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Dispersion and alignment of carbon nanotubes in polycarbonate

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ABSTRACT Dispersion and alignment of carbon nanotubes in thermoplastic polymers such as polycarbonate have been studied. Dispersion was accomplished by mixing in a conical twin-screw extruder and alignment was carried out using a fiber-spinning apparatus. The effects of mixing time and fiber draw rates on dispersion and alignment were investigated. Uniform dispersions were produced with relatively short residence times in the extruder. Excellent alignment of carbon nanotubes in nanocomposite filaments was obtained when the fiber draw rate was greater than 70 m/min. The ability to closely control the dispersion and alignment of carbon nanotubes in polymers is expected to lead to the development of nanocomposites with desirable electronic and structural properties.

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1 Introduction

The fabrication and characterization of polymer-matrix composite materials containing carbon nanotubes (CNTs) including single-wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes (MWNTs) is an active field of research [1–12]. These studies are motivated in large part by the potential that exists to achieve high levels of composite performance, based on the desirable physical properties of carbon nanotubes. These include tensile moduli of over 1 TPa and strengths up to 600 GPa [13].

The need to obtain well-dispersed and aligned CNTs in polymer matrices has been the subject of several recent reports, as this condition is anticipated to give rise to the best composite performance. High-energy sonication of solutions of polymers with dispersed nanotubes followed by solvent evaporation has been used successfully

to achieve homogeneous nanocomposites [6, 14]. Recently, a solvent casting method coupled with a melt mixing procedure was used to make homogeneous SWNTs-polymethylmethacrylate (PMMA) films with enhanced electrical conductivity [10]. Melt spinning of the homogeneous nanocomposite films at high draw ratios produced SWNTs-PMMA fibers with substantial alignment of the nanotubes giving overall improved mechanical properties. Another study investigated the properties of MWNTs-PMMA films fabricated by melt blending and concluded that melt blending does not destroy the nanotubes, produces homogeneous films and increases the storage modulus of PMMA [15].

We report, for the first time to our knowledge, the direct mixing of MWNTs and SWNTs with molten polycarbonate (PC) via a twin-screw extruder to produce nanocomposites with excellent dispersion of nanotubes, followed

by melt spinning of fiber to achieve a high degree of nanotube alignment in the direction of the final PC fibers.

2 Experimental

The MWNTs were produced by chemical vapor decomposition of acetylene on a supported metal catalyst with the assistance of ammonia [16, 17]. The CNTs were washed with aqueous HF to remove the residual catalyst, rinsed with water and dried at 120 °C under vacuum. The average tube dimensions are approximately 20–50 nm in diameter and 20 μm in length. The SWNTs were obtained from Carbon Nanotechnologies (HiPCO process) and dried at 120 °C under vacuum prior to compounding. Makrolon DP1–1265, high flow grade, and Makrolon 2405 PC resin pellets were obtained from Bayer and dried at 120 °C under vacuum prior to use.

Compounding of CNTs with PC (Bayer Makrolon DP1–1265 or 2405) was performed using a DACA co-rotating intermeshing conical twin-screw MicroCompounder (DACA Instruments, Goleta, Calif.) at 80 rpm with temperatures between 250–265 °C. Two kinds of PCs with very different molecular weight (MW) were used to see the effect of viscosity on dispersion of CNTs in PC. The one with lower MW (DP–1265) has lower viscosity so it is easier to mix with the CNTs, but the drawback is that it is also weaker mechanically. Nitrogen gas was used to continuously purge the extruder barrel to prevent oxidation of the polymer. Processing times varied from 1 to 120 min. The compounded nanocomposite material was extruded

through a 2-mm-diameter cylindrical die and immediately cut into approximately 3 mm pellets while still hot.

Melt spinning of nanocomposite MWNTs/PC fibers was carried out on a DACA laboratory SpinLine [17] using a 0.5 mm single hole spinneret. The processing was performed at 265 °C and the fiber draw speed varied between 10 and 70 m/min.

MWNTs/PC nanocomposites were characterized by transmission electron microscopy (TEM) using a JEOL 2010F instrument. Nanocomposite samples were ultramicrotomed using a diamond knife prior to analysis. TEM specimens were prepared by slicing the sample in a direction perpendicular to the fiber axis, to avoid any possible artificial alignment resulting from the diamond knife. The ultramicrotomed TEM specimens were about 0.2 μm thick. The nanocomposites were evaluated to determine the degree of MWNTs dispersion in the materials and the extent of MWNTs orientation in the spun fibers.

3 Results and discussion

It was found that relatively short processing times achieved good dispersion of MWNTs in PC. The TEM images in Fig. 1a, b and c show the extent of nanotube dispersion processed at 1, 5 and 10 min, respectively. White lines, parallel to the arrow direction in Fig. 1a, correspond to cutting traces of the diamond knife. Clearly, the diamond knife did not align the MWNTs during the TEM specimen preparation. From Fig. 1a, we see that the samples processed for only 1 min already show good dispersion of the MWNTs in the polymer matrix though there is still some agglomerate located at the upper left hand corner. With longer and longer processing time, the dispersion gets better and better as shown in Fig. 1b and c.

SWNTs appeared to be more difficult to disperse than MWNTs. Figure 2a, b and c shows the TEM images of samples processed at 1, 10 and 120 min, respectively. Similar with that observed in MWNTs in PC, the dispersion of SWNTs in PC also gets better and better with longer and longer processing time. However, the difference is that the dispersion of SWNTs only happened at the bundle level even after 120 min processing as shown in

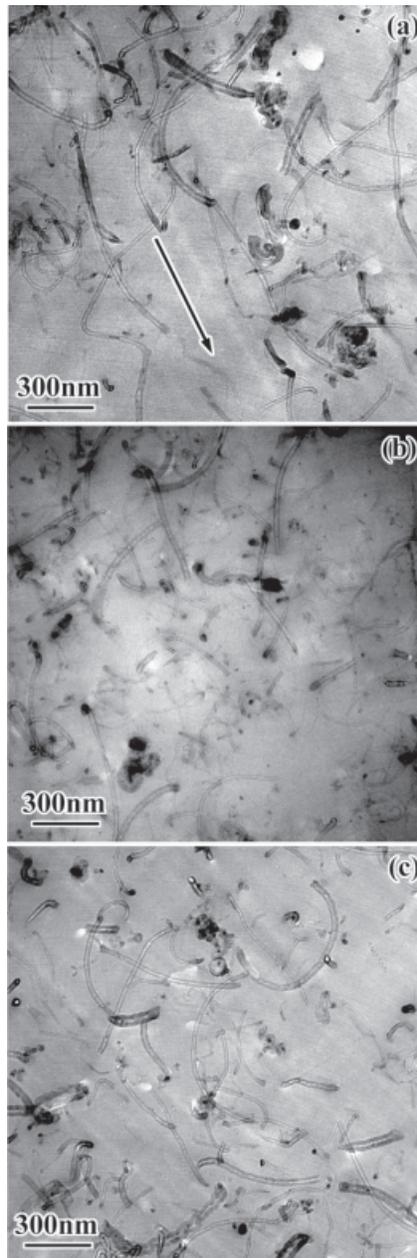


FIGURE 1 5% MWNTs/PC (2405) nanocomposite processed at 265 °C in the twin-screw extruder for **a** 1 min; **b** 5 min; and **c** 10 min

Fig. 2c, since it would not be possible to see any individual SWNTs if they are completely dispersed into individual SWNTs.

It was also observed that, as the fiber draw speed increased, so did the degree of orientation of MWNTs in nanocomposite PC monofilament. Figures 3 and 4 show the TEM images of 5% MWNTs/PC (1265) and 5% MWNTs/PC (2405) nanocomposite monofilament fibers, respectively. The fibers in Fig. 3a and b were produced by draw speeds of 10 and 70 m/min, re-

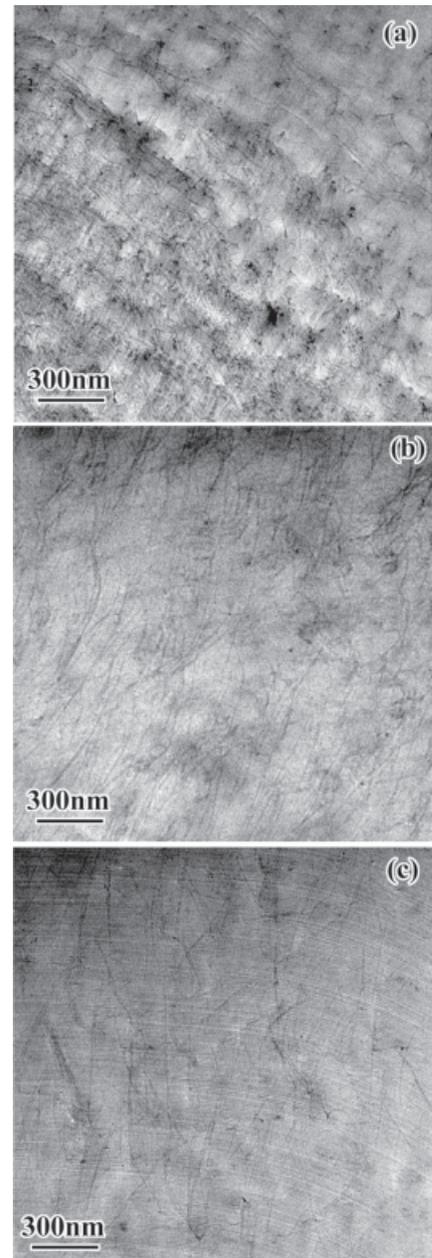


FIGURE 2 5% SWNTs/PC (2405) nanocomposite processed at 265 °C in the twin-screw extruder for **a** 1 min; **b** 10 min; and **c** 120 min

spectively, whereas 30 and 70 m/min were used to obtain the fibers shown in Fig. 4a and b, respectively. For a draw speed of 10 m/min, almost all the MWNTs were still random as shown in Fig. 3a. With increasing draw speeds, the orientation of MWNTs parallel to the fiber axis becomes better and better regardless of the molecular weight of PC (1265 vs. 2405). When the draw speeds reached 30 m/min, noticeable orientation of MWNTs was observed as shown in Fig. 4a. At speeds of 70 m/min, almost complete orientation of MWNTs

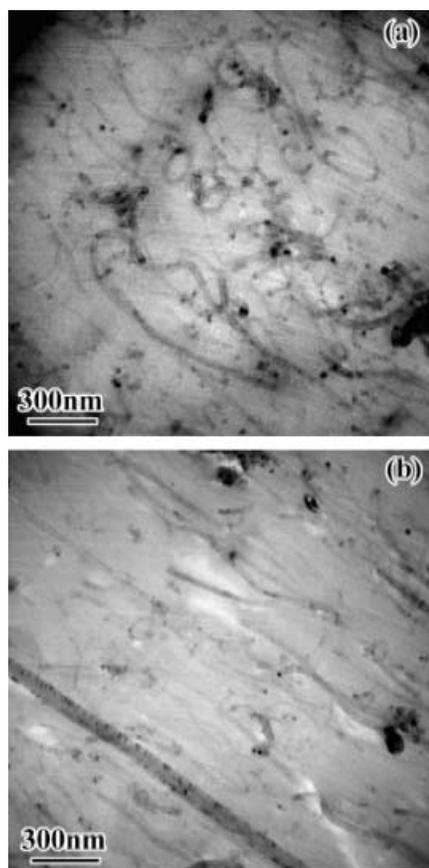


FIGURE 3 5% MWNTs/PC (1265) nanocomposite monofilament fiber drawn at **a** 10 m/min; and **b** 70 m/min

to the fiber axis has been accomplished independent of the polymer molecular weight. For the two PCs with different MW we used, there is no significant difference observed on both the mixing and spinning. The motivation to use the higher molecular weight is to have higher mechanical strength of the final MWNTs/PC fibers. Unfortunately, our first try of spinning SWNTs in PC was not successful (frequent breakage happened during fiber drawing at any draw rate), the reasons for which are not now known. More experiments are under way to figure out the reasons.

With such uniform dispersion and excellent orientation of CNTs parallel to the PC fiber axis, it is expected to see significant improvement of the ten-

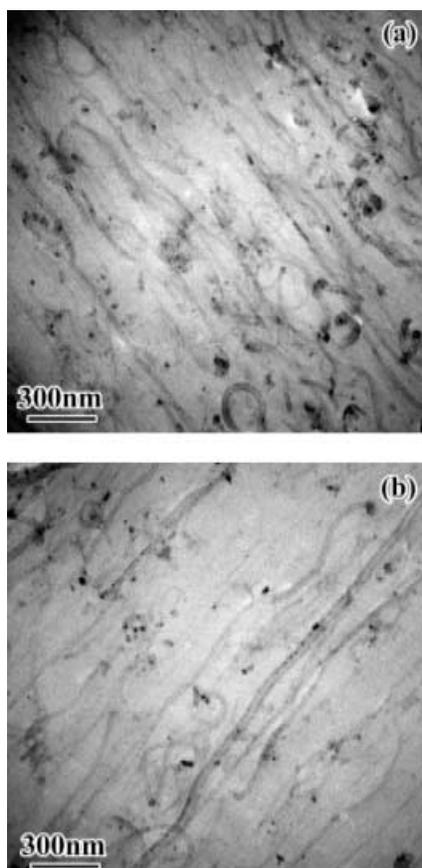


FIGURE 4 5% MWNTs/PC (2405) nanocomposite monofilament fiber drawn at **a** 30 m/min; and **b** 70 m/min

sile strength and electrical conductivity along the fiber axis direction, which is being actively studied and will be reported subsequently. Regardless of the results on tensile strength and electrical conductivity, the uniform dispersion of CNTs in polymers by twin-screw extruding and excellent alignment by drawing is probably going to be very useful.

4 Conclusions

We conclude that both MWNTs and SWNTs can be dispersed into molten thermoplastic PC very efficiently using a twin-screw extruder. The longer the mixing time, the better the dispersion. MWNTs disperse faster than

SWNTs at the same conditions of temperature and extruder speed. MWNTs in MWNTs/PC nanocomposites can be effectively aligned by melt fiber-spinning processes. MWNTs alignment in fiber-spinning processes improves as the fiber draw rate is increased. We anticipate that these extrusion and spinning processes will be an efficient way to create large quantities of polymer-matrix nanocomposite with aligned carbon nanotubes.

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