CHARACTERIZATION OF POLYCARBONATE 3D PRINTING FILAMENTS INFUSED WITH CARBON FROM COCONUT SHELL POWDER

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1 Introduction

The quality of the Earth's environment and climate change challenged mankind for many centuries. Despite the detrimental effects, plastics serve in a wide range of applications due to various properties like high strength, durability, transparency, corrosion resistance, low toxicity, and lightweight. Multifarious industries ranging from food packaging to space exploration tend to use plastics which leads to the immense pollution [1]. Bio-based polymers have proved to be potential countermeasure to for plastic pollution and have thus drawn plentitude attention from the researchers in the recent years [2].

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 [3]. Given that, polycarbonate (PC) based nanocomposites have become an irrefutable source for various commercial and engineering applications. The reinforcement of reduced graphene oxide as the nano-filler in PC matrix has increased its toughness, strength and notch resistance [4]. Electrical and thermal properties are enhanced when carbon is added to PC [5]. Hence, in this work, carbon synthesized from the waste coconut shell powder is used as a filler in PC matrix to enhance the mechanical and thermal properties of the extruded 3D printing filaments.

2 Materials and methods

2.1 Materials

Polycarbonate pellets with melt flow rate of 300ºC/1.2 kg of 34 cm^3/10 min were purchased from Makrolon® LED 2245 produced by Plastics Covestro, Germany. The coconut shell powder (particle size of 150 microns) was received from Essentium Materials LLC, a Texas based company, USA. Carbon was synthesized from the coconut shell powder (CCSP) and was employed as a filler for the polymer matrix.
Chloroform ($CHCl_3$, ≥ 99%) was used to dissolve the PC pellets with the carbon nano-powder in order to create well-dispersed composites. HPLC grade methanol (CH_3OH, ≥ 99.9%) was used to precipitate the polymer composites from the chloroform through methanolysis. Both solvents were purchased from Sigma-Aldrich Inc.

2.2 Synthesis of Carbon Nanopowder

The coconut shell powder of weight 30 gms was added to a custom-built MTI autogenic high temperature/pressure reactor. The powder was heated to 800ºC with a ramp rate of 5ºC/min from room temperature and was held isothermally at 800ºC for 2 hours without application of pressure. Thus collected carbon was ball milled using a vibratory ball mill, 8000D mixer/mill from SPEX SamplePrep, with Zirconia vials and balls. Then the ball mill was allowed to run for 10 hours. The powder was then separated carefully and then, dried, stored and labeled as CCSP10.

2.3 Fabrication of Nanocomposite

The PC pellets were dissolved in chloroform with filler loadings of 0.3, 0.7, 1, and 3 wt% of CCSP10. The solution was magnetically stirred for at least 12 hours and then mechanically stirred for homogenous dispersion. Methanol was added to the solution to precipitate the polymer. The precipitate was then filtered and dried in a vacuum oven overnight. The powder was then crushed with pestle and mortar and was then fed into the EX2 Fil-a-Bot extruder (VT, USA) to extrude filament composites. Extrusion temperature for PC composites was 260ºC. The filaments with a diameter of 1.5 – 1.75 mm were produced.

2.4 Methods

The carbon from coconut shell powder is analyzed using X-ray diffraction (XRD) analysis which was carried out using Rigaku DMAX 2100 diffractometer with monochromatic Cu Kγ radiation (γ = 0.154056 nm) at 40 kV, 30 mA, and 1.2 kW. The diffraction data was collected in the 2θ range (10−80°) at a scan rate of 2° 2θ/min.

The filaments developed were subjected to mechanical analysis using a Zwick/Roell Z2.5 Universal Mechanical Testing-Machine with 2.5kN load cell. The composite filaments underwent tensile testing following ASTM D3379 standard. The testing conditions for the filaments were as follows: gage length was 50 mm, the pre-load tension was 0.1N, pre-load speed was 0.5 mm, and test speed was 0.5 mm/min with TestXpert data acquisition and analysis software.

3 Results and Discussion

3.1 XRD Analysis

The morphology of the ball milled carbon, CCSP10 was analyzed using X-Ray diffraction. Two peaks were observed at 2θ of ~23º and 44.6º for (002) and (101) graphite planes, respectively [6]. The XRD results suggested that the structure of the synthesized carbon was amorphous.

3.2 Microscopic Analysis

The surface morphology and the microstructure of the carbon powder were analyzed using SEM and TEM as shown in figure 1. The SEM micrographs of as obtained carbon (CCSP) and its magnified view is shown in figure 2(a). The micrograph shows that the carbon particles are irregular in shape and size and have sheet like structures. Figure 1(b) shows that the size of the carbon particles was reduced to nano size after ball milling. The size of the particles was observed between 45 to 87 nm. The sheet structures were also observed to be deformed in figure 1(b). The TEM micrograph confirms that the size of the particles is in nano range and the presence of sheet like structures irrespective of the irregular shape of the particles.

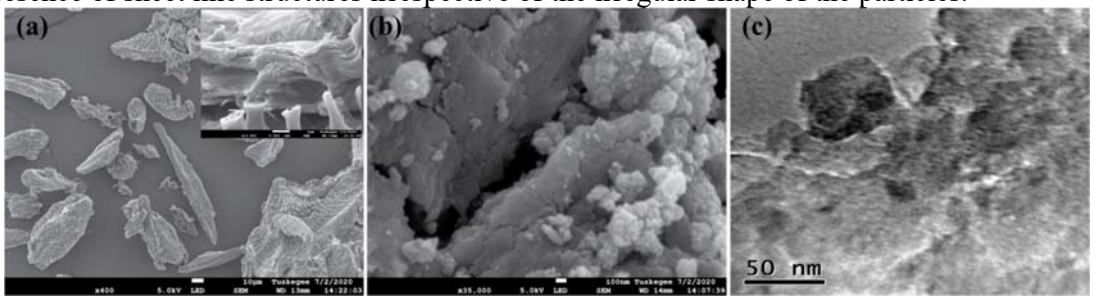

Figure 1: Scanning electron microscopy of (a) CCSP (b) CCSP10 and (b) Transmission electron microscopy of CCSP10.

3.3 Tensile Analysis

Figure 2 displays stress-strain curve of extruded PC-CCSP filament composites. CCSP as a filler increases the mechanical strength in the PC matrix. Table 1 summarizes the tensile properties. Tensile strength of PC increases with the addition of CCSP10 as shown in figure 2. Low loading of CCSP10 significantly increases the tensile strength [4]. Elastic modulus increases with filler content. However, the tensile properties deteriorate with the 3 wt% loading as shown in figure 2 which might be due to the agglomeration of the particles.

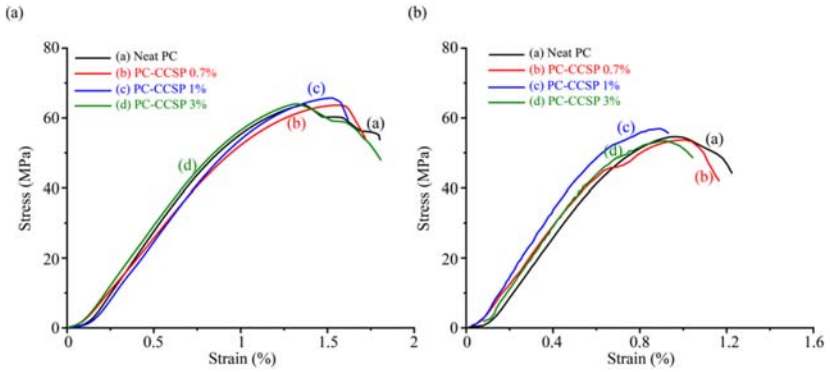

Figure 2: Tensile behavior of carbon infused polycarbonate nanocomposite (a) filaments and (b) 3D printed films

Table 1: Summary of tensile properties

Specimen		Elastic Modulus (GPa)	Tensile Strength (MPa)
Neat PC	filament	3.26±0.62	63.2±1.02
	3D printed film	2.17±0.28	54.61±0.71
PC-CCSP 0.7%	filament	3.77±0.14	63.69±2.8
	3D printed film	2.68±0.84	53.71±1.7
PC-CCSP 1%	filament	4.1±0.28	65.85±1.44
	3D printed film	3.33±0.36	56.91±4.04
PC-CCSP 3%	filament	3.06±0.65	64±1.62
	3D printed film	2.16±0.33	53.44±1.26

Figure 2 displays stress-strain curve of extruded and 3D printed polycarbonate-CCSP composites CCSP as a filler increases the mechanical strength in the polycarbonate-matrix. The tensile. Tensile strength of polycarbonate increases with the addition of CCSP as shown in figure 4a. Moderate loading of CCSP significantly increases the tensile strength. Elastic modulus increases with filler content however the modulus does decrease with the 3 wt% sample shown in figure 4(a). This may be due to agglomeration of particles which have caused the strength to drops significantly at 3 wt%. Similar behavior is observed for the 3D printed films for elastic modulus as well as the tensile strength. PC composite with 1% CCSP loading exhibited superior mechanical properties compared to the other composites. When the loading reached 3% the properties degraded and are lower than the PC. The tensile strength and the elastic modulus of the thin films were lower than the filaments. This might be due to the

formation of voids the between the printed polymer layers. In order to enhance the properties of the 3D printed thin films, they can be subjected to surface treatment process which is considered for future work.

CONCLUSIONS

Carbon nanopowder from waste coconut shell powder is successfully synthesized and then characterized using XRD, Raman, SEM mad TEM. The SEM and TEM results confirmed that the synthesized carbon powder is in nano range and has sheet like structures. The carbon nanopowder thus obtained 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 mechanical properties were enhanced at the lower loadings of the carbon powder. As the filler loading increased the mechanical properties tend to decrease. The thermomechanical analysis of these polycarbonate composite systems suggest that the carbon 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

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REFERENCES

[1] M. Allsopp, A. Walters, D. Santillo, and P. Johnston, “Plastic debris in the world’s oceans,” Greenpeace International, Amsterdam, Netherlands, 2006.

[2] R. P. Babu, K. O’Connor, and R. Seeram, “Current progress on bio-based polymers and their future trends,” *Prog. Biomater.*, vol. 2, no. 1, p. 8, 2013.

[3] A. S. Luyt *et al.*, “Polycarbonate reinforced with silica nanoparticles,” *Polym. Bull.*, vol. 66, no. 7, pp. 991–1004, 2011.

[4] J. Wang *et al.*, “Polycarbonate toughening with reduced graphene oxide: Toward high toughness, strength and notch resistance,” *Chem. Eng. J.*, vol. 325, pp. 474–484, 2017.

[5] E. Lago, P. S. Toth, G. Pugliese, V. Pellegrini, and F. Bonaccorso, “Solution blending preparation of polycarbonate/graphene composite: Boosting the mechanical and electrical properties,” *RSC Adv.*, vol. 6, no. 100, pp. 97931–97940, 2016.

[6] C. O. Umerah, D. Kodali, S. Head, S. Jeelani, and V. K. Rangari, “Synthesis of carbon from waste coconutshell and their application as filler in bioplast polymer filaments for 3D printing,” *Compos. Part B Eng.*, vol. 202, p. 108428, 2020.