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PET-SWNT nanocomposites through ultrasound assisted dissolution-evaporation

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Abstract

Poly(ethylene terephthalate) (PET) based nanocomposites have been prepared with single walled carbon nanotubes (SWNTs) through an ultrasound assisted dissolution-evaporation method. Differential scanning calorimetry studies showed that SWNTs nucleate crystallization in PET at weight fractions as low as 0.3%, as the nanocomposite melt crystallized during cooling at temperature 24 °C higher than neat PET of identical molecular weight. Isothermal crystallization studies also revealed that SWNTs significantly accelerate the crystallization process. Mechanical properties of the PET-SWNT nanocomposites improved as compared to neat PET indicating the effective reinforcement provided by nanotubes in the polymer matrix. Electrical conductivity measurements on the nanocomposite films showed that SWNTs at concentrations exceeding 1 wt% in the PET matrix result in electrical percolation. Comparison of crystallization, conductivity and transmission electron microscopy studies revealed that ultrasound assisted dissolution-evaporation method enables more effective dispersion of SWNTs in the PET matrix as compared to the melt compounding method.
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1. Introduction

For the past one decade, nanocomposites of polymers with carbon nanotubes (CNTs) have been increasingly studied due to their outstanding prop-erties and potential for a wide range of applications [1–6]. In these materials, nanotubes are used as inclusions in various matrices to improve electrical, mechanical or thermal properties. In particular due to their large aspect ratio, mechanical, electronic and conductive properties, single walled carbon nanotubes (SWNTs) [7] are considered to be unique candidates for making polymer-based nanocompos-ites. Several recent reports describe the preparation and properties of SWNT based nanocomposites with epoxy resins [8–11], elastomers [12], thermo-plastics [13–15] and thermoplastic elastomers [16]

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as matrix materials. However, fabrication of polymer-SWNT nanocomposites through conventional melt mixing methods present considerable challenges due to the difficulty of SWNT dispersion at the high viscosity of the polymer melts. Many authors have reported solution evaporation method, *in situ* polymerisation etc. for effectively dispersing nanotubes in various polymer matrices. For example, Qian and his colleagues reported that the addition of 1 wt% multi walled carbon nanotubes into polystyrene matrix by a simple solution evaporation method resulted in ~40% increase in elastic modulus and 25% increase in break stress [17]. Shaffer and Windle prepared poly(vinyl alcohol) based nanocomposites with a wide range of nanotube loadings through a solution evaporation method [2]. Bower et al. fabricated CNTs/poly(hydroxyamino ether) nanocomposites by solution casting and studied their deformation behavior [18]. They estimated the onset buckling strain and fracture strain to be 5% and >18%, respectively. However, the improvement in mechanical properties of the reported polymer nanocomposites with CNTs as fillers are usually limited mainly due to the formation of severe CNT agglomeration and/or poor interfacial interactions with the matrix.

Recently many groups have explored the possibility of using SWNTs as nucleating agents for polymer crystallization. For example, Probst et al. found that single walled carbon nanotubes can nucleate crystallization of poly(vinyl alcohol) at concentrations as low as 0.1 wt% [19]. The crystallization behaviour of polypropylene (PP) in the presence of SWNTs has also been reported [14,15,20]. Nogales *et al.* found that SWNTs did not influence the crystal structure of poly(butylene terephthalate) (PBT) [21], but they did not evaluate the influence on crystallization rate. We have recently shown that melt compounded single walled carbon nanotubes can nucleate crystallization, impart electrical conductivity and provide rheological and mechanical reinforcement in poly(ethylene terephthalate) (PET) [22,23]. Hu et al. have recently employed ultrasonification route for dispersion of multi walled carbon nanotubes (MWNTs) in dichlorobenzene-phenol mixed solvent, followed by mixing with PET [24]. In this communication, we report an ultrasound assisted dissolution-evaporation method for the preparation of PET-SWNT nanocomposites, and examine their crystallization characteristics, as well as electrical conductivity and mechanical properties.

2. Experimental

2.1. Materials

PET pellets (characteristic cylindrical diameter ≈ 2.5 mm, length ≈ 3 mm) were obtained from Acordis Research (Arnhem, the Netherlands). The intrinsic viscosity 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 Inc. (Lexington, USA). 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%. 1,1,1,3,3,3-Hexafluro-2-propanol (99+%, HFIP) was obtained from Lancaster and chloroform (99+%) was purchased from Aldrich.

2.2. Preparation of PET-SWNT nanocomposites

PET pellets were powdered and dried at 150 °C for 12 h under vacuum. HFIP was added in the weight ratio HFIP:PET = 4:1, and allowed to stand for 2 h. Chloroform was then added in the weight ratio chloroform:HFIP = 5:1, and shaken for a few hours to dissolve the PET. Desired amount of pre-dried SWNTs was then added and the suspension (~25 mL) was sonicated for 15 min using a mechanical probe sonicator (13 mm, VibraCell Processor VC 750, operating at 40% of the maximum power 750 W). The solutions were then cast onto glass petri-dishes and allowed to dry slowly at room temperature to get thin films. These films were used for further characterization.

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC Q-100, TA Instruments) was employed to study the effect of SWNTs on the crystallization characteristics of nanocomposites. Indium was used for temperature calibration ($T_m = 156.6$ °C, $\Delta H_m = 28.4$ J/g). All the samples were dried prior to the measurements and analyses were done in a nitrogen atmosphere using standard aluminum pans. Calorimetric measurements were done while the samples (4–5 mg) were exposed to the following temperature scans: heating at a rate of 20 °C/min to 310 °C, holding for 10 min to erase thermal history effects, and then cooling to 50 °C at a rate of 20 °C/min during which the peak of crystallization exotherm was taken as the crystallization temperature, T_c. The heat of fusion (ΔH_m) and

the heat of crystallization (ΔH_c) were determined from the areas of the melting and crystallization peaks during heating and cooling, respectively.

For analysis of the isothermal crystallization characteristics, the samples were subsequently reheated to 310 °C at a rate of 20 °C/min, held at 310 °C for 2 min, and then cooled rapidly (60 °C/min) to the desired temperature for isothermal crystallization (210 °C, 215 °C, 220 °C or 225 °C).

2.4. Mechanical properties

The mechanical properties of PET-SWNT nanocomposite films 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 $30 \times 5 \times 0.2$ mm. 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 were taken to represent each data point.

2.5. DC Electrical conductivity

The DC electrical conductivity of the nanocomposite samples (rectangular strips of dimensions $40 \times 15 \times 0.2$ mm) was measured using a Keithley Nanovoltmeter (model 2182) in dry air at ambient temperature. A standard four-probe electrode configuration is used for the measurements.

2.6. Transmission electron microscopy

The samples were stuck on a stub, blocked and faced using a Leica UCT microtome. The microtoming was carried out at room temperature and sections of about 90 nm thickness were collected on a standard copper grid. The microscopic studies were performed using a JEOL 1200 EX Transmission Electron Microscope using an accelerating voltage of 80 kV.

3. Results and discussion

We dispersed SWNTs by ultrasonication of its suspension in the mixed solvent HFIP-chloroform (1:5) containing dissolved PET ($\sim$8 wt%) (Section 2.2). Fig. 1a shows that the solution containing SWNT (1 wt%) remained stable for at least 6 weeks. On the other hand SWNTs have been ultrasonicated in the mixed solvent but without dissolved PET and it was observed that the nanotubes settle immediately after ultrasonication. This indicates that the polymer PET provides as an effective surfactant for SWNTs in this solvent. Ultrasonication can result in chain scission and decrease in molecular weight of the polymers, depending on the solvent, polymer molecular weight and the ultrasound intensity. However, we found no change in the intrinsic viscosity of the PET recovered after our ultrasonication of the PET solution. SWNT-PET composite films of thickness 0.2 mm were prepared by solution casting (Section 2.2). Fig. 1b compares the appearance of the films corresponding to three different concentrations of the SWNTs. Color uniformity was observed in each sample.

3.1. Crystallization characteristics

The effect of SWNTs on the crystallization of PET was analyzed with non-isothermal DSC experiments.
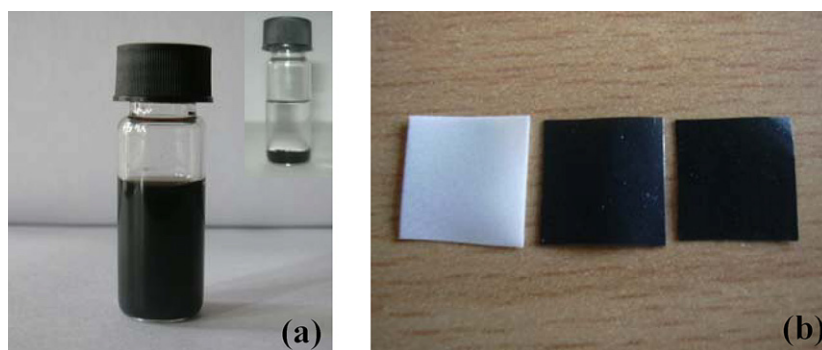

Fig. 1. (a) Vial containing 1 wt% well dispersed SWNTs in PET solution which remained stable even after 6 weeks of its preparation. Shown in the inset is a vial containing the mixed solvent (containing no PET) with nanotubes that settled immediately on ending sonication. (b) Photographs of PET-SWNT nanocomposite films with 0, 1 and 3 wt% SWNT fractions. Each sample is approximately 1 cm in length and breadth.
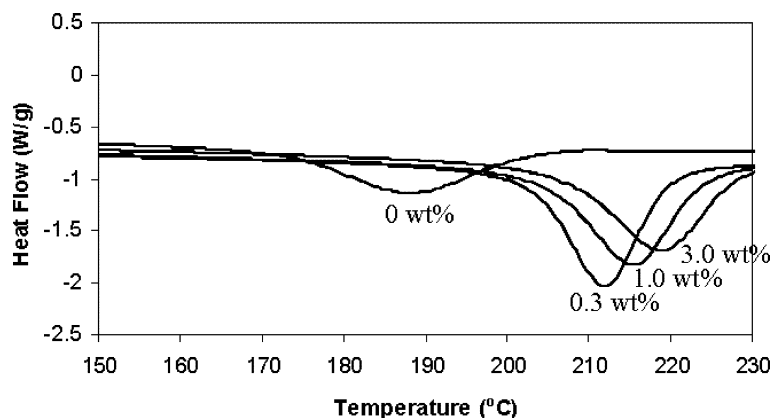
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Fig. 2. DSC cooling scans of neat PET and PET-SWNT nanocomposite samples.

Table 1
DSC-determined thermal parameters for neat PET and PET-SWNT nanocomposite (IV $\sim$0.98 dL/g) samples prepared by ultrasound assisted dissolution-evaporation

Concentration of SWNTs (wt%)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0.0	187.8	23.1	254.8	32.2
0.3	212.1	42.0	252.8	35.4
1.0	215.2	39.5	252.4	36.8
3.0	219.0	42.0	253.5	39.2

Fig. 2 shows the DSC cooling scans of neat PET and SWNT containing nanocomposite samples. The peak crystallization temperatures (T_c) during the cooling scans, peak melting temperatures (T_m) during heating scans, as well as the associated enthalpies are summarized in Table 1. During cooling from the melt, the SWNT containing samples showed crystallization exotherms at higher T_c than the neat polymer. According to the results obtained, the crystallization temperature of PET increased by 24 °C with SWNTs at a concentration as low as 0.3 wt%. The T_c values continue to increase with increasing SWNT concentration indicating that SWNTs act as effective nucleating agents for PET crystallization. However, the rate of rise of T_c decreases with increase in SWNT concentration beyond 0.3 wt%, indicating possible saturation of the nucleation efficiency at low SWNT concentrations. This is possibly related to the large surface area and good dispersion of SWNTs. The melting temperature of the polymer was not significantly affected by carbon nanotubes.

3.2. Isothermal crystallization characteristics

Isothermal crystallization of neat PET and nanocomposite samples is studied at four different tem-
peratures viz., 210, 215, 220 and 225 °C (Section 2.3). After reaching the desired isothermal crystallization quickly from melt (60 °C/min), the time lapsed until the maximum in the heat flow rate, which is proportional to the crystallization rate, was taken as peak time of crystallization (t_{peak}). The peak time of crystallization, t_{peak}, at each of the isothermal temperatures for the neat polymer and the nanocomposite samples is noted and plotted against the isothermal crystallization temperature (Fig. 3). The smaller t_{peak} values for the SWNT containing samples as compared with neat PET indicate that SWNTs enhanced the rate of crystallization. For the case of neat PET, no crystallization is observed at the highest temperature of 225 °C because the crystallization is very slow and would require longer time than the four minutes employed in our DSC programme. On the other hand, for the sample containing 3.0 wt% SWNTs, the rate of crystallization is so fast that most of the crystallization occurs already during the cooling scan (60 °C/min) employed to reach the desired isothermal crystallization temperatures.

In an earlier work [22,23] we had evaluated the crystallization enhancement in PET-SWNT nanocomposite samples prepared by melt compounding. Here we compare those results with the present results with the samples prepared through ultrasound assisted solubilization route. The IV values of the PET dropped from 0.98 dL/g to $\sim$0.88 dL/g after melt compounding. The increase in the crystallization temperatures (T_c), the apparent melting temperatures (T_m) and the enthalpies are reproduced in Table 2 from Ref. [22]. We find that the increase in the T_c values as a result of the SWNT-induced nucleation is much higher for the composite
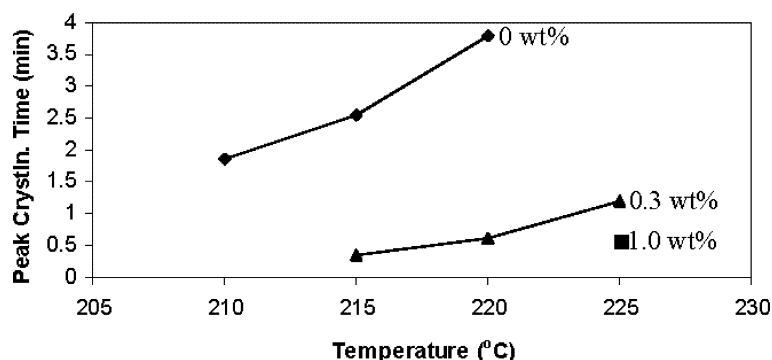
Fig. 3. Effect of SWNTs on the peak crystallization time of PET at different temperatures.

Table 2
DSC-determined thermal characteristics of PET-SWNT nanocomposite samples (IV ~0.88 dL/g) prepared via the melt route [22]

Concentration of SWNTs (wt%)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0.0	199.9	38.2	253.0	36.5
0.3	212.4	37.6	253.5	37.3
1.0	214.3	37.2	251.1	37.7
3.0	219.1	36.8	252.5	38.8

Table 4
Mechanical properties of neat PET and PET/SWNT nanocomposite samples

Concentration of SWNTs (wt%)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
0.0	27.6	1.56	5.21
1.0	35.2	2.52	4.98
3.0	37.2	2.54	4.34

samples prepared via the solution route, indicating a possible improved dispersion of SWNTs by the solution route (Table 3).

3.3. Mechanical properties

Tensile tests were performed on flat $30 \times 5 \times 0.2$ mm samples cut from the solvent cast films. The overall effect of SWNTs on the mechanical properties of PET is given in Table 4. The results indicate that upon incorporation of only 1.0 wt% SWNTs to the PET matrix, the tensile strength of PET is improved by 27%. As the concentration of nanotubes increases, tensile strength increases. The modulus also increases with increasing filler loading; ~60% rise is observed with 1.0 wt% nanotubes.

These results demonstrate that a small fraction of SWNTs substantially enhances the mechanical strength of the polymer or in other words, SWNTs provide effective reinforcement to the PET matrix. The better mechanical performance of the nanocomposites as compared with neat PET can be attributed to the homogeneous dispersion of SWNTs in the PET matrix as well as the strong matrix-nanotube interfacial interactions enabling the effective stress transfer between the matrix and filler.

3.4. Electrical conductivity

Thin electrically conductive films are one possible application of SWNT-PET nanocomposites. The room temperature DC electrical conductivity values of the nanocomposite samples are given in Table 5.

Table 3
Comparison of the T_c rise as a result of the SWNT-induced nucleation in PET-SWNT nanocomposite samples prepared via solution route and melt route

Concentration of SWNTs (wt%)	Increase in T_c (°C)	
	Solution route	Melt route
0.0	187.8	199.9
0.3	24.3	12.5
1.0	27.4	14.4
3.0	31.2	19.2

Table 5
Electrical conductivity of neat PET and nanocomposite films at room temperature

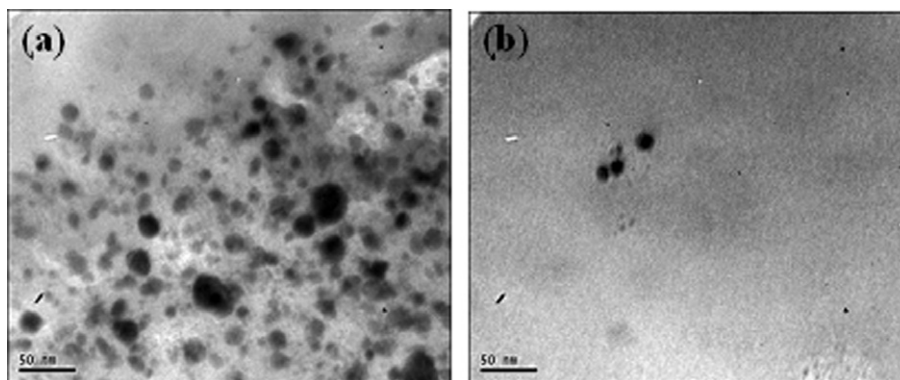| Concentration of SWNTs (wt%)	Conductivity (S cm^{-1})
0.0	1.51×10^{-12}
0.3	1.69×10^{-9}
1.0	1.12×10^{-6}
3.0	2.63×10^{-6}

Fig. 4. Transmission electron micrographs of PET-SWNT (1 wt%) nanocomposite samples prepared through (a) melt compounding method and (b) ultrasound assisted dissolution-evaporation method.

The conductivity of neat PET film was about 1.51×10^{-12} S cm^{-1}. At loading levels exceeding 1 wt%, the conductivity level surpassed the antistatic criterion of thin films (1×10^{-8} S cm^{-1}). However attempt to determine the threshold concentration was abandoned at this stage of the study. Our previous results [23] have shown that the melt compounded SWNTs can impart conductivity to the PET matrix of the order of 10^{-6} S cm^{-1} only at concentrations exceeding 2 wt%. Comparison with results of Table 5 suggests a possibly improved SWNT dispersion during the solubilization route employed here.

3.5. Morphological characterization

Transmission electron micrographs of the nanocomposite samples prepared through the melt compounding method and the dissolution-evaporation method are shown in Fig. 4. In the microtome cut perpendicular to the apparently aligned SWNTs, relatively coarse aggregates are seen (Fig. 4a) for the sample prepared by melt compounding method (as in Refs. [22,23]). In comparison, the dispersion appears to be finer and uniform in Fig. 4b for the sample made by ultrasound assisted dissolution-evaporation. This supports our above observation of higher efficiency of the ultrasound assisted dissolution-evaporation method in enhancing the crystallization and electrical conductivity characteristics of PET.

4. Conclusions

Single walled carbon nanotubes dispersed in PET through the ultrasound assisted solubilization route have been shown to act as effective nucleating agents for PET crystallization. The enhancement in the crystallization temperature of PET on dispersion of SWNTs at a weight fraction as low as 0.3% was roughly 24 °C. As expected, SWNTs are also shown to impart electrical conductivity to the PET matrix, with a percolation threshold at SWNT concentration of 1 wt% in PET matrix. Analysis of the mechanical properties reveals that small fractions of SWNTs can substantially reinforce PET. TEM analysis supports the crystallization and conductivity enhancement based observation that the solution route employed here provides better dispersion of SWNTs as compared to the melt compounding route reported earlier by us.

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