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Fabrication and characterization of polycarbonate-silica filaments for 3D printing applications

Deepa Kodali, Chibu O Umerah, Mohanad O Idrees, S Jeelani and Vijaya K Rangari

Abstract

Owing to its robustness, ability to achieve complex geometries, and ease of use, 3D printing has become one of the noteworthy applications in the field of engineering. Polycarbonate has become a thermoplastic of interest due to its excellent mechanical and optical properties. Especially when infused with nanosilica, polycarbonate becomes a potential candidate for 3D printing with enhanced properties. Polycarbonate nanocomposite filaments infused with AEROSIL (nanosilica) have been melt extruded with various filler loadings of 0.5, 1, and 3 wt% and are then 3D printed. The thermal analysis of the filaments has shown that thermal stability of the filaments increases with increase in filler loading. Tensile tests have shown that addition of nanosilica have enhanced the mechanical properties of the filaments as well as 3D printed films. The addition of silica in low concentrations exhibit higher transmittance of UV light, as silica restricts the mobility of polycarbonate. Despite 3D printing causing voids in bulk materials, silica at low concentration (0.5 and 1 wt%) can improve the mechanical and optical properties. These improvements are promising for applications in thin film interfaces and the automotive industry.

Keywords

3D printing, nanosilica, AEROSIL, polymer nanocomposites, polycarbonate

Introduction

Driven by the excellent properties such as extensive design freedom and high functionality while lowering the weight of the parts, additive manufacturing (AM) has revolutionized the manufacturing technology techniques.[1] The emergence of additive manufacturing (AM) techniques over the past few decades have garnered plentitude of attention from the researchers due to its undeniable contributions in the technological advancement of wide variety of industries such as aerospace, biomedical, automotive, electronics and so on.[2–4] AM also known as 3D printing can fabricate intricate parts with complex geometries with ease by using layer by layer deposition technique.[5,6] Reduced waste, energy consumption and production timing combined with inherent customizability made AM remarkable and thus made it into the spotlight research.[3,7]

According to ISO ASTM standard 52900:2015 AM techniques are categorized as vat polymerization, material jetting, binder jetting material extrusion, sheet lamination, powder bed fusion and directed energy deposition.[8,9] Owing to its simplicity and reliability, fused deposition modeling (FDM) has become the most prominent one among the various available techniques for 3D printing.[3,10] In the FDM technique, the filaments are melt and are extruded from the liquefier head and are then solidified forming the desired part.[11,12] The extrusion of the melt follows the layer by layer deposition process guided by the enumerated design from the computer-aided design (CAD) or Stereo Lithography (STL) geometry file.[13]

Due to the freeform fabrication ability of FDM, thermoplastics are widely used in FDM process because of their flexibility to be converted into

Department of Materials Science and Engineering, Tuskegee University, USA

Corresponding author:
Vijaya K Rangari, Department of Materials Science and Engineering, Tuskegee University, Tuskegee, AL 36088, USA.
Email: vrangari@tuskegee.edu

filaments with desired sizes.[14] Moreover, the filament softening and extrusion characteristics of the thermoplastics enabled them for low volume applications such as in automotive, aeronautical and medical industries.[15] A comprehensive range of plastics such as polylactic acid (PLA), acrylonitrile butadiene Styrene (ABS), nylon/polyamide (PA), thermoplastic polyurethane (TPU), high impact polystyrene (HIPS) and polycarbonate (PC) are widely used for 3D printing to improve the functionality.[3,13,16,17] Although numerous advancements were made in FDM, the substandard mechanical properties of the 3D printed parts still remains as a challenge.[18] Despite the vast availability of the engineering plastics with excellent characteristics, they cannot be used in FDM because of their poor printability and unyielding processibility.[19] For instance, polyamide-6 (PA6) products have experienced warpage due to shrinkage stress accumulation.[20] PEEK, which is a high performance semicrystalline polymer can only be used to print small parts with mediocre quality because of its high melting temperature.[21] Thus the dearth of suitable materials that conforms to the existing 3D printing techniques primarily contributes to the limited performance of printed products.[22]

Numerous research efforts have been made in the preparation and characterization of nanocomposites obtained by infusion of nanofillers of different nature in polymer matrices. The homogenous dispersion of the nanofillers in transparent polymer matrices allows them to enhance their mechanical properties without compromising their optical clarity.[23] Furthermore, the reinforcement of the fillers in polymer matrices facilitates the refinement of thermomechanical properties.[24] Given that, polycarbonate (PC) based nanocomposites have become an irrefutable source for various commercial and engineering applications such as electrical, electronics, automobile, construction, marine, and aerospace applications. Owing to its strength, toughness and transparency PC is widely used for conventional applications such as safety eye glasses/shields, CDs and DVDs, automobile headlights, bullet proof windows and so on.[25] However, when PC is used in heat dissipation domains, it is prone to life time reduction with the deterioration of mechanical properties and color fading.[26] Hence, it is worthwhile to enhance the properties of PC by incorporating fillers.

The reinforcement of reduced graphene oxide as the nano-filler in PC matrix has increased its toughness, strength and notch resistance.[27] Electrical and thermal properties are enhanced when carbon is added to PC.[28] PC filled with multi-walled carbon nanotubes (CNT))/expanded graphite (eG)/CNT-eG composite powder has shown significant improvement in electromagnetic interference shielding effectiveness.[29] The scratch resistance and impact resistance of the PC has increased with the incorporation of hydrophilic nanosized silica particles.[23] Despite the efforts, with the reinforcement of various organic/inorganic fillers, there has been not much improvement in increasing the mechanical strength of PC with the minimal amount of fillers, while maintaining the optical clarity.[30] Hence, it is inevitable to focus on the development of the polymer composites to meet the existing demand for industrial applications.

Thus far, silica nanoparticles are added to the PC to understand the sound absorption phenomena[31,32] and very limited research is focused on enhancing the mechanical properties.[23] Hence, this work focuses on developing a 3D printable PC composite filament infused with AEROSIL silica. AEROSIL® silica is extensively used as a reinforcement filler material in elastomers to improve their mechanical properties and duration of life. Furthermore, it can significantly enhance the strength of the coatings even at low concentrations.[33] That being the case, the PC-silica composite filaments are extruded and are analyzed for thermal and mechanical properties. The extruded filaments are used for 3D printing to produce thin films which are further characterized and analyzed for optical and mechanical properties.

Experimentation

Materials

Polycarbonate pellets were purchased from Makrolon® LED 2245 produced by Plastics Covestro, Germany with melt flow rate at 300 °C/1.2 kg of 34 cm^3/10 min. The AEROSIL 200® was purchased from Evonik Corporation and has a specific surface area of 200 m^2/g and melting point of 1700 °C. The specifications of AEROSIL were listed in Table 1. AEROSIL 200® is hydrophilic and non-porous. A JOEL 2010 TEM was used for transmission electron microscopy (TEM) of AEROSIL at an operating voltage of 200 kV. The nanosilica was dispersed in ethanol and then administered on Cu grid for characterization.

Table 1. Product Specification of AEROSIL® 200.

Vendor	Evonik Corporation
Product number	132138
Phase structure	Amorphous
Composition	Si, O (SiO_2>99.8%)
Specific surface area	200 m^2/g
Applications	Nanosilica can be used in paints and coatings, adhesives and sealants, printing inks, cable compounds and gels, plant protection and so on.

The particle size is observed to be within the range of 15 nm to 50 nm as shown in Figure 1.

Extrusion of composite filaments

The polycarbonate pellets of 50 gms were mixed with 0.5%, 1%, and 3% of silica nanopowder and were compounded into a blend. This polymer blend was processed in an oven at 120 °C for 6 hours. The polymer blend thus obtained is taken out of the oven and is fed into the EX2 FilaBot extruder (VT, USA) continuously to extrude PC-silica composite filaments. The Fil-a-Bot extruder which is shown in Figure 2(a) is equipped with three stage single screw with progressive compression section to promote mixing capability of the material. It is provided with a hopper of 26 in^3 volume to feed the material and 1.75 mm nozzle to extrude filament. The speed control associated with the extruder helps to regulate the screw RPM and thus controls the material flow. The extrusion temperature was maintained between 260°–265°C for all the PC blends with different loadings. As the melt temperature of the origin PC pellets was 280 °C, extrusion beyond 265 °C resulted in a liquid flow with very less viscosity making it unable to extrude in the desired form. Also, the temperature plays a critical role in producing a filament with the highest transparency. The extruded PC filament was shown in Figure 2(b). The guided airpath of the Filabot uses forced convection for cooling the filament as it travels along the path. Once the filaments were cooled, they were spooled by passing through Filabot spooler. The extruded filaments were chopped into few millimeters length and were extruded again to maintain uniformity in diameter. The spooled PC filaments with 0.5 wt% and 3 wt% nanosilica are shown in Figure 2(b) and (c), respectively. The filaments with diameter of 1.5 to 1.6 mm with at least 2 to 5 meters in length were developed which are suitable for 3D printing application.

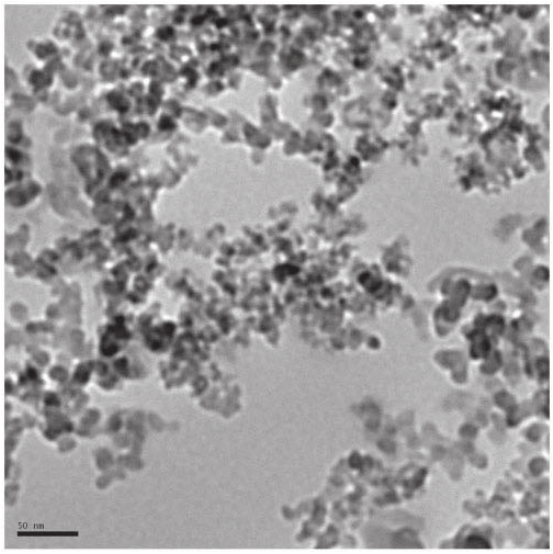

Figure 1. TEM of AEROSIL® 200.

3D Printing of thin films

The PC-silica filaments were 3D printed using Hyrel Systems 3D printer which is shown in Figure 3(a) and (b) with a bed temperature set to 90 °C and the printing temperature of 260 °C. The printing temperature was chosen depending on the viscosity of the melt filament that is suitable for printing. MK-450 hot head was used for printing the film. FreeCAD and Slic3r was used to design the samples for the printing process. The dimensions of the single layer were $120 \times 20 \times 0.11\ mm^3$. The first layer printed was in a 0° motion with the printing speed of 30 mm/s. The rectilinear infill was 100%. Retraction length was 1 mm while the retraction speed was 30 mm/s. The considered nozzle diameter

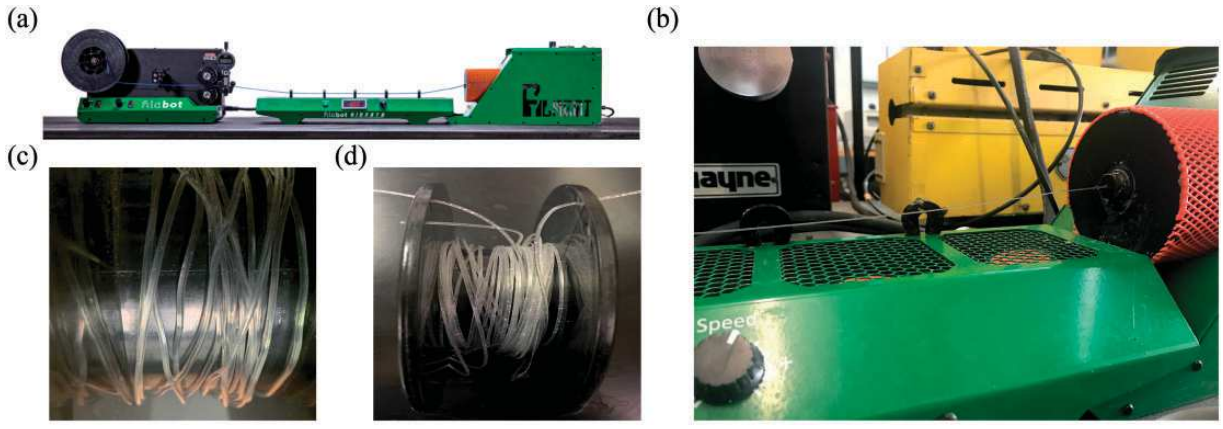

Figure 2. (a) Schematic of EX2 Filabot extruder complete set up, (b) Filabot with extruded PC filament, (c) Extruded PC-SiO_2 composite filaments with 0.5 wt% of nanosilica and (d) PC-SiO_2 composite filaments with 3 wt% of nanosilica.

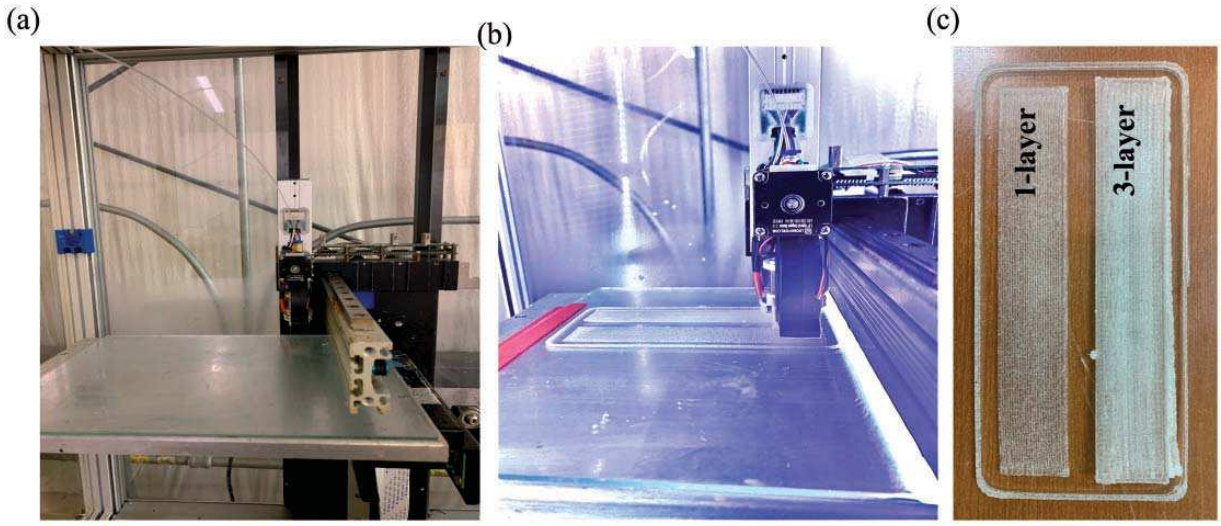

Figure 3. (a) Hyrel 3D printer set up with PC filament attached before printing, (b) Printing process of PC-SiO_2 1 wt% filament, and (c) 3D Printed PC-SiO_2 films with 1 layer and 3 layers.

was 0.6 mm to ensure the smooth feeding of the composite filaments that are reinforced with nanoparticles. The second layer was printed in 90° motion and third layer in 0°. The printed films with one-layer and three-layers are shown in Figure 3(c). Similar description of the printing technique was discussed in similar study by Umerah et al.[34] The materials were printed in such a way that they fit dimensions of ASTM D3379-75 standards.

Characterization of nanocomposites

Thermogravimetric analysis. A TA Q500 TGA was used to carry out thermogravimetric analysis (TGA) to obtain decomposition temperatures and the weight of the residue left from the heat flow of the specimens. The sample of approximately 15 mg was placed in platinum pan and is heated at a rate of 10 °C/min from 30 °C to 500 °C in the presence of nitrogen gas.

Differential scanning calorimetry. A TA Q20000 DSC was used to analyze the thermal behavior of the composite filaments. The sample of approximately 10 to 12 mg was sealed in aluminum pan and is heated at a rate of 5 °C/min from 30 °C to 380 °C and then again cooled down to 30 °C in the presence nitrogen gas.

Tensile test. The tensile test was performed using the Zwick/Roell Z2.5 Universal Mechanical Testing-Machine of 2.5 kN load cell was used to determine the mechanical properties of the filaments as well as the thin films. The composite filaments were tested following ASTM D3379-75 standard. The gage of the filament was 50 mm with the specimen length being 100 mm, the pre-load tension of 0.1 N, pre-load speed of 0.5 mm, and test speed of 3 mm/min. The gage length for the thin films was considered as 20 mm with the pre-load tension being 0.1 N, and with pre-load speed of 0.5 mm, and test speed of 3 mm/min. The 3D printed samples with 1- layer were tested using tensile standard ASTM D638T. Five specimens for each blend system were tested and the average of the results was considered. The data was acquired from TestXpert data acquisition and analysis software and tensile modulus and strength were evaluated from the data obtained. The filaments with 5 wt% silica were not printable due to high filler content and hence are not considered for the analysis.

Scanning electron microscopy. The surface morphology of the PC composite filaments were analyzed using JEOL JSM-7200F field emission scanning electron microscope (FESEM, JEOL USA, Peabody, MA) at 2 kV. The samples were sputter coated with gold/palladium (Au/Pd) for 3 mins at 10 mA using Hummer sputter coater.

Spectrometry. Genesys 10S UV-Vis Spectrophotometer by Thermo Scientific was used to investigate the optical properties of the nanocomposite. The wavelength was set from 200–600 nm to determine the differentiation of the transmittance from the 3D printed one layer to the 3D printed three-layered, as well as the neat polycarbonate with the various polycarbonate-silica composites.

Results and discussion

Thermal analysis of the filaments

The thermal properties of the PC filaments infused with AEROSIL were analyzed by TGA and DSC as shown in Figure 4. The percentage weight change of the filaments was shown in Figure 4(a) which exhibited single stage decomposition process. The addition of nanosilica particles have shown improvement in the onset and major degradation temperatures of the filaments suggesting that the filaments with nanosilica has higher thermal stability compared to that of the neat polycarbonate filament (Figures 4(a) and (b)). Although not significant, the filaments with 1 wt% nanosilica particles have shown highest onset and major degradation temperatures. Increasing the filler percent beyond 1 has slightly decreased the thermal stability of the filaments as shown from Table 2. Furthermore, it is observed the weight loss has decreased with the increase in silica content.[35] The residue at 600 °C increases with increase in silica content (Table 2) suggesting that the addition of the AEROSIL causes hindrance to the mobility of volatile products and heat during the thermal degradation.[36] Although with the improvement in thermal stability PC-SiO_2 cannot be considered as flame retardant, fewer flame retardant additives can achieve desired flame retardancy with the infusion of nanosilica.[23]

The glass transition temperature (T_g) is evaluated from DSC thermographs as shown in Figure 4(c) to further analyze the thermal stability of the filaments. The T_g of the neat polycarbonate filament is obtained at 148.75 °C. The glass transition temperature has slightly increased with the addition of nanosilica as shown in Table 2. Similar results were observed in the studies of nanosilica infused composites by Motaung et al.[37] and Feng et al.[36] The filament with 1 wt% of nanosilica has demonstrated highest glass transition temperature. Increasing the filler content beyond 1 wt% has decreased the glass transition temperatures. However, the change is insignificant. The increase in the glass transition might be due to the modularized mobility of the polymer chains which suggests that the stresses induced at the polymer particle interface during melt extrusion process have resulted in rigid polymer chains.[35]

Mechanical analysis

The tensile properties of the neat polycarbonate and silica infused polycarbonate composites are reported in Figure 5(a) and (b) and the results are summarized in Tables 3 and 4 for filaments and 3D printed parts with one-layer, respectively. It is noted that the results for PC composites with 5 wt% nanosilica are excluded as those filaments were not printable because of high particle content. The tensile results (Figure 5(a) and Table 3) showed that filaments with 1 wt% nanosilica exhibited superior properties compared to other composites with elastic modulus of 0.63 GPa (16% increase), tensile strength of 62.02 MPa and with

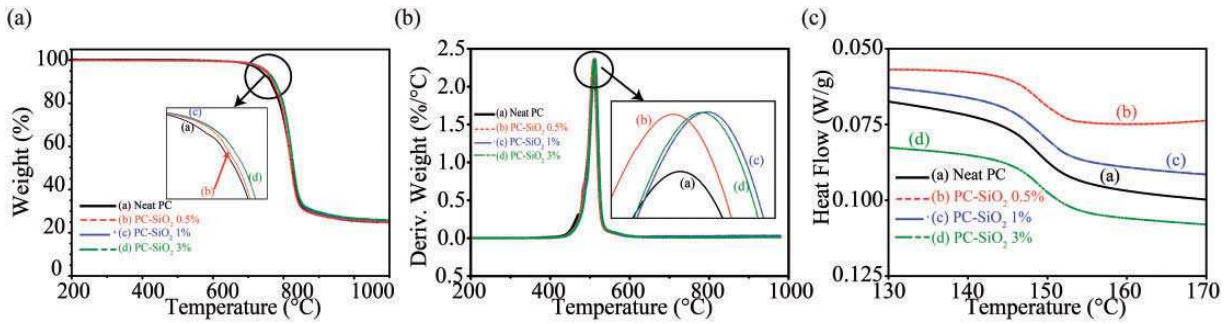

Figure 4. Thermal analysis of PC filaments infused with AEROSIL (a) weight change from TGA, (b) derivative weight change from TGA and (c) DSC thermographs.

Table 2. Summary of thermal analysis.

Specimen	Onset temperature (°C)	Major degradation (°C)	Weight loss at degradation (%)	Residue left at 600°C (%)	Glass transition temperature (°C)
Neat PC	478	509.9	46	25.56	148.75
PC-SiO_2 0.5%	488.35	509.28	45	25.69	148.84
PC-SiO_2 1%	494	512.17	44.64	26.2	149.62
PC-SiO_2 3%	493.38	511.67	43.48	26.74	148.78

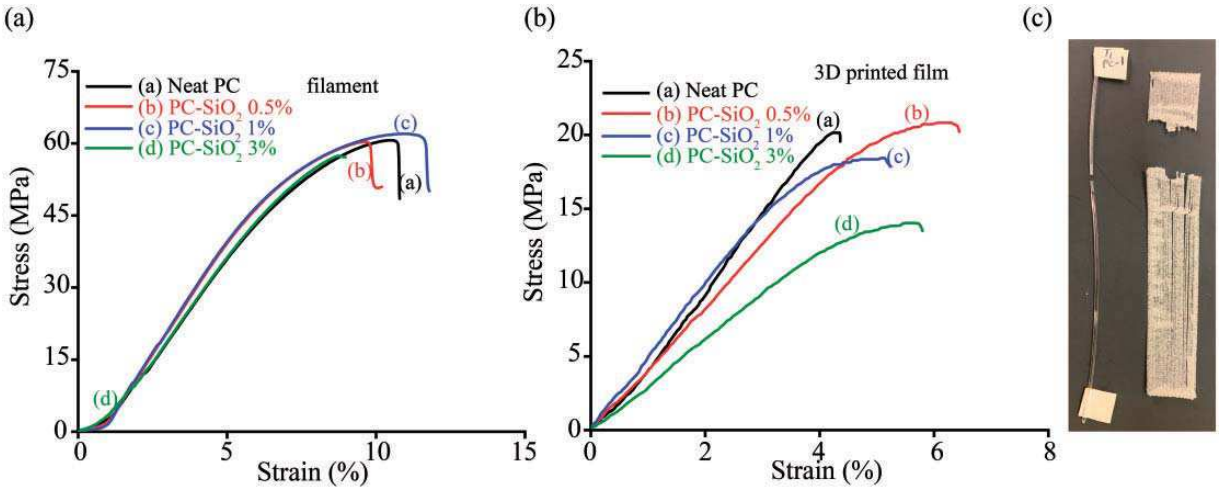

Figure 5. Tensile behavior of AEROSIL infused polycarbonate nanocomposite (a) filaments and (b) one-layer 3D printed films, and (c) fractured PC-SiO_2 1 wt % composite filament and 3D printed film.

Table 3. Summary of tensile properties of filament.

Specimen	Elastic modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PC	0.54 ± 0.065	60.66 ± 0.345	10.80 ± 0.185
PC-SiO_2 0.5%	0.59 ± 0.158	60.31 ± 0.234	11.82 ± 0.39
PC-SiO_2 1%	0.63 ± 0.04	62.02 ± 0.02	21.89 ± 0.86
PC-SiO_2 3%	0.57 ± 0.114	57.42 ± 3.574	8.78 ± 0.523

Table 4. Summary of tensile properties of one-layer 3D printed film.

Specimen	Elastic modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PC	0.485 ± 0.015	19.255 ± 0.855	4.37 ± 0.48
PC-SiO_2 0.5%	0.435 ± 0.025	20.645 ± 0.075	6.42 ± 0.445
PC-SiO_2 1%	0.5 ± 0.04	18.32 ± 0.125	5.22 ± 0.18
PC-SiO_2 3%	0.325 ± 0.005	13.63 ± 0.34	5.79 ± 0.545

elongation of 21.89% at break. The fractured filament and 3D printed film for 1 wt% nanosilica infused PC composites were shown in Figure 5(c). The gradual increment in elastic modulus for filaments with 0.5 wt % and 1 wt% nanosilica suggests that the addition of nanosilica has induced the stiffening effect of nanoparticles which offers resistance to the deformation and thus enhancing the strength and modulus.[35,38] However, as the filler content is increased to 3% the tensile properties deteriorated and the tensile strength and elongation at break are less than neat polycarbonate filaments. The increase in the filler content might have caused the particle agglomerations which resulted in poor properties due to induced stress concentration in polymer matrix.[38] The fracture surface of the filaments can be observed from SEM micrographs in Figure 6. The fracture surface of the neat filaments (Figure 6(a)) and 0.5 wt% SiO_2 (Figure 6(b)) infused composite filaments exhibit clean surface without any voids. Figure 6(b) suggests the homogenous dispersion of the nanosilica into the polymer. As the filler content increases to 1 wt% the inconsistencies due to agglomerations started to show up and the surface roughness increases as shown in figure (Figure 6(c)). When the filler content increases to 3 wt% the fracture surface is inhomogenous due to high filler content which is evident from Figure 6(d). Due to the presence of inhomogeneity the strength of the filaments decreased with the increase in filler content.

The tensile properties of 3D printed 1- layer polymer composites (Figure 5(b)) were compared to the melt extruded filaments. The tensile properties of the 3D printed films are inferior to that of the filaments. However, the film with 1 wt% of nanosilica exhibited

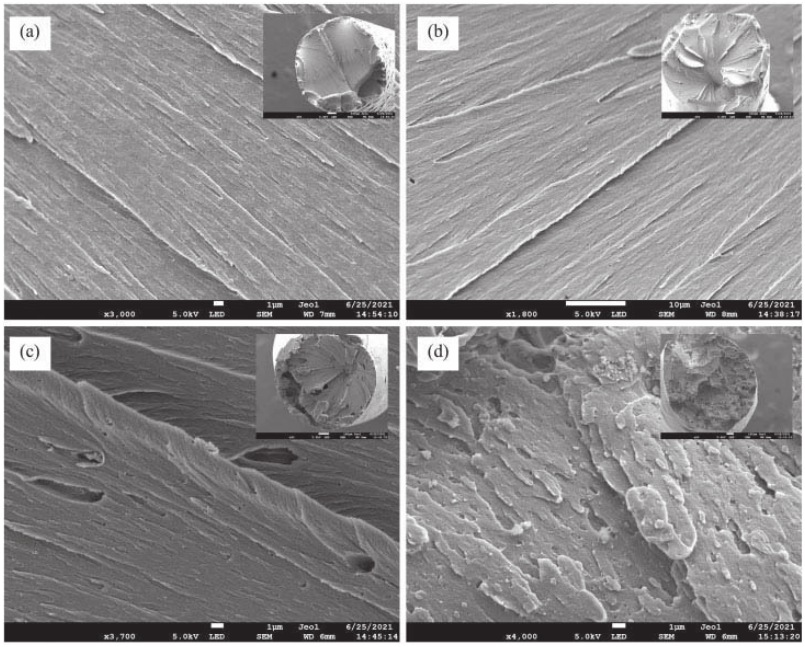

Figure 6. SEM micrographs of the polycarbonate filaments for surface analysis infused with (a) Neat, (b) 0.5 wt%, (c) 1 wt% and (d) 3 wt% of AEROSIL.

more desirable properties compared to the other 3D printed films as shown in Table 4. Furthermore, the one-layer 3D film with 0.5 wt% of nanosilica has exhibited higher tensile strength and high elongation at break which might be due to the homogenous dispersion of the filler in the matrix as observed from Figure 6(b). The 3D printing of polymer composites often decreases the strength of a polymer which might be due to the formation of voids in between the printed polymer layers.[18,39] The printing parameters such as extrusion temperature and printing speed also might have affected the strength of the 3D printed films. Furthermore, the filaments with 1 wt% SiO_2 has shown high surface roughness compared to 0.5 wt% as shown in Figure 6(b) and (c) which might have resulted in the presence of voids in the 3D printed films during the printing process. It is to be noted that the filaments are lab-made and hence, factors like moisture absorption, inconsistency in diameter, presence of air bubbles might also have affected the properties of the 3D printed films. The properties of the 3D printed thin films can be enhanced by surface modification which is considered for future work.

Optical analysis

Polycarbonate is known to degrade easily when exposed to UV light due to its chemical structure. The presence of the phenolic group undergoes oxidation when exposed to ultraviolet radiation. Materials such as silica are often used to coat polycarbonate to prevent UV degradation. Silica is a material that resists damage caused by UV radiation due to its optical density. However, infusing nanosilica might affect the transparency of the polycarbonate which also depends on particle size, particle content and the dispersion of particles.[38,40] Figure 7 depicts the optical properties of neat and silica infused 3D printed polycarbonate composites with one and three layers. The results showed that the neat polycarbonate has the highest transmittance of ultraviolet visible (UV-Vis) light compared to the other silica infused composites. However, the neat 3D printed film with 1 layer has shown transmittance of 80% within the visible light range of 525 nm to 600 nm whereas the origin PC pellets has luminous transmittance of 90%. The slight decrease in the transparency might be due to the extrusion process parameters while fabricating the filaments as well as 3D printing. The composite filaments are subjected to the extrusion temperatures lower than the melt temperatures which might have affected the clarity of the 3D printed films. Despite these factors, the neat PC films have exhibited satisfactory transmittance values. The increase in the silica concentration in polymer lowers the transmittance of the composite. It is anticipated that the increase in the nanosilica content might increase the light reflection at polymer particle interfaces thus reducing transmittance.[38] The silica nanoparticles block the transmission of light in the UV range, unlike the neat polymer.

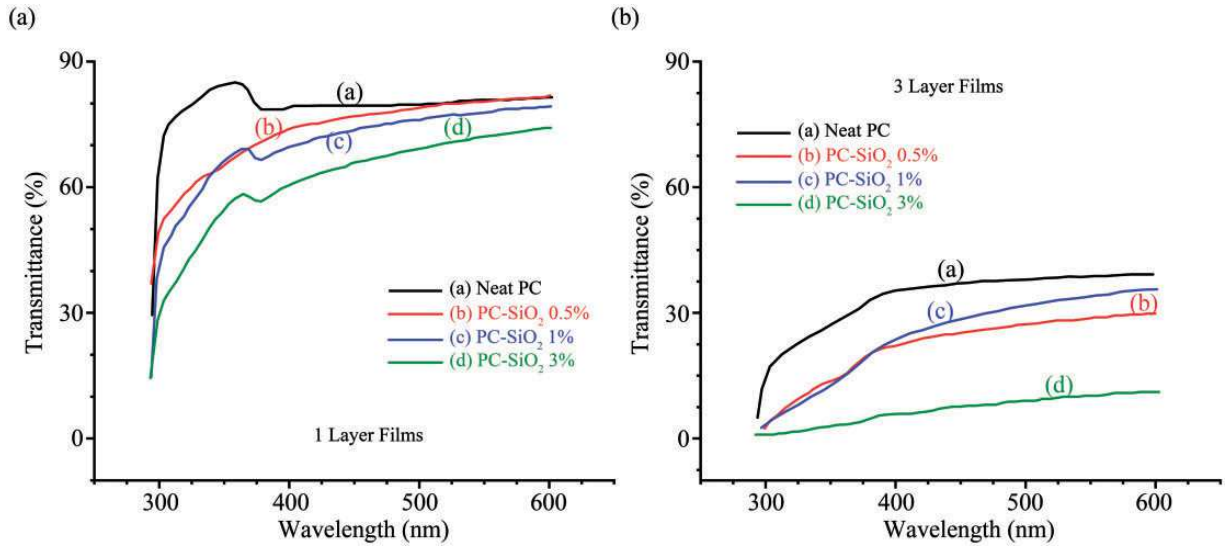

Figure 7. UV-visual spectrometry of 3D printed (a) one-layer films and (b) three-layered films.

For single layer films (Figure 5(a)), a sharp rudimentary edge is observed with two absorption steps between 300-350 nm and 350-400 nm.[41] These steps were also observed for nanosilica infused composites. As for the range of visible light, the neat and 0.5% silica begins to overlap from 525 nm to 600 nm. Figure 5(b) displays high transmittance for neat PC followed by 1% and 0.5% unlike single layer films. However, the transmittance is less for all the 3 layered films compared to single layer films. This might be because of large number of interfaces within the three-layered wafers which caused a decrease in transmittance.

Conclusions

The AEROSIL (nanosilica) is infused into the polycarbonate matrix to obtain polymer nanocomposite systems at various loadings. These blends were extruded into polymer nanocomposite filaments and then were 3D printed into thin films. The thermal properties of the filaments were analyzed using TGA and DSC which showed that the onset temperature, major degradation temperature and glass transition temperature increased with increase in the nanosilica content upto 1 wt %. As the silica content increases beyond 1 wt%, due to inhomogenous dispersion and agglomeration of particles, the thermal stability of the composites decreased. The residue amount was significantly increased due to the emission of volatile gases. The mechanical properties also comply with the thermal results as they were enhanced at the lower loadings of 1 wt% of silica. As the filler loading increased the mechanical properties tend to decrease. Melt extruded polymer filaments exhibit higher mechanical properties compared to 3D printed composites which might be due to the formation of voids during the 3D printing process. Although silica does not transmit UV rays, it transmits visible light in the same manner as polycarbonate due to the chemical and crystal structure. Despite 3D printing causing voids in bulk materials, silica at low concentrations improved the mechanical and optical properties. Hence, the thermomechanical and optical analysis of these polycarbonate composite systems suggest that the nanosilica can be used in moderate quantities as a filler to enhance the properties of the filaments and can be successfully used for 3D printing applications. This study was mainly aimed to check the printability of the fabricated filaments with the reinforcement of nanosilica and was successfully proved that the filaments are printable. It was observed that the addition of lower amounts of nanosilica is feasible for 3D printing. The further investigation of influence of 3D printing parameters is left for future work.

Declaration of Conflicting Interests

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ORCID iD

Vijaya K Rangari https://orcid.org/0000-0002-3962-1686

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