of resistivity and conductivity for different filaments are listed in Table 2. The resistance measured for PLA1%NC, PLA2%NC and PLA6%NC was found to be infinite, suggesting zero conductivity. The resistance dropped drastically when NC percentage was increased from 10% to 15%, suggesting percolation threshold between 10% and 15%. The resistivity and conductivity for higher NC% are plotted in Fig. 2.

3.2. *Tensile testing*

Each composite filament was tested to study tensile characteristics. Several filament samples of each composition were tested and stress versus strain

Table 2. Average resistivity and conductivity of prepared filaments.

Name	Resistivity* (ohm-m)	Conductivity (S/m)
PLA1%NC	∞	0
PLA2%NC	∞	0
PLA6%NC	∞	0
PLA10%NC	83.40 ± 22.37	0.01 ± 0.01
PLA15%NC	0.97 ± 0.39	1.18 ± 0.46
PLA20%NC	0.28 ± 0.06	3.76 ± 0.84

Note: *Resistivity value ∞ means resistance is very large which is beyond multimeter's limit.

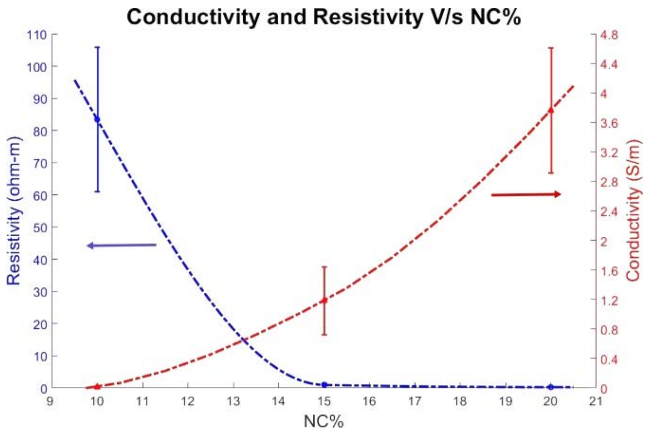


Fig. 2. Resistivity and conductivity versus NC% for different filaments. Measurements were taken from eight samples for each composition, the average and standard deviation (error bar) are reported here.

graphs were plotted (Fig. 3). To clearly understand how the increase in NC% affects the mechanical properties of the filament, the mean yield stress at break for each filament with NC% was also plotted (Fig. 4). The tensile strength of pure PLA from the vendor MakerBot is 46 MPa (std) and 65 MPa (max). Other resources such as Jiang *et al.* stated that it is 60 MPa[18] and we also measured it and confirmed the range to be 60 MPa. It was clearly seen that tensile strength was reduced significantly from 60 MPa[18] to ~24 MPa for 1%NC filament. There is a small increase in strength when NC was increased from 1% to 2% (~27 MPa for PLA 2%NC filament), however, with further increase in NC% (up to 10%), the strength was reduced. The strength was minimum for PLA10%NC filament,

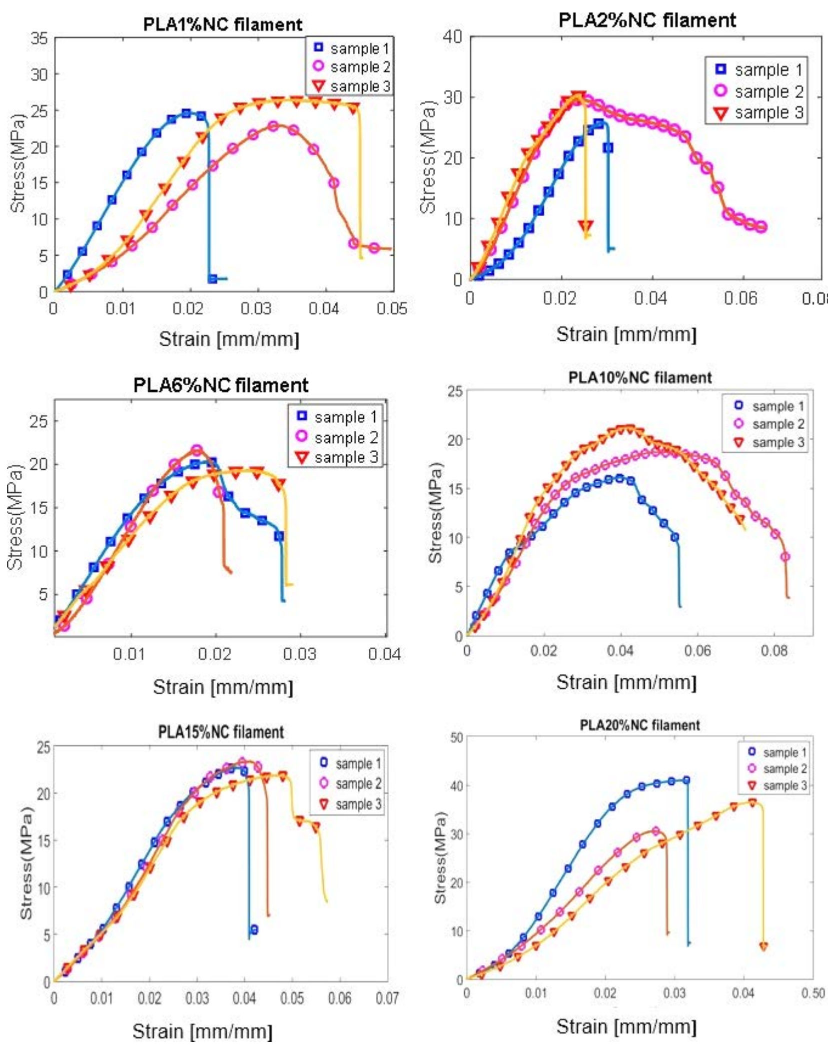


Fig. 3. Tensile testing results for different NC % filaments. Three samples from each composition were used for the measurement. The samples were cut from a long filament due to which had slight different diameter that are in the range of 1.6–1.8 mm and length variation from 26 mm to 37 mm. The stress is the normalized force by area as described by Eq. (2) and the strain is the ratio of displacement to the original length of the filament.

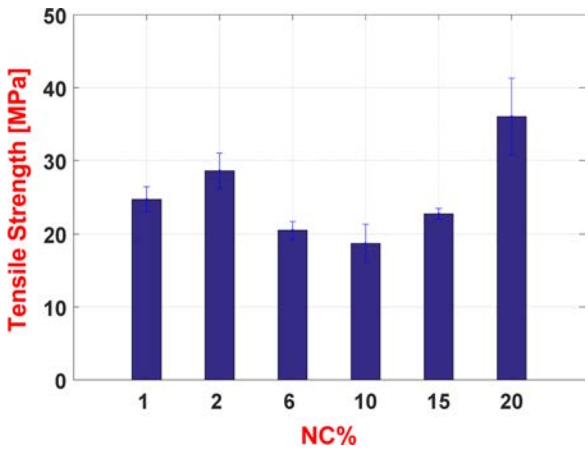


Fig. 4. Mean tensile stress at yield (yield strength) of PLA-NC filament at various concentration of NC. Error bars in this figure are standard deviation of tensile stress at yield for three samples.

which was ~17 MPa. The strongest filament was obtained for 20% NC loading, which reached a tensile strength of ~36 MPa. Several small samples for each NC% filament were tested (at least 3 samples for each composition). One of the reasons for the less strength for all compositions 1–20% NC compared to the original PLA filament as received could be the weakening of the polymeric chain of the PLA by the DCM. The trend of the strength, which increases and decreases and again increases as the percentage of NC is increased (Fig. 4), is not known and needs further investigation. More samples should be tested for different compositions and different filler materials. Improvement in mechanical strength was observed in many nanomaterials which were used as a filler in thermoplastics as discussed in Table 1. Even though there is a decrease in strength from the original PLA filament (as received), the increase in NC loading from 10%, 15%, and 20% NC showed an increase in strength (Fig. 4), these results are consistent with other studies due to the chemical bonding between the groups in the PLA and the molecules in the filler nanomaterials.[31] Detailed study such as XRD patterns should be done to examine further.

The samples used for tensile test were cut from a long filament due to which, the samples had slightly different diameter that are in the range of 1.6–1.8 mm and length variation from 26 mm to 37 mm. However, the stress in (Fig. 3), is the normalized value i.e., the force divided by the area as described by Eq. (2), and the strain is the ratio of displacement by the original length of the sample during tensile testing. In a related study, Jahantigh and Nazirzadeh showed the elastic modulus and tensile strength of the composite of polycarbonate (PC) and Titanium oxide (TiO_2) nanocomposite increased slightly with increasing weight fraction of nanoparticles.[12]

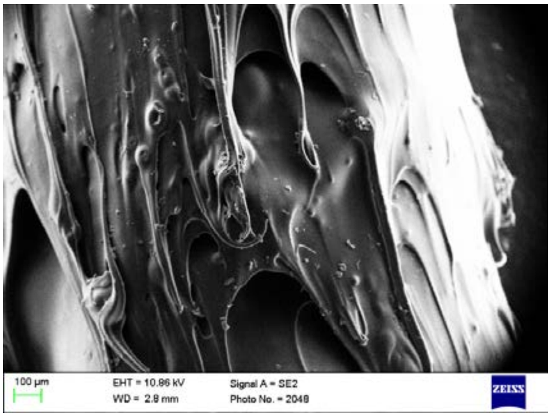
3.3. *Scanning electron microscopy*

Figure 5(a) shows SEM image of PLA15%NC at low resolution. This image shows presence of pores in the filaments created while extruding out of the extruder machine. When the composite was extruded, bubble formation was noticed such that a small size bubble was coming out from the filament surface. It can be concluded that some amount of DCM was present in the composite even after drying in air for 12 h and the bubbles formed while DCM was escaping from filament surface at the time it was leaving the extruder nozzle. Figures 5(b) and 5(c) are low resolution SEM images for PLA10%NC and PLA20%NC filament, respectively, which also confirm presence of pores in the filament. Low content of NC (1%, 2% and 6% NC) are not presented as the image SEM images were completely dark and excluded from the results (Figs. 5 and 6). All of SEM images presented here were taken without any preprocessing of the filaments.

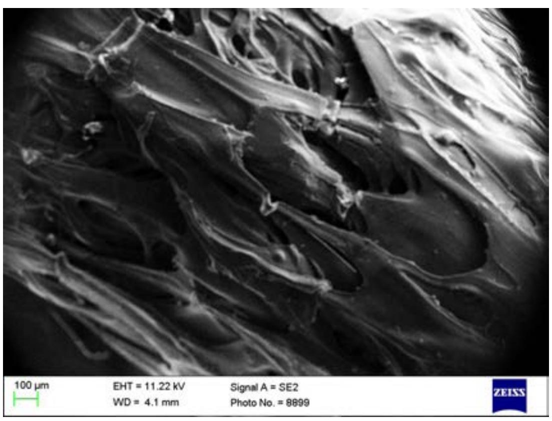
Figures 6(a) and 6(b) are SEM images for PLA15%NC and PLA20%NC filament sample respectively. Both these images show relatively uniform dispersion of NC in the polymer matrix. Also, no cluster or coagulation of NC was present in the filaments. Comparing to the literature, our SEM images can prove that the dispersion of NC is uniform. Lee *et al.*[24] used direct melt mixing of polymer with CNT for fabrication of nanocomposite which is very similar to the fabrication method used in this work. However, they used injection molding to form disc shaped specimen which cause presence of small lumps of CNT in polymer matrix, but, in this paper, there is no lump observed even at high loading (15% and 20%).

3.4. *Differential scanning calorimetry*

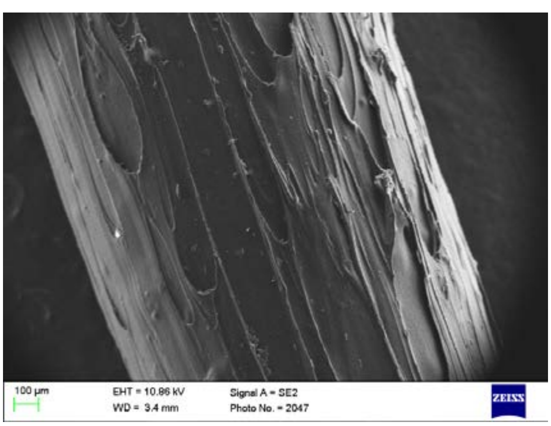
The prepared filament samples were tested using heating–cooling–heating cycle to get transition temperatures. Heat flow versus temperature graph for the first and the second heating cycles are shown in Figs. 7 and 8, respectively. As the percentage of NC increases, the heat flow increases and the curve



(a)

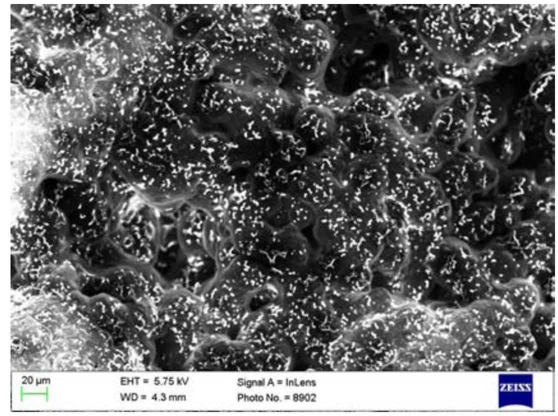


(b)

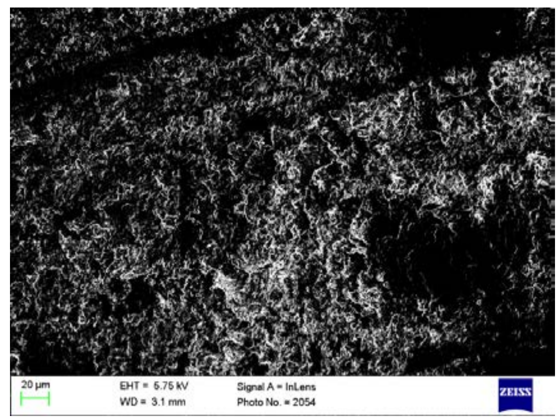


(c)

Fig. 5. SEM images of prepared filaments (a) at surface of PLA15%NC filament, (b) at surface of PLA10%NC filament, (c) at surface of PLA20%NC filament.



(a)



(b)

Fig. 6. Magnified SEM images of prepared filaments (a) PLA15%NC filament, (b) PLA20%NC filament.

moves upwards. Since the filament needs to be heated above its glass transition temperature (T_g) then cooled to room temperature after printing, T_g is the most vital parameter for any FDM filament. T_g for the composite filament should be the same (or near to) base material so that it can be used in place of the base filament directly without any change in setting of printer. Another important aspect for FDM filament is melting temperature (T_m). The melting temperature should not be changing significantly with addition of filler. It is to be noted that the melting temperature of

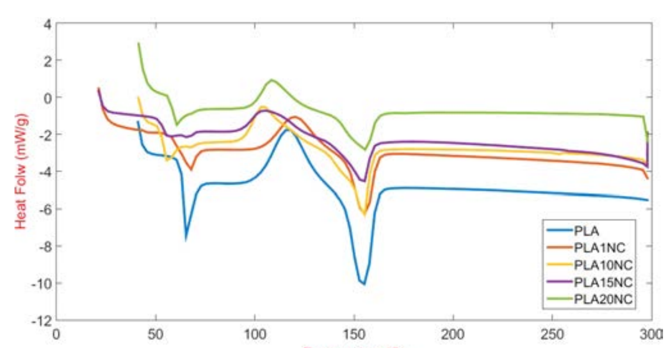


Fig. 7. DSC curves for different filament samples during first heating cycle.

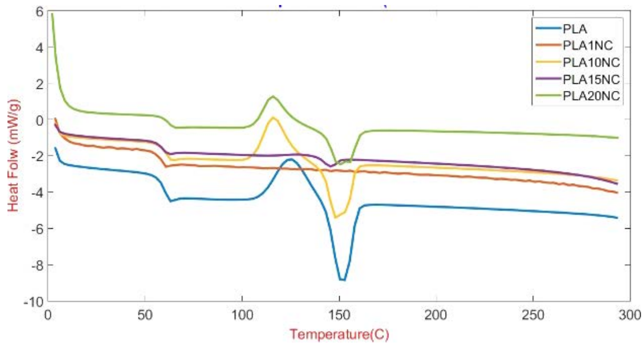


Fig. 8. DSC curves for different filament samples during second heating cycle.

Table 3. Glass transition temperature and melting temperature obtained from DSC data.

S. no.	Sample name	Tm (°C)	T_g (°C)
1	PLA	155.2	59.35
2	PLA1NC	155.38	59.4
3	PLA10NC	155.39	61.92
4	PLA15NC	155.39	59.35
5	PLA20NC	155.61	62.17

nanocarbon (approximately 3500°C) is much higher than PLA and since filler content is small, it should not affect the melting temperature. The T_g increases as the NC% is increased except the slight variation of the PLA15% NC sample which might be due to error in measurement. The test was done on one sample and the variation is not very much significant. All transition temperatures obtained after analyzing DSC plots are summarized in Table 3. We focused on NC 10% to 20% since good conductivity and strength were obtained in these compositions.

4. Discussion

From the results presented in the previous section, it is very clear that high NC% filaments had very good conductivity while lower NC% filaments had almost zero conductivity. Average unit length resistance for PLA20%NC filament was $1.28 \pm 0.27 \times 10^5\,\Omega/\text{m}$ equivalent to resistivity of 0 $.278 \pm 0.065\,\Omega - \text{m}$ and conductivity of $3.76 \pm 0.84\,\text{S/m}$, which is comparable to electrical properties of salt water. There are few conductive filaments available commercially. For example, composite PLA-electrically conductive graphite[32] has resistivity of $1.15\,\Omega{-}\text{m}$, which is almost 4 times higher than the resistivity obtained in this study. However, the advantage of NC is that much higher filler percentage can be used. Another commercial ABS based conductive filament is the one supplied by Maker-geeks,[33] which has per unit resistance of $10^6\,\Omega/\text{m}$ compared to our filament which has average unit length resistance of $1.3 \times 10^5\Omega/\text{m}$. This resistance is almost 10 times higher than ours. Recently, a company, Graphene 3D Lab Inc,[34] announced a conductive graphene filament having volume resistivity of $6 \times 10^{-3}\,\Omega - \text{m}$, which is about 100 times less than resistivity reported in this paper. They stated that the composition of the filament as graphene (CAS 7782-42-5) and polylactic acid (CAS# 26100-51-6), but the percentage of the composition and other fabrication parameters are not described. Even though it is used in 3D printed structures,[35] no data related to mechanical properties of the filament is available. It was stated that the mechanical strength is higher than PLA and ABS but there is no experimental data available to compare. The Graphene-containing filaments that had good conductivity are emerging in the market and inexpensive compared with others (Conductive Graphene PLA Filament 100 g in $100, https://www.blackmagic3d.com/accessed April 2018). Another MWCNT based liquid nanocomposite was reported in a technical paper of Sigma-Aldrich Corporation[36] that showed a very high conductivity of 1200 S/m for 20% loading for MWCNT, which is much higher compared to conductivity obtained in this study. They also report the 40 MPa mechanical strength of the material. Again, the MWCNT costs a lot compared to NC and their nanocomposite can only be used in solvent-cast 3D printing which is much more complex that FDM printing.

Several researchers reported conductive nanocomposites. Sun *et al.*[22] reported ABS composite having log resistivity value of $4.5\,\Omega - \text{cm}$ equivalent to resistivity value of $316.22\,\Omega - \text{m}$, which is 1000 times higher than resistivity found in this study. Meincke *et al.*[20] presented two polymide-6(PA) based composite with carbon nanotube and carbon black filler. They reported resistivity value of $0.1\,\Omega - \text{m}$ for 16 wt.% filler of carbon nanotube. They also reported resistivity of $1\,\Omega - \text{m}$ for 20 wt.% filler of carbon black. The current resistivity mentioned in this study at 20 wt% is four times better than carbon black composite while almost half for carbon nanotube composite. Bose *et al.*[19] reported AC conductivity of 10^{-2} S/m at 5% filler loading of carbon nanotube in polymide-6(PA). McNally *et al.*[21] described resistivity value of $1000\,\Omega - \text{m}$ at

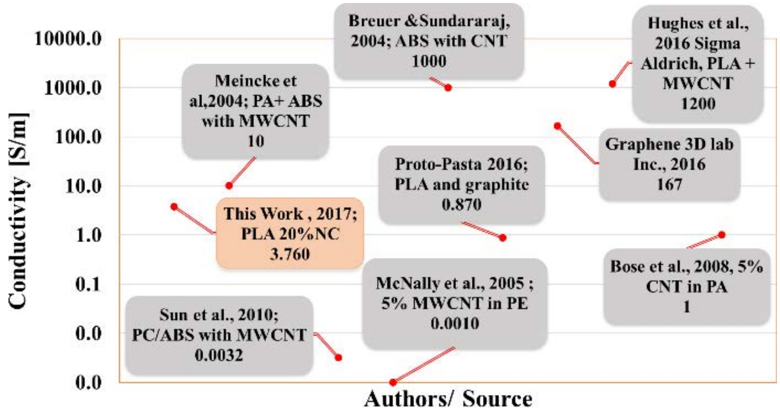
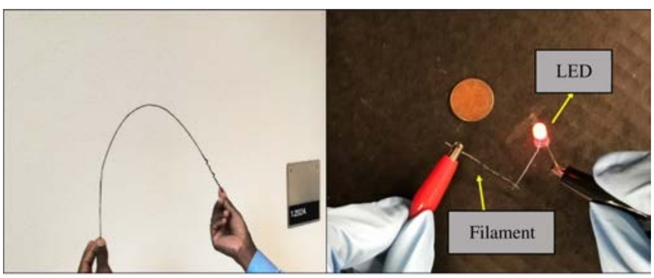


Fig. 9. Comparison of conductivity of various additives (nano filler) in host thermoplastic polymer.[13,19–22,32,34,36]



(a) (b)

Fig. 10. Flexibility and use of PLA20%NC filament (a) Flexibility of filament displayed by bending. (b) Use of filament in wiring to light LED bulb.

5 wt.% loading of MWCNT in PE. This resistivity value is 10^3 higher than what is reported here. Breuer *et al.*[13] showed several carbon nanotube polymer composites. They reported resistivity values that are similar or better than all composites, except the one that had a resistivity of 10^{-3}–$10^{-2}\,\Omega-\mathrm{m}$. This particular composite was fabricated by expensive and complex powder technology method. Figure 9 shows the comparison of conductivity values obtained from the literature and commercial filament suppliers. The plot also shows the exact magnitude of the conductivity in the third row.

Pure PLA has T_g and T_m value of 59.35°C and 155.2°C, respectively. While for PLA1%NC, PLA10%NC, PLA15%NC and PLA20%NC, the value of T_g was 59.4°C, 61.92°C, 59.35°C and 62.17°C, respectively. T_m values for PLA1%NC, PLA10%NC, PLA15%NC and PLA20%NC were 155.38°C, 155.39°C, 155.39°C and 155.61°C, respectively. T_g for all samples were within 2°C range of pure PLA. These results clearly shows that T_g was not changing too much with increase in filler content which was similar to that found in literature.[27,29] From presented data, it is clear that T_g and T_m did not change considerably with increase in filler content. This fact is very important for using

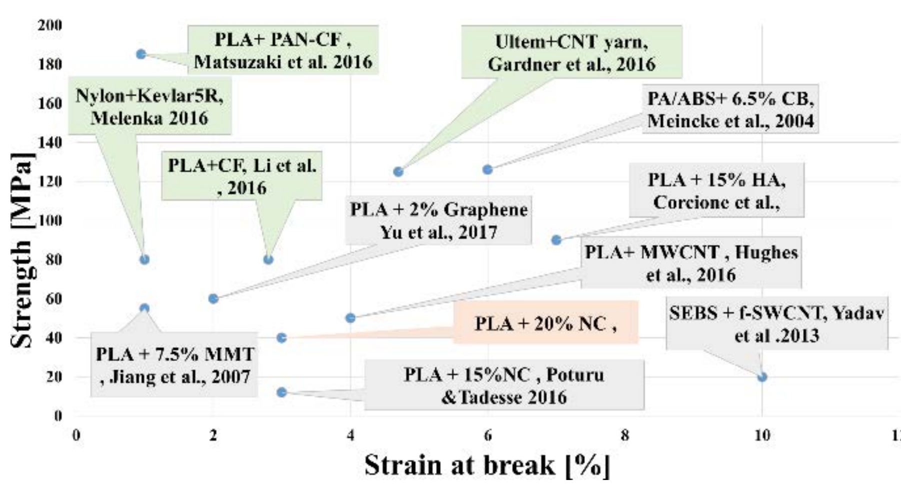


Fig. 11. (Color online) Comparison of the strength of composite conductive filaments[17,18,20,27,29,30,36] (gray) and other polymer composite consisting of fibers[37–40] (green).

this filament in commercial FDM printers and with same printing parameter as PLA.

Tensile testing of the prepared filaments showed significant drop in strength compared to PLA (yield stress of 60 MPa). This drop is because as PLA dissolved in DCM, the polymer links were broken causing loss of strength. At lower NC composition, the strength is slightly higher than middle range loading. At high loading of NC (more than 10%), the strength increases with increase in NC%. In general, the flexibility Fig. 10(a) and strength at 20%NC filler loading is enough to print electrical wiring routes and can be used to 3D print wiring lines in 3D printed robots as described in the beginning. Figure 10(b) demonstrates the use of this filament in wiring to light LED bulbs. Some portion of the filament had nonuniform cross sectional area. The nonuniformity in cross-section was due to absence of proper winding while extruding the filament. If a winder is employed with the extruder, more uniform cross sectional area of filament can be fabricated. Another comparison of the strength of the polymer materials that are conductive (grayish color) and those that consist of fibers (greenish color) are shown in Fig. 11. It can be seen that adding fibrous structure improves the strength of the composite in most cases.

5. Conclusion

A brief review of nanofiller materials in thermoplastics and other host materials was made in this paper along with the unique characteristics obtained. Composite filament consisting of carbon nanopowder (NC) in PLA matrix that ranges from 1% to 20% NC was successfully fabricated in this study using melt extrusion. The melt extrusion can be used for long filament fabrication and mass manufacturing. Mechanical, electrical and thermomechanical properties of the filaments were determined and a conductivity of $3.76 \pm 0.84\,\mathrm{S/m}$ and a mechanical strength of 36 MPa at 20% loading of NC was obtained. The glass transition temperature was not affected significantly as the NC% is increased and the SEM images showed the uniform dispersion of the nanoparticles. This conductive filament can be a promising solution for 3D printing of wire lining in robots, orthotics and prosthetics using commercial FDM printers. Further research should be done to print prototypes, determine the characteristics of the structures and the efficacy of the approach, and investigate higher concentration and other additives.

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