EFFECT OF INJECTION MOLDING PARAMETERS ON THE ELECTRICAL CONDUCTIVITY OF POLYCARBONATE/CARBON NANOTUBE NANOCOMPOSITES

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Abstract

Polycarbonate (PC) was compounded with carbon nanotubes (CNT) using a co-rotating twin screw extruder followed by injection molding. Two 1.8 wt% PC/CNT nanocomposites produced from the direct compounding and solution masterbatch approach were injection molded into ASTM D638 standard tensile bars and underwent electrical conductivity measurement in accordance with the ASTM D4496 standard along the flow directions of the tensile bars. It was found that the resulting electrical conductivity was sensitive to injection speed and melt temperature, as well as the location of the injection molded specimens. High electrical conductivities were achieved at high melt temperatures, but high injection speeds resulted in a non-uniform distribution of conductivities across the specimen width. Finally, higher electrical conductivities were found at locations farther away from the gate.

Introduction

Carbon nanotubes were discovered by Iijima in 1991 and have since undergone extensive research in fields such as chemistry, physics, materials science, and a whole range of engineering disciplines [1]. The unique nano-structure of carbon nanotubes, which have excellent mechanical and physical properties, enables them to be used as potential fillers in composite systems, especially for the development of lightweight, high-performance polymer nanocomposites.

It is known that carbon–carbon covalent bonds are some of the strongest bonds in nature, and the characteristics on how these bonds are arranged in carbon nanotubes has made them one of the strongest materials with an extremely high strength-to-weight ratio [3]. Carbon nanotubes, especially single-wall carbon nanotubes (SWNT), exhibit high flexibility and strength with high stiffness. This enables them to be stiff at low loads and soften at high loads, thus accommodating large deformations without breaking [4]. The tensile strengths of these nanotubes were measured to be approximately 100 to 600 GPa, which is two orders of magnitude higher than that of the high strength carbon fillers [5]. Furthermore, the density of carbon nanotubes is about 1.3 g/cm^3 [6], which is lower than that of carbon fillers whose density is around 1.8 g/cm^3. The Young's moduli of carbon nanotubes are 1 to 5 TPa, as compared to 750 GPa for carbon fibers [1,7]. Finally, carbon nanotubes also have unique electrical characteristics ranging from semi to high electrical conductivity depending on the chirality of the hexagon cylinders [8]. In fact, the electrical conductivity of the nanotubes can be several times as high as copper with the ability to carry immense current densities higher than 100 MA/cm^2 [9]. All of these superior properties, as well as the extremely high surface-to-weight ratio, suggest that carbon nanotubes can be used to replace commercial carbon fibers to produce enhanced composites with significantly reduced weight.

In addition to the general dispersion state of the carbon nanotubes, the overall alignment of the nanotubes also plays an important role in the nanocomposite's properties. Jin et al. studied uniaxially stretched carbon nanotube polymer composites at 100 °C and found that the degree of alignment depended on the stretching ratio [10]. Similarly, Haggenmuller et al. prepared single-wall carbon nanotubes and PMMA composite films and fibers via melt processing and found that the elastic modulus and yield strength increased with the draw ratio [11]. Finally, Thostenson and Chou extruded multi-wall nanotubes and polystyrene through a rectangular die and drew composite films prior to cooling and obtained a 137% and a 49% increase in tensile strength and modulus, respectively [12].

Injection molding is one of the most widely used material processing methods for mass-production of plastic parts with complex geometry. Thus, it lends itself as a perfect process for producing nanocomposite components. However, various process parameters used in the injection molding process would significantly affect the performance of the molded parts, and to the best of our knowledge, very few studies have been performed on the effects of injection molding parameters on the conductive properties of composites [13]. Therefore, this study is aimed at investigating the effects of injection molding parameters on the electrical conductivity of polycarbonate carbon nanotube nanocomposites.

Materials and Experiments

Carbon nanotubes (CNT) were supplied by Carbon Nanotechnologies, Inc., and GE Lexan polycarbonate (PC) was used for the matrix. Two compounding processes were utilized in preparing the PC/CNT nanocomposites. The first method employed a direct compounding of the PC and CNT. Both PC and CNT were hand mixed to a 1.8 wt% concentration and extruded using a Davis–Standard 32 mm (L/D = 36/1) co-rotating twin screw extruder that has been configured with a set of mixing elements to provide better CNT dispersion at 200 rpm. The second compounding method involved a solution process to prepare a 9.1 wt% masterbatch of PC/CNT nanocomposites. CNT were sonicated in chloroform for one hour and then mixed with PC (also dissolved in chloroform) with a mechanical stirrer. The mixture was sonicated for another hour, followed by solvent removal in a RotaVapor, oven drying, and finally grinding into powder. The 9.1 wt% PC/CNT masterbatch was then diluted with PC to a 1.8 wt% CNT concentration using the same twin screw extruder. The two 1.8 wt% PC/CNT nanocomposites produced from the direct compounding and solution masterbatch approaches were then molded into ASTM D638 standard tensile bars using an Arburg injection molding machine under the conditions listed in Table 1. The molding parameters labeled as "Control" in Table 1 were based on the recommended settings supplied by the manufacturer for molding polycarbonate neat resin; whereas the two factorial designs were based on the maximum or minimum processing windows that would generate appropriately molded tensile bars. When either the melt temperatures or injection speeds were too high or too low (with the other parameters held constant), the injection molded tensile bars would show imperfections such as short shots or jetting on the surface.

A LEO 1530 field emission scanning electron microscope (FESEM) was employed to investigate the dispersion state of the nanocomposites. The electrical conductivities were measured in accordance with the ASTM D4496 standard along the flow directions of the tensile bars (cf. Figure 1). Each sample was cut at different locations while maintaining a constant thickness. Both ends of the sample parallel to the flow direction were then coated with conductive carbon paint, and the resistance was measured from the center. The electrical conductivity (ρ) was then calculated using Equation 1:

$$\rho = \frac{d}{A \cdot R} \qquad (1)$$

where d is the distance between the electrodes, A is the cross sectional area, and R is the measured resistance.

Results and Discussions

The electrical conductivities of the injection molded specimens along the gage length of 46 mm (cf. Figure 1) at various processing parameters are shown in Figure 2. Since the electrical conductivity depends largely on the carbon nanotube alignment, dispersion, and distribution, injection speeds and melt temperature were the two controllable parameters that would most likely affect the conductivities. This is because injection speed dictates the distributions of shear/elongation stresses and shear/elongation rates while the melt temperature affects the viscosity, diffusion, relaxation time, and solidification time. Moreover, although the injection molding screw is capable of providing a degree of mixing, it is not aggressive enough to promote further carbon nanotubes dispersion. As observed in Figure 2, the conductivity of the direct compounded nanocomposites exhibited the lowest electrical conductivity, which suggests poor carbon nanotube dispersion. The strong van der Waals attraction between the carbon nanotubes caused the nanotubes to form ropes where multiple strands of nanotubes adhered to one another. Furthermore, these ropes eventually bundled and entangled, thus creating agglomerates. In addition to the poor dispersion, it is possible that the polymer matrix did not penetrate the voids between the carbon nanotube bundles during direct compounding, thus resulting in discrete agglomerates with poor contact and connection, thereby ultimately reducing the electrical conductivity of the nanocomposites. On the other hand, the masterbatch sample made from the solution method allowed the polycarbonate to fully penetrate and separate the carbon nanotube bundles, thereby resulting in better contact and a higher degree of dispersion.

Because the direct compounded nanocomposite exhibited much lower electrical conductivity, the injection molding parameters studied were only performed on the nanocomposites made from the solution masterbatch process. Figure 2 shows that the electrical conductivities were sensitive to the melt temperature during injection molding, whereas the injection speed appeared to have only moderate effects. It can be seen that, in general, the high temperature settings would yield nanocomposites with considerably higher conductivities when compared to the specimens molded at lower melt temperatures. Figure 2 shows the freeze fractured FESEM images of PC/CNT nanocomposites molded with different melt temperatures but identical high injection speeds. As seen in Figure 2, the voids (dark/black region) on the carbon nanotube bundles were more visible at low melt temperatures (cf.

Figure 2a) whereas hardly any voids were present on the samples injection molded at high melt temperatures (cf. Figure 2b). One of the immediate effects of having a higher melt temperature while holding the remaining parameters constant during injection molding was the reduced melt viscosity and higher diffusivity, which enabled better polymer penetration into the carbon nanotube bundles, resulting in better contact, and thus higher electrical conductivities. Also, note that spherical particles can be seen on the nanocomposite surface. It is not clear what those particles are, as they might be impurities from the carbon nanotubes or carbon soot. Again, the spherical particles were less visible in the samples injection molded at high melt temperatures, implying better surface coverage. Finally, the lower melt viscosity allowed less restriction to the carbon nanotube bundles, enabling the ropes to disentangle. One of the representative micrograph is shown in Figure 2 where the carbon nanotube bundles were less tightly bound when injection molded at high melt temperatures.

The injection speed showed moderate effects on the resulting electrical conductivities but a clear trend of their effects could not be observed directly from Figure 2. This could be due to the complex interactions among many factors during injection molding that affected the final distribution of the nanotubes in the specimens. Therefore the effects of injection speed on the resulting electrical conductivities require further study as discussed below. Hong et al. performed a study on the shear-induced migration of conductive fillers during injection molding and showed that during injection molding the fillers are pushed toward the core leaving very small concentrations in the skin region. This filler migration strongly depended on injection speed, with more particles leaving the surface under higher injection speeds [13]. Our preliminary results of the injection molding of PC/CNT nanocomposites have revealed a similar phenomenon, although the thickness of the resin-rich skin layer was affected by the melt temperature. At present, the conductivity measurements were performed across the width of the tensile bar for practicality.

In order to investigate the effects of injection speeds on the electrical conductivities, measurements were taken at two different locations along the gage length, namely, one near and one farther from the gate. Furthermore, each location was divided into three specimens of equal width along the flow directions as depicted in Figure 1. The effects of injection speed at both low and high temperatures at various locations are shown in Figures 4 and 5. It can be seen that the effects are more pronounced at the high temperature. As seen in Figure 4, the injection speed did not show any trend when performed at the low melt temperature. At present, it is not yet understood why such behaviors were observed. Conceivably, the viscosity of the melt may be so high that particle migration was hindered and the flow behavior of the melt may have been affected as the melt temperature was lower than the recommended setting.

At the high melt temperature, it can be seen in Figure 5 that more agglomerates are pushed toward the core. This was supported by the electrical conductivities at the center, where they were in general, the highest at any distance from the gate. Further observations on the figure reveal that both the distance from the gate and the injection speed affect the electrical conductivity of the injection molded specimens. At high melt temperatures and low injection speeds, the electrical conductivity distribution farther from the gate is more uniform than the distribution from the samples produced at high temperatures and high injection speeds. The fountain flow effect occurs during injection molding where material layers on the melt front that entered the cavity are pushed outward. And although particle migration toward the core also occurs at the same time, the low shear gradient at the low injection speed reduces the particle’s tendency to migrate toward the core. In fact, the combination of low melt viscosity and higher shear gradient from the higher injection speed promoted more particle migration toward the core which caused one side of the gage length to lose its conductivity whilst the center conductivity increased dramatically. However, Figure 5 also shows that one side (right) of the gage length retained some of its conductivity which may be caused by uneven cooling. The injection mold was designed such that the cooling line was positioned at one side of the tensile bar. Because of the cooler mold wall temperature, the melt viscosity at this side was higher and thus hindered particle migration to the core. Also from Figure 5, the overall conductivities at the location nearest to the gate were lower than the farther location, although the center was still the most conductive, and injection speed did not have any effect on the electrical conductivity distributions. The core of material at the location closest to the gate experienced less residence time in the cavity and because the polymer melt did not undergo any significant flow length, the effects of injection speed were minimized and thus there were fewer particle migrations. Furthermore, the melt flow at this region did not see as much side wall effect (which also caused particle migration toward the center region) as the far end, resulting in reduced concentration of the carbon nanotubes and thus decreasing the overall conductivities.

Summary

In order to achieve uniformly distributed high electrical conductivity, polycarbonate carbon nanotube (PC/CNT) nanocomposites should be processed at high melt temperatures and low injection speeds to ensure proper and uniform electrical conductivities. Furthermore, higher electrical conductivities were found at locations farthest from the gate. Finally, the effect of mold wall temperatures on the resulting electrical conductivity will be investigated in future study.

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Table 1. Injection molding parameters.

	Barrel Temperature [°C]					Injection Speed [cm^3/s]
	Zone 5	Zone 4	Zone 3	Zone 2	Zone 1	
Low Temperature, Low Injection Speed [LT/LI]	265	255	245	235	225	5
Low Temperature, High Injection Speed [LT/HI]	265	255	245	235	225	9
Control	280	270	260	250	240	7
High Temperature, Low Injection Speed [HT/LI]	295	285	275	265	255	5
High Temperature, High Injection Speed [HT/HI]	295	285	275	265	255	9

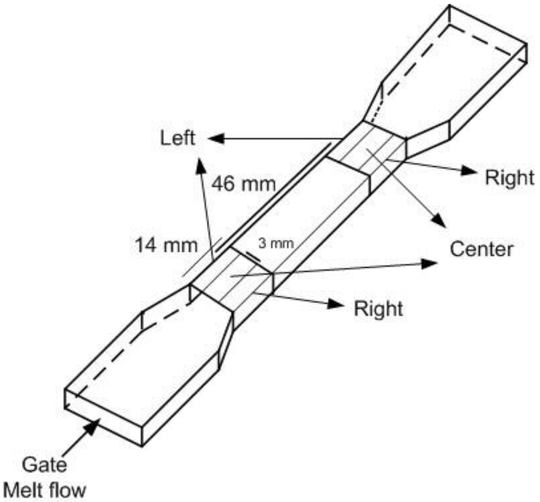
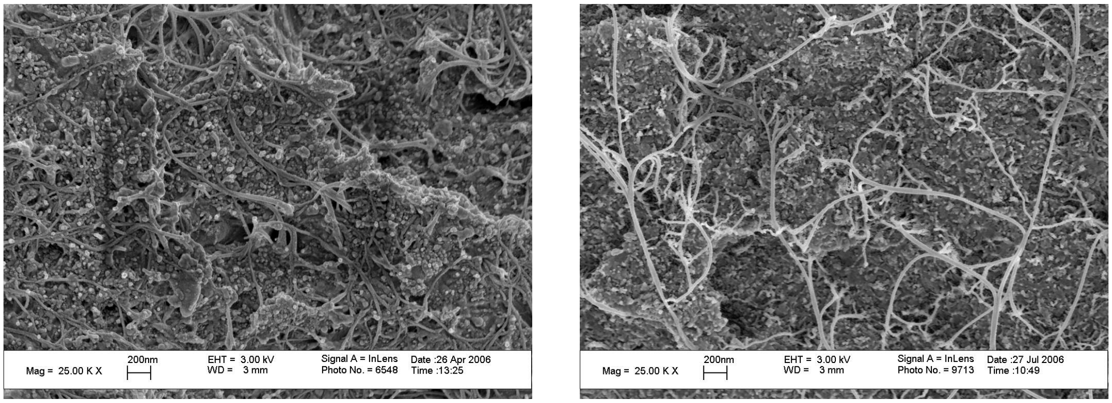


Figure 1. Electrical conductivity measurement locations across specimen width and length.



(a) (b)

Figure 2. Freeze fractured surfaces of the PC/CNT nanocomposites; (a) low melt temperature, (b) high melt temperature (both were molded at high injection speed).

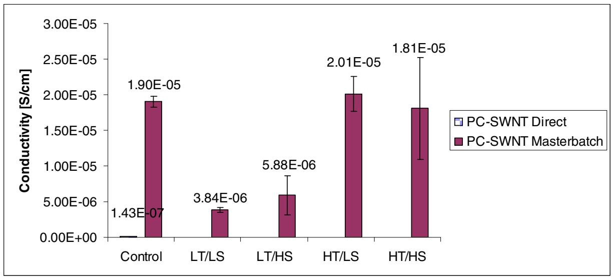
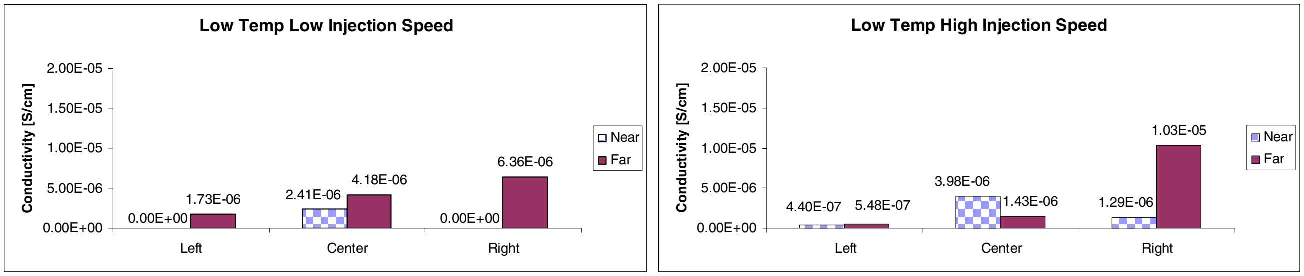
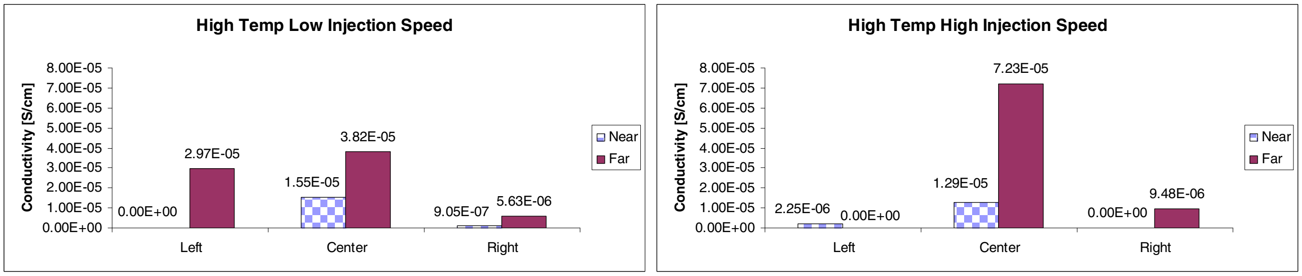


Figure 3. Electrical conductivity of PC/CNT nanocomposites from the direct compounding and solution masterbatch process.



(a) (b)

Figure 4. Electrical conductivities of PC/CNT nanocomposites injection molded at low melt temperatures (a) low injection speed, (b) high injection speed (Values of zero indicate that the conductivities were too low to be measured).



(a) (b)

Figure 5. Electrical conductivities of PC/CNT nanocomposites injection molded at high melt temperatures; (a) low injection speed, (b) high injection speed (Values of zero indicate that the conductivities were too low to be measured).

Keywords: Polycarbonate, carbon nanotubes, extrusion, injection molding.