Carbon Nanotubes-Reinforced PET Nanocomposite by Melt-Compounding

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ABSTRACT: Poly(ethylene terephthalate) (PET) nanocomposites with single-walled carbon nanotubes (SWNTs) have been prepared by a simple melt compounding method. With increasing concentration (0–3 wt %) of SWNTs, the mechanical and dynamic mechanical properties improved, corresponding to effective reinforcement. Melt rheological characterization indicated the effective entanglements provided by SWNTs in the melt state as well. Thermogravimetric analysis suggested no influence of SWNTs on the thermal stability of PET. Electrical conductivity measurements on the composite films pointed out that the melt compounded SWNTs can result in electrical percolation albeit at concentrations exceeding 2 wt %. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3090–3095, 2007

Key words: carbon nanotubes; polyester; reinforcement; conductivity

INTRODUCTION

Single-walled carbon nanotubes (SWNTs), the long thin cylinders of carbon, are considered to be unique for their size, shape, and remarkable physical and electrical properties. Since their discovery in early 1990s by Iijima, considerable effort has focused on producing functional composite materials with SWNTs.[1–14] This is because of their outstanding characteristics like high Young's modulus, electrical and thermal conductivity, stiffness, flexibility, large aspect ratio, and chemical inertness.[15–17] Their mechanical properties, coupled with relatively low density, make SWNTs ideal candidates for weight-efficient structures and for the same reason, they are considered to be the ultimate reinforcement in polymer composites. However, the effective utilization of SWNTs in composite applications depends on the ability to disperse them homogeneously throughout the matrix without destroying their integrity.[18] Furthermore, good interfacial bonding is required to achieve load transfer across the filler-matrix interface, a requisite for improving the mechanical properties of the composites. Fabrication of polymer-SWNT nanocomposites present considerable challenges because of the difficulty of SWNT dispersion at the high viscosity of the polymer melts. Several recent reports describe the preparation and properties of SWNT-based nanocomposites with epoxy resins,[19–23] elastomers,[24] thermoplastic polymers,[25–27] and thermoplastic elastomers[28] as matrix materials.

This study investigates the effect of 0–3 wt % melt compounded SWNTs on the mechanical, dynamic mechanical, rheological, thermal, and electrical conducting characteristics of poly(ethylene terephthalate) (PET). In an earlier work, we have found that melt compounded SWNTs are acting as effective nucleating agents for PET crystallization.[29] PET is one of the most extensively used thermoplastic polyesters, which has assumed a role of primacy in fibers, films, packaging, and molding materials. Owing to its excellent performance characteristics, it has worldwide consumption next only to polyolefins.[30–32]

EXPERIMENTAL

Materials

PET pellets (characteristic cylindrical diameter ≈ 2.5 mm, length ≈ 3 mm) were obtained from Acordis Research (Arnhem, The Netherlands). The intrinsic viscosity (IV) of the polymer was determined to be 0.98 dL/g in 1/1 phenol/1,1,2,2-tetrachloroethane at 30°C. SWNTs were purchased from CarboLex (Lexington). They were prepared by arc discharge method and the average diameter of an individual tube was 1.4 nm and length in the range of 2–5 µm. The purity of as-prepared grade of SWNTs was 50–70%.

Preparation of PET–SWNT nanocomposites

A simple melt-compounding route was adopted for the preparation of PET–SWNT nanocomposites. The

polymer and SWNTs were vacuum dried at 150°C for 12 h to avoid moisture-induced degradation. The melt compounding was performed using a laboratory scale (60 cm^3) Haake Kneader (model-HBI System-90) operating at 40 rpm for 4 min at 270°C. Nanocomposites at different concentrations (0.0–3.0 wt %) of SWNTs were prepared. A mixing time of 4 min was fixed since the torque stabilized to constant values during this time. The stabilization of torque may be related to the attainment of a stable structure.

After melt compounding, the samples were compression-molded at 270°C for 4 min in an electrically heated hydraulic press. The samples were quenched from the melt to avoid excessive degradation during the otherwise slow cooling, and then annealed at 150°C for 1 h before using for further characterization.

Intrinsic viscosity measurements

Relative viscosities (η_{rel}) of (c = 0.5 g/dL) solutions of PET or PET–SWNT samples in 1/1 mixture of phenol and 1,1,2,2-tetrachloroethane were determined using a Schott-Gerate viscometer at a constant temperature of 30°C. The solutions were prepared by dissolving the polymer samples at 70°C in the solvent, which is predried with regenerated molecular sieves. They were filtered prior to the measurements so that the presence of small amounts of undispersed components from SWNTs in the nanocomposite samples did not affect the measurements. The intrinsic viscosity (IV) values were calculated using a single-point determination method according to the relation:[33,34]

$$IV = (1/c)[2(\eta_{rel} - 1) - 2 \ln(\eta_{rel})]^{1/2} \quad (1)$$

Mechanical properties

The mechanical properties of the compression-molded samples of PET–SWNT nanocomposites were studied using a Shimadzu Universal Testing Machine (model-AG1) with a load cell of 10 kN capacity. The specimens used were rectangular strips of dimensions 40 × 5 × 0.5 mm^3. The gauge length between the jaws at the start of each test was adjusted to 20 mm and the measurements were carried out at a cross-head speed of 1 mm/min. Average of at least six sample measurements was taken to represent each data point.

Dynamic mechanical analysis

Dynamic mechanical analyzer (DMA Q-800, TA instruments) was used to study the effect of SWNTs on the viscoelastic properties of PET. The rectangular-shaped specimens of dimensions 20 × 4 × 0.5

mm^3 were exposed to a series of increasing isothermal temperatures from room temperature to 200°C at a temperature increment rate of 2.5°C and isothermal soak time of 5.0 min. At each temperature, the material was deformed at constant amplitude of 10.0 μm over a frequency of 1 Hz and the properties were measured.

Melt rheology

Rheological measurements were performed using an Advanced Rheometric Expansion System (ARES) oscillatory rheometer (Rheometric Scientific). Plate–plate geometry with a plate diameter of 25 mm was employed. Prior to the experiment, the samples were dried at 150°C under vacuum for 2 h to limit hydrolytic degradation during the measurement at 280°C. Solid samples of diameter 25 mm and thickness 1 mm were placed between the preheated plates and were allowed to equilibrate for ~10 min before each frequency sweep run. Data were recorded in a frequency range of 0.1–100 rad/s. The strain region in which the material can be regarded as linear viscoelastic was determined by amplitude sweep measurements and it was in the order of 10%. All the measurements were conducted under nitrogen atmosphere to minimize thermooxidative degradation.

Thermogravimetric analysis

Thermogravimetric analyzer (TGA, Q-50, TA Instruments) was used to study the effect of SWNTs on the thermal stability of PET. Approximately 5 mg of the samples were heated at a rate of 20°C/min from ambient temperature to 700°C. The chamber was continuously swept with nitrogen at a rate of 60 mL/min.

dc electrical conductivity

The room temperature dc electrical conductivity of the nanocomposite samples (rectangular strips of dimensions, 40 × 15 × 0.5 mm^3) was measured using a Keithley Nanovoltmeter (model 2182). A standard four-probe electrode configuration was used for the measurements.

RESULTS AND DISCUSSION

Effect of melt processing on the molecular weight of PET

Considering the sensitivity of properties of PET to molecular weight, an evaluation of the effect of SWNTs on PET properties requires comparison at similar molecular weights. For this purpose, neat PET was also subjected to melt compounding and

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TABLE I
Mechanical Properties of PET–SWNT Nanocomposite Samples

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Concentration of SWNTs (wt %)	Intrinsic viscosity (dL/g)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
0.0	0.794	42.1	1.17	5.9
0.03	0.796	42.9	1.23	5.7
0.1	0.793	45.5	1.40	5.4
0.3	0.798	45.6	1.47	4.6
1.0	0.783	52.3	1.85	4.1
3.0	0.790	54.9	1.87	3.9

compression-molding processes under identical conditions as that for the PET–SWNT nanocomposite preparation, and hereafter called the 0 wt % (SWNT concentration) sample. The decline in molecular weight of PET as a result of thermal/hydrolytic/oxidative degradation during melt processing was monitored by IV measurements. It was observed that the IV of PET drops from 0.98 to 0.88 dL/g during melt compounding and to 0.79 dL/g during compression-molding. As shown in Table I, the nanocomposite samples also had comparable IV after the processing steps. The reported IV values are the average of at least five concordant measurements. Since all the samples had comparable IV (or molecular weight) after processing under identical conditions, we infer that we have reasonably eliminated the possible dependence of our property measurement studies on the molecular weights of the samples.

Mechanical properties

Tensile tests were performed on flat tensile bars cut from the compression-molded films. The results in Table I show the expected increase in the tensile modulus and strength of PET with increasing concentration of SWNTs. For example, incorporation of SWNTs at the level of 1 wt % increases the modulus by over 50% and strength by about 25%. The elongation to break is found to decrease with the increasing loading of SWNTs, indicating that the nanocomposites become somewhat brittle. These results demonstrate that even a small fraction of SWNTs provide effective reinforcement to the PET matrix. These improved mechanical properties of PET–SWNT nanocomposite is similar to observation of Dickey and coworkers, who found that the addition of 1 wt % nanotubes into a polystyrene matrix results in 25% increase in tensile strength and 36–42% increase in modulus.[35]

Temperature dependence of the solids' viscoelastic characteristics

The DMA results for the dynamic storage modulus of the PET–SWNT nanocomposite samples as a function

of temperature at 1 Hz are shown in Figure 1(a). Following a slow decrease of the modulii with temperature in the glassy state, a rapid decrease in the modulii is observed corresponding to the glass–rubber transition at about 75°C. The storage modulii of the nanocomposite samples below glass transition increases substantially with the SWNT concentration (about 50% increase with 1 wt % SWNTs) because of the stiffening effect of nanotubes, and indicating effi-
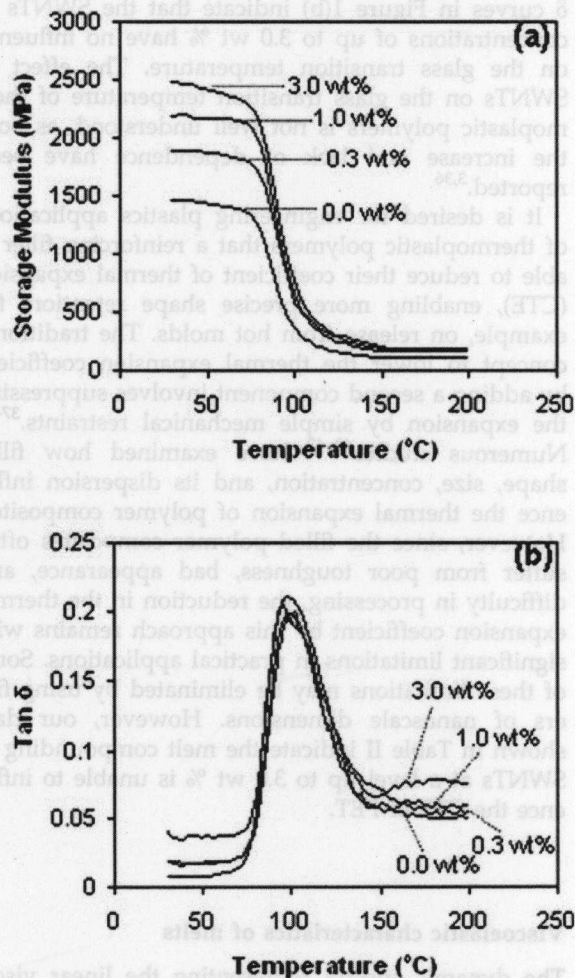

Figure 1 Effect of SWNT concentration on the (a) storage modulus and (b) tan δ of PET–SWNT nanocomposite samples.

TABLE II
Coefficient of Thermal Expansion for PET–SWNT Nanocomposites at Different Temperature Ranges

Concentration of SWNTs (wt %)	Coefficient of thermal expansion ($\times 10^{-5}$) (°C)		
	−20 to 80	0–80	20–80
0.0	6.3	6.4	6.4
0.03	6.5	6.6	6.7
0.3	6.5	6.6	6.6
3.0	6.1	6.2	6.3

cient stress transfer between the polymer matrix and SWNTs.

Although the storage modulus values are significantly enhanced by SWNTs (about 50% increase with 1.0 wt % SWNTs in the glassy region), the tan δ curves in Figure 1(b) indicate that the SWNTs at concentrations of up to 3.0 wt % have no influence on the glass transition temperature. The effect of SWNTs on the glass transition temperature of thermoplastic polymers is not well understood, as both the increase and lack of dependence have been reported.[3,36]

It is desired for engineering plastics applications of thermoplastic polymers that a reinforcing filler is able to reduce their coefficient of thermal expansion (CTE), enabling more precise shape retention, for example, on release from hot molds. The traditional concept to lower the thermal expansion coefficient by adding a second component involves suppressing the expansion by simple mechanical restraints.[37–39] Numerous studies[40–42] have examined how filler shape, size, concentration, and its dispersion influence the thermal expansion of polymer composites. However, since the filled polymer composites often suffer from poor toughness, bad appearance, and difficulty in processing, the reduction in the thermal expansion coefficient by this approach remains with significant limitations in practical applications. Some of these limitations may be eliminated by using fillers of nanoscale dimensions. However, our data shown in Table II indicate the melt compounding of SWNTs at a level up to 3.0 wt % is unable to influence the CTE of PET.

Viscoelastic characteristics of melts

The dynamic spectra representing the linear viscoelastic properties of PET–SWNT nanocomposites at different concentrations of SWNTs are shown in Figure 2. It is noticed that with the increasing SWNT loading, the storage (G') and loss (G'') modulii increase at all frequencies [Fig. 2(a,b)]. In particular, G' at low frequencies increases 100-fold on incorporation of 3.0 wt % SWNTs.

Figure 2(c) illustrates the frequency dependence of complex viscosity (η^*) of the PET–SWNT nanocomposites. It is noticed that the samples with low
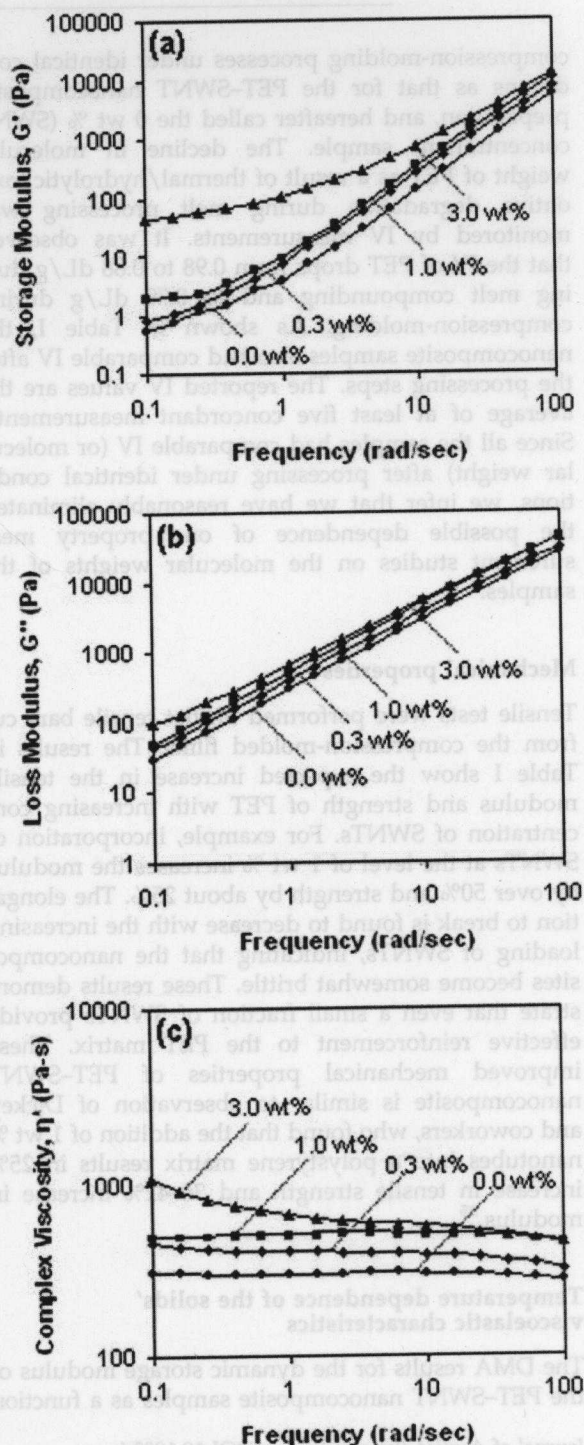

Figure 2 Effect of SWNT concentration on the (a) storage modulus, (b) loss modulus, and (c) complex viscosity (T = 280°C, strain = 10%) of PET–SWNT nanocomposites.
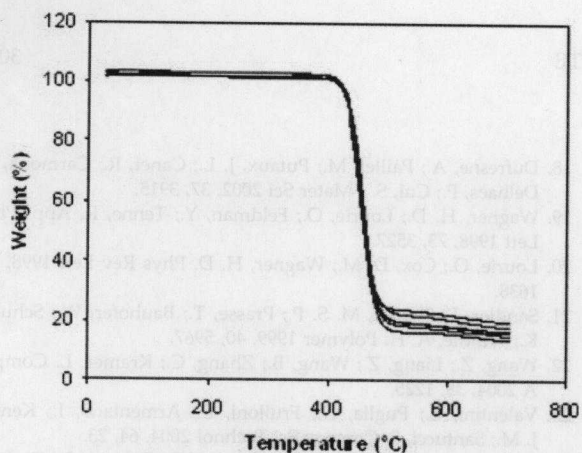
Figure 3 Temperature dependence of the weight loss characteristics (TGA) of PET–SWNT nanocomposite samples (upper curves with increasing concentration of SWNTs).

SWNT content display the expected Newtonian behavior at low frequencies, and shear thinning behavior at higher frequencies. However, the 3.0 wt % SWNTs sample shows a marked enhancement in the complex viscosity and strong shear thinning behavior even at the lowest frequency examined here. These results are in agreement with those reported by Li et al. who observed the decrease of shear viscosity of PET composites with MWNTs.[43] Pötschke et al. also observed shear thinning even at low frequencies for polycarbonate nanocomposite samples with carbon nanotube concentration exceeding 2.0 wt %.[44] Hu et al. have also studied the dynamic rheological characteristics of PET-based nanocomposites.[45] They observed that the viscosity of neat PET is almost independent of frequency, and the nanocomposite at MWNT loading of 0.5 wt % shows a weak shear thinning behavior, whereas the nanocomposites with higher MWNT loadings exhibit strong shear thinning behavior and the viscosities are orders of magnitude higher than that of neat PET at low frequency. However, Shin et al. reported that the addition of MWNTs to PET leads to an increase in complex viscosity but the viscosity does not depend on the nanotube content up to the nanotube concentration of 1.0 wt %.[46]

Thermal degradation

Some workers in the past have reported the enhancement of thermal stability of polymers with SWNTs.[47,48] Therefore, we examined the temperature dependence of the weight loss characteristics of our PET–SWNT nanocomposite samples. The TGA plots of nanocomposite samples in Figure 3 indicate that decomposition of all samples starts at around 420°C irrespective of the SWNT concentrations and thus

the thermal stability of PET is inferred to be unaffected by the presence of SWNTs.

dc electrical conductivity

Insulating polymers can be imparted electrical conducting properties by dispersion of electrically conducting particles that may form a conducting network through the sample at concentrations exceeding certain minimum value called the percolation threshold. This approach reduces the manufacturing and maintenance costs of components when compared with those previously coated with an antistatic paint. The technology is also relevant to other applications where static electrical dissipation is needed such as computer housings or exterior automotive parts. Although carbon black is traditionally used as the conductive filler, the small diameter and the large aspect ratio of SWNTs has enabled achievement of very low percolation threshold concentrations, depending on the quality of their dispersion.[13,49]

Neat PET is an excellent insulating material and had a conductivity value of the order of 10^{-17} S cm^{-1}.[45] The room temperature dc electrical conductivity values of our PET–SWNT nanocomposite samples are shown in Figure 4, and these indicate that SWNTs at concentrations ≥2.0 wt % are indeed effective in imparting electrical conductivity when melt blended to the PET matrix. A particularly impressive report by Ounaies et al. presented a similar kind of result for polyimide nanocomposites.[9] The conductivity of the pristine polyimide was increased from an order of magnitude of 10^{-18} to 10^{-8} S cm^{-1} at concentrations between 0.02 and 0.1 vol %. It is also well known that the percolation threshold is sensitive to the polymer matrix in which the nanotubes are dispersed.[50] This effect is because of the role of enhanced interfacial properties found in the case of nanocomposites.
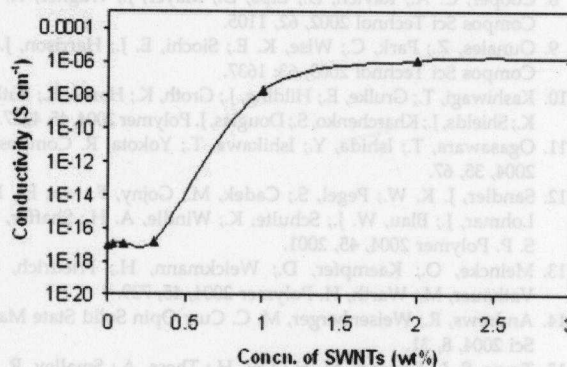

Figure 4 dc electrical conductivity of PET–SWNT nanocomposites.

CONCLUSIONS

PET–SWNT nanocomposites have been prepared by melt compounding followed by compression-molding. The improved mechanical properties and dynamic mechanical analysis of the nanocomposite samples revealed that a small concentration of SWNTs could substantially reinforce PET. The glass transition temperature, however, was not affected by the SWNT concentration of up to 3.0 wt %. Thermogravimetric analysis and thermal expansion studies indicated that carbon nanotubes did not improve the thermal stability and dimensional stability of PET. The dynamic rheological characteristics indicated that carbon nanotubes act as effective entanglements in melt state. Similarly, SWNTs at concentrations ≥2.0 wt % were found to impart electrical conductivity to the PET matrix.

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