On the Feasibility of Printing 3D Composite Objects Based on Polypropylene/Multi-walled Carbon Nanotubes

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Abstract. In this paper, the feasibility of 3D printing polypropylene/multi-walled carbon nanotube (PP/MWCNT) composites by fused deposition modeling. First, the rheological behavior of PP with 0.3, 0.5 and 1 wt.% of MWCNT was investigated in order to determine the printability in terms of melt shear viscosity and flow activation energy. Second, the filament extrusion process was optimized by the trial-and-error method in order to obtain round and constant filaments. Finally, tensile specimens were printed and tested in order to determine the mechanical properties at various printing direction. Experimental results show that the PP/MWCNT composite filaments with MWCNT loading up to 1 wt.% have good printability characteristics and can be successfully 3D printed with good mechanical performance.

1 Introduction

Fused Deposition Modeling (FDM) is an additive manufacturing (AM) process that uses thermoplastic filament by fused deposition which creates part geometry along trajectories generated by slicing [1]. This manufacturing process provides the ability to fabricate prototypes in the early stages of designing, but the part is made from triangles and not true arcs, splines etc. thus it loses resolution [2].

In the last years, different industrial sectors, including automotive and aerospace, have exploring the potential of additive manufacturing for printing composite materials with different fillers such as carbon fiber in PLA [3,4], ABS [4], and PA [5]; graphene oxide in ABS [6]; carbon black in ABS [7], PLA and PA [8]. However, 3D printing with composite filaments can be difficult due to fiber agglomerations and/or breaking and high shear viscosity that cause lower mechanical properties at high loadings [9]. Thus, an alternative printing with carbon nanotubes (CNTs) in ABS [9-12], PLA [8,13-15], PEEK [16], PA [8], and TPU [17,18] was considered, due to outstanding properties of CNTs such as chemical resistance, high electrical and thermal conductivity, high elastic modulus and strength [19-21]. However, printing of polymer/CNT composites is currently under development mainly due to the absence of commercially available polymer/CNT filaments and the difficulty at printing due to lack of adhesion on the building platform and nozzle clogging [9]. Thus, in

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this paper, the feasibility of 3D printing polypropylene/multi-walled carbon nanotube (PP/MWCNT) composites is investigated. In general, scientific literature results provide extensive information on both mechanical and electrical properties of PP/CNT composites [21-33] as well as on the rheological properties [21,24,26-36], mostly at low shear rates; however, the filament extrudability and 3D printability of PP/MWCNT composites were not investigated.

2 Materials and methods

2.1 Materials

The material studied in this paper is a commercially available polypropylene (grade Lyondell Basell Moplen HP400R) filled with 0.3, 0.5, and 1 wt.% of multi-wall carbon nanotubes (MWCNTs) supplied by Nanocyl (Sambreville, Belgium). The composites were prepared by dilution of the PP masterbatches with 20 wt.% of NC7000TM [37] at 230°C. Based on the DSC measurements (10°C/min rate) the peak melting temperature of these composites with MWCNT loading up to 1 wt.% was found to be ~172°C and 167°C for first and second heating, respectively, while the crystallization temperature was noticed to be ~122°C, regardless of the carbon nanotube loading.

2.2 Melt Shear Rheological Measurements

Polymer manufacturing processes, such as filament extrusion and 3D printing, have a range of different shear rates associated with them, thus, in order to determine the extrudability and 3D printability windows, the rheological properties of PP/MWCNT composites were measured on a capillary rheometer (Rheograph 75, Göttfert, Germany) across a wide range of shear rate (75 to 5×10^3 s⁻¹) and temperature (190 to 230°C). It is important to note that the measurements were carried out on a capillary die with a length/diameter (L/D) ratio of 30/1. The PP/MWCNT pellets were dried in a vacuum drying system (Raypa, Spain) for 4 h at 80°C before testing.

2.3 Fabrication of filaments

Filaments of PP/MWCNT composites filled with 0.3, 0.5 and 1 wt.% were produced using a single screw extruder with 25-mm diameter and a 3-mm diameter die (NEXT 1.0 Advanced Silver, 3devo, The Netherlands). The extruder operates with a flood feeding system, dual air cooling system with adjustable fan speed and 4 heating zones along the barrel. During the extrusion process, the melt is extruded through the die, and then the filament passes through an optic sensor and a puller system that work together to achieve the 3D printing filament. Generally, the standard commercial filament diameter is 1.75 ± 0.05 mm. However, due to the presence of nanotubes, which have the tendency to re-agglomerate during the extrusion process, in this paper, the filament diameter was set to 1.7 mm.

The filament roundness is achieved by adjusting the temperatures and speed of the screw. Since the viscosity of the PP/MWCNT composites increases with increasing nanotube loading, a trial-and-error method was applied in order to identify the optimum extrusion parameters (Table 1). The temperatures of the four heating zones are given from the feed hopper (T_4) to the die (T_1).

Table 1. Filament extrusion parameters.

MWCNT (wt.%)	Barrel zones temperatures (°C)				Screw speed (rpm)	Fan speed (%)
	T ₄	T ₃	T ₂	T ₁		
0.3	190	190	170	165	3.5	10
0.5						
1	195	195	175	170		

2.4 3D printing of PP/MWCNT composite

The 3D printing of PP/MWCNT filaments was carried out using an in-house designed 3D printer equipped with a standard 0.4-mm nozzle. The 3D specimens (Figure 1) were modeled using Inventor and exported as STL files, while the software Ultimaker Cura Version 3.6 (Ultimaker B.V.) was used to prepare the code for 3D printing. Three printing directions (0, 90, and 45°) were considered in order to investigate the effect of printing direction on the mechanical properties of 3D printed PP/MWCNT composites (Figure 2).

Fig. 1. Geometry of the 3D printing specimens. In-house designed 3D printer.

Fig. 2. The printing directions of the tensile specimen.

The printing was performed at a constant speed of 30 mm/s with a 0.2-mm layer height, and 50% filament flow feeding. Following preliminary 3D printing tests, the melt temperature was set to 175°C for 0.3 and 0.5 wt.% filaments and to 185°C for the filament with 1 wt.%. At temperatures higher than 185°C, the filament starts to melt above the liquefier reservoir and affects the filament feeding. The printing platform was maintained at 25°C to ensure the same bed temperature for all specimens.

First, the wall of the 3D printed specimen, which consists of 3 roads (marked in red in Figure 2), was created then the layer of 0.2-mm height was printed. The PP/MWCNT specimens were printed on a PP-based packing tape to improve the adhesion between the 3D printed part and the build platform. It was found that for a good print, the part should

not have geometries that need sudden trajectory changes when the wall is building (e.g. 90° corners).

2.5 Tensile testing

Mechanical testing of PP/MWCNT filaments and 3D printed tensile specimens was carried out on a universal testing machine (Testometric, Model M350 – 5AT, UK), at room temperature, with a cross-head speed of 5 mm/min. The filaments with a length of 100±2 mm were tested at a 50 mm distance between the grips, whereas for the 3D printed specimens the distance between the grips was set to 110 mm (according to ISO 527-2-1B). A minimum of 10 specimens were tested for each MWCNT loading and printing direction.

3 Results and discussion

3.1 Flow curves

Figure 3 presents the variation of apparent melt shear viscosity as a function of MWCNT wt.% for different shear rates at 190°C. The melt viscosity increases linearly with nanotube loading and decreases with increasing apparent shear rate, as can be seen in Figure 3. A linear relationship was used to estimate the dependence of the melt shear viscosity on the MWCNT wt.%. Both the slope and the intercept of the straight line decrease with increasing shear rate (Table 2), indicating that the sensitivity of PP/MWCNT composites is weakened with increasing apparent shear rate [38].

Fig. 3. Effect of MWCNT wt.% on apparent shear viscosity of PP/MWCNT composite at 190°C.

Table 2. Dependence of viscosity on MWCNT loading at 190°C.

App. shear rate (1/s)	Slope (a) (Pa s/ wt.%)	Intercept (b) (Pa s)
75	46.594	404.69
500	2.859	158.24
1000	2.961	97.834
3000	0.704	45.653
4000	0.037	37.454

The variation of the apparent shear viscosity with the reciprocal absolute temperature ($1/T$) for different shear rates is illustrated in Figure 4. In the temperature range of 190 to 230°C, the dependence of shear viscosity on the $1/T$ was found to follow the Arrhenius equation [38,39], thus the activation energy for flow, E_a , was calculated from the slope of the straight line in Figure 4 (Table 3). As shown in Table 3 the activation energy for flow decreases significantly with increasing shear rate. However, for MWCNT loadings up to 1 wt.%, the activation energy is not significantly affected by the addition of nanotubes, which is beneficial for the 3D printing process.

Fig. 4. Effect of melt temperature on the melt shear viscosity of PP with (a) 0.3, (b) 0.5, and (c) 1 wt.% MWCNT.

Table 3. Activation energy for flow.

App. shear rate (1/s)	E_a (KJ/ mol K)		
	0.3 wt.%	0.5 wt.%	1 wt.%
75	28.033	28.761	27.404
250	21.093	21.349	19.936
500	17.852	17.923	17.671
1000	14.491	14.701	13.928
4000	12.287	12.857	11.881

During the 3D printing, relative low shear rates are developed at the entrance of the extruder head, while the polymer melt reaches shear rates as high as 200 s^{-1} when passes the printing nozzle [40]. Thus, the Carreau-Winter viscosity model was used to model the composites flow behavior [39,41].

The equation for the Carreau-Winter model is given as follows [39,41]

$$\eta(\dot{\gamma}) = \frac{\eta_0}{(1 + \lambda \dot{\gamma})^{m_c}}, \quad (1)$$

where η_0 is the zero-shear viscosity, λ is the characteristic time (the inverse of the shear rate at which the shear-thinning begins), m_c is the viscosity exponent.

Figure 5 shows the effect of nanotube loading and shear rate on the melt shear viscosity at 190°C . The solid symbols represent the experimental data, while the solid lines represent the viscosity calculated from the Carreau-Winter model, including the extrapolation to low shear rates. It can be seen that the melt shear viscosity decreases with increasing shear rate, and all composites display shear thinning behavior at high shear rates (Figure 5). In the experimental shear rates region, the Carreau-Winter model predicts very well the experimental data.

Fig. 5. Melt shear viscosity for PP/MWCNT composites at 190°C .

For each nanotube loading, a master curve was generated using the Time-Temperature-Superposition (TTS) principle [39] as shown in Figure 6. The master curves allow the prediction of the melt shear viscosity over a wide range of shear rates and at a particular temperature. The parameters for the Carreau-Winter model obtained using the master curve are listed in Table 4. It was found that all PP/MWCNT composites display shear-thinning behavior, which is practically independent of the nanotube loading ($m_c = 0.724 \pm 0.0045$).

Fig. 6. Master viscosity curves for PP/MWCNT composite at a reference temperature of 210°C.

Table 4. Carreau-Winter parameters at a reference temperature of 210°C.

Parameter	MWCNT (wt.%)		
	0.3	0.5	1
η_0 (Pa s)	440.603	453.429	509.062
λ (s)	0.009	0.009	0.011
m_c (-)	0.718	0.727	0.728

3.2 PP/MWCNT filaments

Figure 7 shows the optical microscopy for the filaments with 0.3, 0.5 and 1 wt.%. With increasing nanotube loading, the filament surface goes from a smooth to a coarse aspect, due to the re-agglomeration of nanotubes during the filament extrusion.

Figure 8 shows the distribution of the measured filament diameter. It can be seen that the filament diameter is normally distributed around the mean value of 1.700 ± 0.0434 mm, 1.699 ± 0.0383 mm, and 1.699 ± 0.053 mm, for 0.3, 0.5, and 1 wt.% MWCNTs, respectively. Recall that the filament diameter was set to 1.7 ± 0.05 mm.

The representative stress-strain curves for PP/MWCNT filaments are illustrated in Figure 9. It can be seen that the PP with MWCNT loading up to 1 wt.% exhibits elastoplastic behavior with yielding, softening and hardening. Overall, the tensile strength of the PP/MWCNT filaments increased with increasing nanotube loading (33.35 ± 1.27 MPa, 37.93 ± 0.31 MPa and 36.71 ± 0.31 MPa for 0.3, 0.5 and 1 wt.%, respectively). On the other hand, the results reveal that the brittleness of PP/MWCNT filaments increased significantly with MWCNT loading.

Fig. 7. Optical microscopy of PP with (a) 0.3, (b) 0.5, and (c) 1 wt.% MWCNT filament.

Fig. 8. Filament diameter distribution of PP with (a) 0.3, (b) 0.5, and (c) 1 wt.% MWCNT.

Fig. 9. Stress-strain curve for PP/MWCNT filaments.

3.3 3D printing of PP/MWCNT composite

The 3D printed specimens with 0.3 wt.% MWCNT printed with 0, 90 and 45° direction are presented in Figure 10, while Figure 11 shows the corresponding optical images of the top and bottom printed layer. These images show well diffused roads with no gaps or voids. However, the top surface appears to be slightly rough as compared with the bottom surface. The application of the packing tape onto the printing platform can have a negative effect on the bottom surface, e.g. a cavity/intent into the print can be formed if air bubbles are trapped between the packing tape and the printing platform.

Fig. 10. 3D specimens with 0.3 wt.% MWCNT at (a) 0°, (b) 90° and (c) 45° printing directions.

Fig. 11. Optical microscopy of 3D specimens with 0.3 wt.% MWCNT at (a) 0°, (b) 90° and (c) 45° printing directions.

3.4 Mechanical properties of 3D printed parts

The representative stress-strain curves for PP/MWCNT 3D printed specimens are shown in Figures 12 and 13. The effect of printing direction on the mechanical behavior of 3D printed PP/ 0.3 wt.% MWCNT composite is given in Figure 12. It can be seen that the printing direction has a significant effect on the tensile behavior of the PP/MWCNT 3D printed specimens. All printed specimens display a brittle behavior as shown in the inset image.

Fig. 12. Stress-strain curve for PP with 0.3 wt.% MWCNT.

The effect of nanotube loading on the tensile behavior of PP/MWCNT 3D printed specimens is shown in Figure 13. The average tensile strengths and strain at break of the 3D printed specimens are presented in Table 5 and 6, respectively.

The specimens with 0° printing direction have higher tensile strength as compared with 45° and 90° printing directions. However, overall, the experimental data indicate that the adhesion between the printed roads/layers was very good. The strain at break was influenced by the printing direction more than the nanotube loading.

Table 5. Tensile strength (MPa) of the printed specimens.

Printing direction	MWCNT (wt.%)		
	0.3	0.5	1
0°	29.434±0.60	29.425±1.23	28.350±2.14
45°	23.882±1.06	27.162±0.80	26.657±1.69
90°	24.562±2.18	29.523±0.83	24.724±1.03

Table 6. Strain at break (%) of the printed specimens.

Printing direction	MWCNT (wt.%)		
	0.3	0.5	1
0°	4.709±0.14	3.701±0.21	4.564±0.85
45°	4.559±0.43	4.371±0.71	5.307±0.44
90°	3.305±0.59	4.350±0.43	3.513±0.30

Fig. 13. Stress-strain curve for PP/ 0.3 wt.% MWCNT printed specimens at (a) 0°, (b) 45°, and (c) 90° printing direction.

Regarding the effect of MWCNTs on the mechanical properties of the 3D printed PP/MWCNT composites, although there is a tendency that the tensile strength increases with increasing nanotube loading, no general relationship can be identified for all nanotube loadings. However, the 3D printed PP/MWCNT specimens retain good tensile strength (25-30 MPa), indicating good adhesion between PP layers.

The trajectory of the printing code was setup by default in the Cura software, as shown in Figure 14 (point A). To investigate if the point A has an influence on the fracture initiation point, manual adjustments in the settings of the printing code were performed so

that the starting point was set outside the active zone of the tensile specimen (point B in Figure 14). However, tensile tests (not presented here) showed that the fracture initiation is not related to the starting printing point. It could be attributed to the changes in the specimen cross-section.

Fig. 14. Starting printing point for 45° printing direction: A (by default in Cura), B (manual settings).

4 Conclusions

In this paper, the 3D printability of polypropylene filled with 0.3, 0.5 and 1 wt.% multi-walled carbon nanotubes was investigated. PP/MWCNT filaments with 1.7-mm diameter were extruded and tensile specimens were 3D printed using the fusion deposition modeling. The mechanical properties of the PP/MWCNT 3D printed specimens were characterized as a function of printing direction and nanotube loading. The following conclusions were drawn based on the experimental results:

(i) For MWCNT loadings up to 1 wt.%, the melt shear viscosity and activation energy of PP/MWCNT composites are not significantly affected by the addition of nanotubes. All PP/MWCNT composites display solid-like behavior at high shear rates;

(ii) PP/MWCNT filaments with good surface finish were extruded; however, the roughness of the PP/MWCNT filament increased with increasing nanotube loading, especially at 1 wt.%, due to nanotube agglomeration;

(iii) The 0.3 and 0.5 wt.% filaments exhibited very good printability characteristics, and were successfully 3D printed with good mechanical performance. The 1 wt.% filament was also printable, but some clogging were experienced due to nanotube agglomeration;

(iv) Overall, the filaments and 3D printed specimens exhibited good mechanical properties with good-interlayer adhesion. Printing direction was found to have a significant effect on the tensile strength. The MWCNT loading was also affected the tensile strength but with a lower impact.

Although experimental results showed that the PP/MWCNT composites are suitable for 3D printing, further investigation on filament extrusion and 3D printing are needed in order to 3D print reliable objects.

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