Production and Characterization of Polymer Nanocomposites with Highly Aligned Single-Walled Carbon Nanotubes

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We report the production and characterization of polymer nanocomposites with single-walled carbon nanotubes having improved mechanical properties and exceptional nanotube alignment. High-pressure carbon monoxide nanotubes (HiPco) were efficiently distributed in polystyrene (PS) and polyethylene (PE) with a twin-screw compounder. Nanotube concentrations were 1, 5, 10, and 20 wt% in PE composites and 0.7 wt% in PS composites. PE composites were melt-spin into fibers to achieve highly aligned nanotubes. Polarized Raman spectroscopy shows that the degree of alignment increases with decreasing fiber diameter and decreases with increasing nanotube loading. The orientation distribution function of a 1 wt% HiPco/PE composite had a full width at half-maximum of ~5°. The elastic modulus increases up to 450% relative to PE fibers for 20 wt% nanotube loading at an intermediate fiber diameter of 100 μm.

Keywords: Polymer, Nanotubes, Composite, Alignment, Modulus.

1. INTRODUCTION

Carbon nanotubes have attracted considerable attention and generated intense research activities on nanotubes and their composites with polymers. The interest in this extraordinary carbon form is based on exceptional mechanical, electrical, and thermal properties.1-4 These properties, combined with the very high aspect ratio, make nanotubes an excellent candidate for novel composite materials.

Several previous studies focus on the fabrication and characterization of carbon nanotube-polymer nanocomposites.5-12 An increase in thermal conductivity of 125% was observed for a 1 wt% SWNT-epoxy composite, where the nanotubes were randomly dispersed in the epoxy resin before curing.5 The same composite showed a low percolation threshold for an electrical conduction of 0.2 wt%. A solvent-evaporation method was applied for multiwall carbon nanotube-polystyrene composites with enhanced mechanical properties.7 The modulus of a 1 wt% MWNT-polystyrene composite was within ~10% of a theoretical prediction, suggesting both good dispersion and effective load transfer from the matrix to the nanotubes. The orientation of the nanotubes in the composite is a critical issue regarding the electrical, thermal, and mechanical properties of the composite. Two-dimensional (2D) X-ray diffraction was used to measure the alignment of nanotubes in a solvent cast thermoplastic composite film that was mechanically stretched at elevated temperature.11 The full width at half-maximum (FWHM) of the data fits was 46.4° for a stretched 50 wt% MWNT-poly(hydroxy aminoether) composite.11 Raman spectroscopy on a thermo-set composite that was sheared before curing showed a correlation between deformation and alignment.12

This report describes advanced, efficient fabrication methods for SWNT-polymer composites that are applicable to both amorphous and semicrystalline matrix polymers. A twin-screw compounder is used for the fabrication of the composites, which permits a direct mixing of the SWNT with the molten polymer, resulting in a good distribution of the SWNT. Melt-spinning of composite fibers produced extraordinary alignment of the SWNTs as determined by polarized Raman spectroscopy. The improved mechanical properties are measured in a tensile test and compared with theoretical values.

2. EXPERIMENTAL DETAILS

The matrix polymers were polystyrene (PS) (MW ~250,000 g/mol, supplied by Scientific Polymer Products) and polyethylene (PE) (high density, supplied by Aldrich). Single-walled carbon nanotubes (SWNTs) for the PS composites were synthesized by the high-pressure carbon monoxide method (HiPco) (Rice University)13 and used

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The SWNTs were mixed with the polymer matrix with the use of a twin-screw MicroCompounder from DACA Instruments with a barrel capacity of 5 cm³. HiPco nanotubes were sonicated in a 0.05 wt% dimethylformamide (DMF) suspension for 3 h. The compounder was filled to two-thirds of capacity with PS at 145 °C, and the HiPco/DMF suspension was added dropwise until the compounder was full. Then the temperature was increased to 155 °C to evaporate the DMF, after which the temperature was lowered to 145 °C and more HiPco/DMF suspension was added. This was repeated until 0.7 wt% loading was reached.

 Tubes@Rice were sonicated in a 0.3 wt% toluene suspension for 1 h. The Tubes@Rice suspension was then added dropwise to the compounder at 145 °C, which was filled to two-thirds of capacity with PE. The toluene boiled instantly, leaving the Tubes@Rice in the PE matrix. After evaporation of the toluene more Tubes@Rice/toluene suspension was added. Tubes@Rice/PE composites of 1, 5, 10, and 20 wt% nanotube loading were obtained.

Transmission light microscopy was used to evaluate the distribution of SWNTs within the composites. HiPco/PS films for light microscopy were pressed at 150 °C to a thickness of ~150 μm. At this thickness the films appear dark brown in transmission. The semicrystalline structure of the Tubes@Rice/PE composites produces an opaque sample that prevents transmission light microscopy.

Composite fibers were melt-spun with a DACA Spin-Line consisting of a single spinneret hole (diameter 500 μm, length ~1.7 mm) attached to a heated barrel with a piston extruder. The extruded fiber was air-cooled and drawn under tension with a variable-speed winder. Pristine PE, 1, and 5 wt% Tubes@Rice/PE composites were spun at 150–160 °C at a windup speed as high as 50 m/min. Composites with 10 and 20 wt% Tubes@Rice were spun at 175–180 °C, the maximum windup speed for the 10 wt% composite was 5 m/min, whereas the 20 wt% composite could not be wound up continuously. The HiPco/PS composite could be spun at 155 °C with windup speeds up to 60 m/min.

SEM images for composite fiber characterization were obtained with a JEOL 6300FV SEM at 2 kV. Samples were Pt/Au coated.

Orientation of SWNTs within the composite fibers was assessed with a Renishaw micro-Raman spectrometer in VV polarization geometry (1-μm beam spot) and 514.5-nm excitation. To minimize experimental errors, five positions along the fiber were measured at θ = 0 and 90°, where θ is the angle between the fiber axis and the polarization vector. Polarized Raman spectra were recorded for selected fiber diameters on 1, 5, 10, and 20 wt% Tubes@Rice/PE composite fibers. In VV geometry the Raman intensity of a single SWNT is proportional to cos⁴θ. For fibers, we can integrate cos⁴θ weighed by an orientation distribution function of the SWNTs to get the relative distribution function of SWNTs that are to be at different fiber angles. A good 2D model describing the orientation distribution is to consider a constant for the unaligned fraction, representing nanotube agglomerates without a preferred orientation, and to use a Lorentzian or Gaussian function to describe the aligned part. A 3D model with a cylindrical Lorentzian function resulted in a slightly different FWHM. Here we report the results from the simpler 2D model, because these are adequate for comparing the alignment in different fibers. For the Tubes@Rice/PE composite fibers, a Lorentzian function alone works very well because of the good alignment of the SWNT. The constant for the unaligned fraction can be neglected, because the tail of the Lorentzian function at θ = 90° accounts well for the nonzero Raman response. The Raman intensity ratio (I₀/I₀₀) was used to determine the FWHM of the distribution function, which is a good measure of the alignment of the SWNT in the composite fibers. An error of ±5% is estimated for the FWHM because of the roughness of the fiber surface and the focus uncertainty. Furthermore, Raman spectroscopy is surface sensitive since the penetration depth is generally no more than several micrometers, depending on the SWNT loading. Although it is possible that the alignment inside the fiber could be different from that on the fiber surface, we believe that the Raman ratio measured on the fiber surface is a reasonable representation of the overall alignment.

Mechanical properties of pristine PE fibers and 5, 10, and 20 wt% Tubes@Rice/PE composite fibers were obtained from tensile tests on an Instron 4206 (10 N load cell). The gauge length was 1 cm. The fibers were fixed on paper frames and tested at room temperature at a deformation rate of 1 mm/min.

The crystallinity of the PE in Tubes@Rice/PE composite fibers and pristine PE fibers was obtained from DSC measurements performed on a Perkin-Elmer differential scanning calorimeter at a heating rate of 10°/min.

3. RESULTS AND DISCUSSION

The SWNT/PS composite with 0.7 wt% HiPco from DMF suspension is homogeneous, with a good distribution of the SWNTs on the 10-μm scale (Fig. 1). A few particles are detected that we believe originate from SWNT agglomerates in the DMF suspension. DMF has a boiling point slightly higher than the process temperature of PS at ~145–150 °C. Thus the SWNT/DMF suspension can be added below the boiling point of the solvent where the DMF swells the PS and incorporates the nanotubes. Thus, agglomeration of the SWNTs is probably prevented when the DMF is evaporated at elevated temperatures.

Toluene is a good dispersant for Tubes@Rice SWNT, and it is able to soften the PE melt at 145 °C. It is not
ideal for that temperature because it boils and evaporates quickly. If too much suspension is added, the toluene evaporates before the nanotubes are incorporated in the PE matrix. Thus, a careful balance between adding the toluene suspension and the evaporation rate is necessary to prevent intense boiling that causes nanotube agglomeration.

The compounding method is efficient in preparing modest quantities of SWNT/polymer composites and could be modified into a continuous process for larger-scale fabrication. Furthermore, it is applicable to a wide range of thermoplastics and selected thermosets. The key is to isolate the SWNTs in a well-dispersed state. SWNT suspensions should be incorporated into the polymer matrix before the suspending solvent is evaporated completely to prevent nanotube agglomeration. Therefore, the suspending solvent should be able to swell or soften the polymer at the melt mixing temperature to incorporate the SWNTs, and the boiling temperature of the solvent should be ~10–20 °C above the process temperature to remain high enough to accomplish this.

Fibers were successfully spun from the HiPco/PS composite and from the Tubes@Rice/PE composites. Pristine PE and Tubes@Rice/PE composites with a SWNT loading up to 10 wt% were spun and wound up continuously. The 20 wt% Tubes@Rice/PE composite broke frequently and thus could not be wound up. As the weight fraction of the SWNTs increases, the smallest attainable fiber diameter increases somewhat, for example, 50 μm for 5 wt% Tubes@Rice and 100 μm for 20 wt%. The surface roughness and striations increase with the addition of SWNT, a typical sign of increased melt viscosity (Fig. 2). No steps, such as lubricating the spinneret, were taken to improve the surface quality. The 10 and 20 wt% nanocomposite fibers also exhibit non-uniform diameters along the fiber axis.

The polarized Raman spectroscopy indicates an extraordinarily good alignment with a FWHM of the orientation function of ~5° for the 1 wt% composite fibers with diameters of ~50 and 65 μm (Fig. 3). For a 75-μm 20 wt% composite fiber a FWHM of ~23° was
obtained. The alignment of the SWNT in the composite fibers shows two clear trends: the FWHM decreases with both decreasing fiber diameter and decreasing SWNT loading. Fibers with smaller diameters have experienced greater extensional flow, which produces better alignment. The SWNTs in composites with lower loading have more freedom to flow during shear, which results in better SWNT alignment. The SWNTs in composites with higher loading are restricted in motion by neighboring nanotubes and cannot align as well. Furthermore, the SWNTs could tend to agglomerate at higher loadings, which prevents good alignment. Overall, the high extensions achievable in melt fiber spinning produce highly aligned SWNTs in a wide range of composite loading.

The mechanical properties of the PE and Tubes@Rice/PE composite fibers were measured as a function of fiber diameter and SWNT weight fraction (Fig. 4). Linear fits are shown for each SWNT loading. Both better SWNT alignment in fibers with small diameter and higher nanotube loading result in substantial increases in the elastic modulus. The modulus increases with SWNT content, for example, ~625, ~800, ~1000, and ~1750 MPa for 0, 5, 10, and 20 wt% Tubes@Rice for a diameter of 160 μm (Fig. 4). At a diameter of 100 μm, the moduli are ~650, ~1250, ~1750, and ~3050 MPa for 0, 5, 10, and 20 wt% Tubes@Rice. This is an enhancement of more than 450% for the 20 wt% composite relative to the PE fiber. DSC showed that the crystallinity of the PE in the composite fibers is ~70% independent of the loading (5–20 wt%) and the fiber diameter (50–200 μm). Thus, variations in the PE crystallinity can be excluded as a reason for the increased moduli in smaller-diameter fibers.

The effects of alignment and concentration of the SWNTs on the mechanical properties of composite fibers are summarized in Figure 5, which is a combination of Figures 3 and 4. The elastic moduli were taken from the linear fits in Figure 4 at diameters and SWNT loadings corresponding to the 10 fibers characterized in Figure 3. At a fixed FWHM, the modulus increases with SWNT concentration, for example, ~1200 to ~2000 MPa for 5 and 10 wt% with a FWHM of 15 (Fig. 5). Furthermore, the modulus increases with better alignment for a given composite composition, for example, from ~800 to 3600 MPa for the 20 wt% composite. The elastic modulus is more sensitive to alignment for higher loaded composites. Thus, alignment and SWNT concentration both contribute to improving the mechanical properties of the composite fibers.

The Tubes@Rice/PE composite fibers have demonstrated very promising mechanical properties. A theoretical limit of these materials can be calculated with models for the longitudinal elastic modulus of composite fibers. The rule of mixtures is a first approach:

$$E = E_r V_r + E_m V_m$$

where $E_r$ and $E_m$ are the elastic moduli of the reinforcing filler and of the matrix, respectively, and $V_r$ and $V_m$ are the volume fractions. This model predicts realistic moduli for continuous fiber composites where the load is carried directly by the fibers. Here it gives the upper limit for the modulus of a discontinuous–SWNT composite (Fig. 6). Moduli were calculated for SWNT volume fractions up to 0.5, for a density of 1.6 g/cm³ for SWNT and 0.96 g/cm³ for PE. Elastic moduli of 1000 GPa for the SWNT and 0.65 GPa for the PE matrix were assumed.

A more realistic model for SWNT composites includes the aspect ratio $l_d/d_i$ of the filler, where $l_d$ is the length and $d_i$ is the diameter of the nanotubes. The following equations are derived from the Halpin-Tsai equations, with the assumptions of a circular cross section, uniform
Fig. 6. Calculated and experimental data for elastic modulus of SWNT/PE composite fibers as a function of SWNT loading: continuous SWNTs (—), SWNTs with an aspect ratio of 1000 (—), SWNTs with an aspect ratio of 100 (—), and experimental data from Tubes@Rice/PE composite fibers with a diameter of 100 µm (■).

Fiber distribution, and void free matrix:

\[
E = \frac{1 + 2(\frac{l}{d})\eta V_f}{1 - \eta V_f} E_m
\]

\[
\eta = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l/d)}
\]

where the factor \(\eta\) also depends on \(E_f\) and \(E_m\). The modulus was calculated for composites with SWNT aspect ratios of 1000 and 100. The calculated moduli for the realistic aspect ratio of 1000 is within 30% of the curve of the continuous model showing the potential of SWNT composites.

For comparison, the experimental data from the Tubes@Rice/PE composite fibers with a diameter of 100 µm are shown. The experimental data lie far below the calculated values. The reasons for this large difference can be discussed by inspecting the assumptions for the model: (a) perfect bonding of the nanotubes to the matrix, (b) complete dispersion of the nanotubes, and (c) perfect alignment of the nanotubes. The Raman data show that the nanotubes are highly aligned, so that the nanotubes interact with the load in their strong longitudinal axis, which is consistent with the mechanical model. Further improvements to the already quite good alignment are possible but will probably not result in order-of-magnitude improvements in properties. On the other hand, nanotube waviness can influence the mechanical performance of the composites and result in a modulus reduction. The nanotubes are well distributed in the composites, but it is not clear if they are dispersed on the nanoscale. SWNT ropes have a decreasing modulus with increasing rope diameter. Thus, a complete dispersion is essential for obtaining the predicted properties. The interface that transfers the load from the matrix into the nanotubes has not been specifically modified in the present work, so we can expect substantially better properties once the SWNT/matrix interface has been optimized.

4. CONCLUSIONS

In summary, we have demonstrated the successful fabrication of nanocomposite fibers consisting of a PS or PE matrix with up to 20 wt% SWNT. The fabrication method with a twin-screw compounding is efficient and promotes nanotube distribution. Furthermore, it is applicable to a wide range of matrix polymers. Melt fiber spinning results in highly aligned nanotubes with a distribution function FWHM as small as 5°. The alignment decreases for higher nanotube loading but is still good compared with other published results. High loading and good alignment of SWNT in PE results in enhanced mechanical properties. Improvement of dispersion and interface properties of the nanotubes is necessary to further improve the composite properties. Composite models predict promising mechanical properties for nanocomposites with discrete SWNTs in a polymer matrix. We have demonstrated that good alignment is essential and can be achieved by melt fiber spinning.

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References and Notes


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