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Nanotube composites produced from single-walled carbon nanotubes and polycarbonate

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Single-walled carbon nanotubes (SWCNTs) were dispersed in a polycarbonate (PC) matrix in a solution system and the composite was characterised by wide-angle X-ray diffraction technique, differential scanning calorimetry, a mechanical testing equipment and by FTIR-spectroscopy. The results showed a 58% increase in Young's modulus of PC with the addition of 0.5-5 wt% SWCNTs to the polymer matrix. Changes in the x-ray diffraction patterns, heats of melting etc. of the composite system were measured and are correlated to the changes in crystallinity and other molecular parameters.

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1. Introduction

Since the report on carbon nanotubes (CNTs) by Iijima [1] in 1991 there had been a spate of research activities on the production, characterization and application of these amazing materials. Single-walled carbon nanotubes (SWCNTs) are cylinders with a single wrapped graphene sheet. Multi-walled carbon nanotubes (MWCNTs) are a collection of concentric SWNTs. These have been found to have relatively better defined atomic structure with higher length to diameter ratios, and better chemical stability than structures formed in polymeric chains [2]. Theoretical and experimental studies have shown that SWCNTs possess a Young's modulus of the order of 1-5 TPa [2] and a tensile strength as high as 60 GPa [3]. These unique properties of CNTs offers the potential for synthesizing nanotube composites with highly increased mechanical strengths due to reinforcement. Such reinforcement has been considered to depend on the efficiency of the process of transferring load from CNTs to the polymer matrix [4]. However, there are only a few examples of successful use of CNT's as a reinforcing agent [5] in polymers, and the aggregation of CNTs and the poor interactions between CNTs and polymer matrices are generally attributed to the lack of functionality in such composites. Several approaches, e.g. melt blending [6] have been tried to improve the functional properties of such composites, and different polymers have been used as matrix materials for CNT/polymer composite system for various applications. Research on a polycarbonate (PC) and SWCNT composite system [7] has not been widely reported. Physical properties of polymers, particularly, the PC are important parameters because of its myriads engineering applications. The improvement of these properties through the introduction of CNT into its matrices will be very useful for both scientific studies and application oriented investigations. In this paper we investigate the changes in mechanical properties and the morphology of the PC polymer due to the introduction of CNTs using a variety of conventional physical measurement methods and correlate the results with the changes in the molecular structures.

2. Experimental

For the formulation of the composite bisphenol A polycarbonate (PC, from Aldrich) having an average molecular weight of 64 kDa and density of 1.2 g. cm^{-3} was used without further treatment as a 10% (w/v) solution in CHCl3 (laboratory grade). SWCNTs were added to the polymer solution, and stirred vigorously for at least 48 hours prior to placement in a high-energy ultrasonic bath for 24 hours for dispersion of the SWCNTs in the polymer matrix. Films were cast on a glass substrate using a stainless steel applicator, and were dried for 24 hours at the room temperature before being placed under a constant vacuum at 50 °C for 48 hours.

Wide angle X-Ray Diffractometer (WAXRD) was used to evaluate the structure of the materials. The X-ray spectra were recorded from $2\theta = 2^{o}$ to 80^{o}, using a graphite monochromator and using Nickel-filtered Cu K_{α} radiation at $\lambda = 0.1542$ nm (40 kV, 40 mA). The results were analyzed using commercial software (MDI Jade 5) to determine the d-space and the crystallinity (Xc). The Xc was calculated as the ratio of the intensity under the crystalline peaks above the background to the total intensity.

Thermal properties of the samples (about 6-8 mg) were studied by differential scanning calorimery (DSC) using a thermal analyzer instrument (DSC 2010). The analysis was carried out under nitrogen atmosphere at a flow rate of 50 ml min^{-1} and at a heating rate of 10 °C min-1. The DSC instrument was calibrated for temperature and energy with indium and tin reference samples.

Fourier Transform Infrared (FTIR) spectroscopy was carried out using ABB Bomem, MB Series (Model MB-100) FTIR spectrometer.

Measurements of the mechanical properties were performed using a computer-controlled material testing machine Zwick (Zwick GmbH & Co.). A calibrated load cell of 1 kN at a crosshead speed of 5 mm min^{-1} with an internal extensometer with automatic break detector having a constant gauge length of 10 mm was used. Parameters such as the tensile stress, percentage of strain and Young's modulus at which the samples were ruptured were determined. The numerical values were calculated as an average of the 3 measurements for each type of sample, and the results were presented with standard deviation.

3. Results and discussion

The main features of the X-ray diffraction pattern of SWCNTs, as expected, were similar to those of graphite, as shown in Fig. 1 a. A graphite-like peak (002) plane at 26.4° was present and a family of (h k 0) peaks due to the honeycomb lattice of the single graphene sheet was observed. The peak position for graphite is at 26.5^{o}, giving a shift of ~0.1° in the SWCNT. Additionally, the line strength of the peaks in SWCNT is reduced and somewhat broadened on its low diffraction angle part compared to those in graphite. The asymmetry in SWCNT is caused by the presence of different crystalline species which are difficult to separate. The SWCNT materials consist of a stack of graphene sheet and the wrapped graphitic plane constituting a carbon nanotube. The intensity and width of the (002) peak has a d-space of 3.37 Å and are related to parameters such as: the number of layers, interlayer spacing, lattice distortions and orientation of the SWCNT with respect to the direction of the incident X-ray. The observed peak profiles were similar to those reported [8]. Fig. 1b illustrates the intensity distributions measured for the pure PC homopolymer film and the PC/SWCNT nanotube composites with different concentrations of SWCNTs. The X-ray diffraction pattern shows several crystalline reflections with a d-space = 3.54 Å [(124), (302), (312)], 5.104 Å (210) and 10.82 (002) Å in the case of PC, which correspond to an orthorhombic crystals structure. Here, the monoclinic crystals form, e.g. d = 8.05 Å and 4.75 Å were not recorded in the PC film as studies of the crystal structure itself is beyond the scope of this article. Initial peak at smaller angles (0-3°) are due to air scattering, and in this range the crystal reflections were not detected. The intensity of the peaks decreased with the addition of SWCNTs, indicating a disruption of the PC crystallites by the SWCNT in the matrix. A small increase of the intensities of peaks of the (002) and (100) reflections at 26.4^{o} and 44.34^{o} with the increase in the concentration of SWCNTs confirms the transition from PC crystallites to tubostratic organization of the carbon layer planes[9]. The crystallinity of the PC as estimated from the X-Ray diffraction results was found to be reduced to only 9% in the composite having 5 % SWCNTs' from a value of ~18% in the unmodified PC sample. This was calculated from the diffraction trace for the PC without the addition of SWCNTs. The crystallinity was reduced to ~ 9 % with the addition of 5% SWCNTs in the PC.

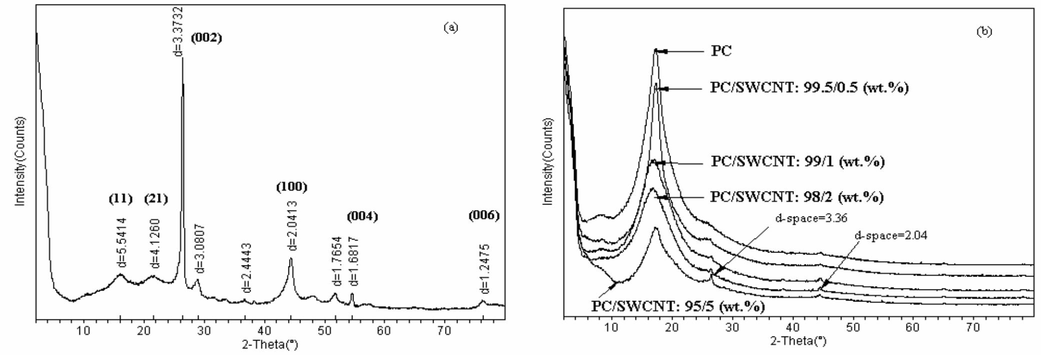

Fig. 1. Wide-angle X-ray diffraction patterns of (a) SWCNT and (b) PC and PC/SWCNT nanotube composites.

The crystallinity was also measured by using the enthalpy of fusion detected from the DSC thermogram, for the different proportions of PC/SWCNTs recorded under a nitrogen atmosphere and with at a heating rate of 10 °C min^{-1}. Fig. 2 shows the changes in enthalpy of the samples with temperature for different loading of SWCNT. For PC film with no SWCNT, a broad melting endotherm at ~ 222 °C appeared with heat of fusion of ~ 6.9 Jg^{-1}, and the midpoint T_g was evaluated to be ~155 °C. The thermogram (Fig. 2 (i)) also showed a distinct endotherm at 260 ^{o}C. With 0.5 (wt.%) of SWCNTs, the heat of fusion was reduced to 4.6 J.g^{-1} without any changes in the melting temperature, and glass transition temperature is decreased by 7 °C. The heat of fusion (ΔH) decreases drastically with the increase of SWCNT contents (Fig. 2) and the ΔH could not be measured for higher concentrations of SWCNTs (e.g. for 2% and 5% of SWCNTs), although the T_g was found to decrease by 13 °C. The degree of crystallinity was calculated using 100% crystalline PC films, having ΔH = 109.7 J/g [10], to give a crystallinity of ~ 6.3%, in the case of PC film. The measured value of crystallinity using DSC was significantly lower than the value obtained by WAXRD. The difference in the crystallinities for the two different measurements suggests that the requirements for a long-range order of the chains in semicrystalline samples are less rigorous for the X-ray measurements than those for melting enthalpy using DSC. However, the observed differences in the crystallinity in composites having different concentrations of SWCNT are attributed to the differences in the interfacial region between crystalline and amorphous phases characterized by partial ordering of the chain units. The SWCNTs in the PC matrix act as a plasticizer, which increases the amorphous phase and thus reduces the crystallinity and glass transition temperature. For PC (Fig. 2), the glass transition occurs over a broad temperature range (e.g. 125-175 °C) and therefore the values determined from such data are inherently not unique and are usually quoted with a large error margin. However, a well-defined thermogram giving a unique value of T_g is observed in the case of PC/SWCNT nanotube composites, particularly for concentrations of SWCNT > 0.5%.

The mechanical parameters, i.e. the Young's modulus, tensile strength and percentage of elongation at which the samples were ruptured, were measured. The numerical values were calculated as an average of 3 measurements for each type of sample. The typical stress-strain curves of PC and its composite are presented in Fig. 3a. The Young's modulus, the tensile strength and the elongation of the nanotube composites were found to increase with the increase in the SWCNT loading as shown in Fig. 3b. The increase of tensile strength was as high as 53% compared to that of PC film at a SWNT loading of only 2 %. The superior mechanical properties of nanotube composites are attributed to the reinforcement effect created by the incorporation of SWCNTs within the PC matrix.

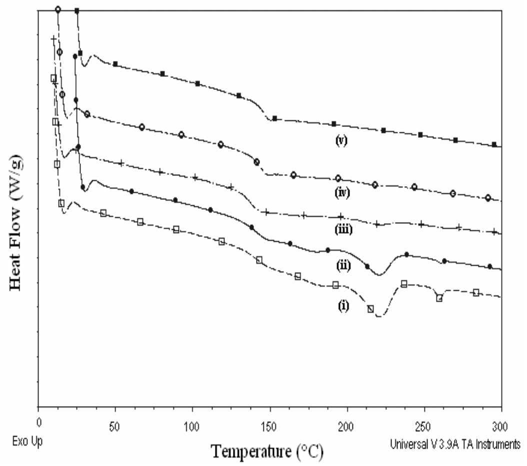

Fig. 2. Differential scanning calorimetry thermograms of PC and nanotube composites: (i) PC film, (ii) PC/SWCNT: 99.5/0.5 (wt.%), (iii) PC/SWCNT: 99/1 (wt. %), (iv) PC/SWCNT: 98/2 (wt. %), and (v) PC/SWCNT: 95/5 (wt. %).

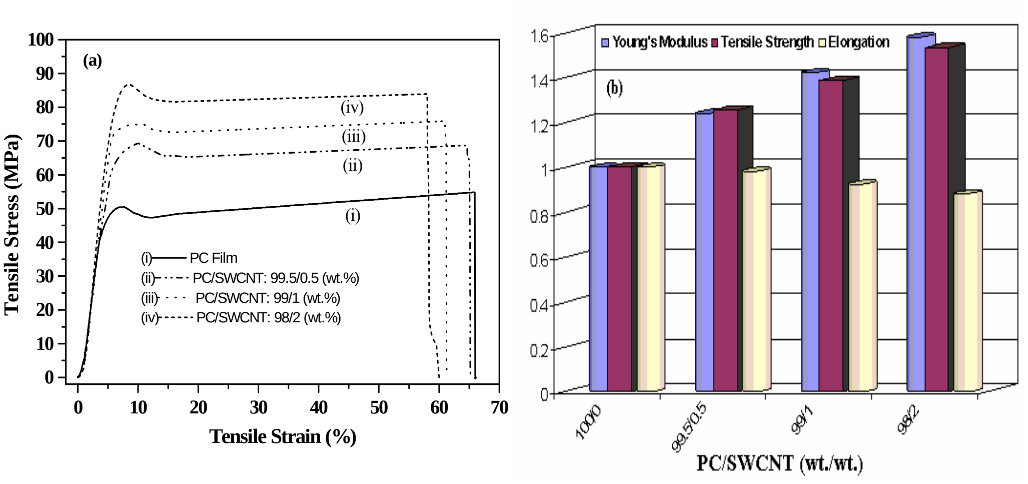

Fig. 3. The graphical representation of the mechanical properties of PC/SWCNT nanotube composites, (a) typical stress-strain curves of PC film and PC/SWCNT composites, (b) Young's modulus, tensile strength and elongation are plotted as a function of different composition of SWCNT in PC (these parameters were normalized with the values obtained from the 100% PC film).

Fourier Transform Infrared (FTIR) spectroscopy was carried out using ABB Bomem, (Model MB-100) FTIR spectrometer. The FTIR spectra of as received SWCNT (Fig. 4 a) exhibited characteristic bands at 748 cm^{-1}, 873 cm^{-1}, 1452 cm^{-1}, 1634 cm^{-1} and 2914 cm^{-1}. The band at 873 cm^{-1} is attributed to the A2u mode out-of-plane vibration and the band at 1634 cm^{-1} is considered to be due to the E_{1u} mode in-plane-vibration. The phonon modes at 873 and 1598 cm^{-1} have been reported [11] and the first of which matches exactly with our results. The band at 557 cm^{-1} (Fig. 4b) has been attributed to the skeletal vibration of carbonate group in PC [12]. In the present study the carbonyl band in the spectrum of PC film at 1779 cm^{-1} shifted to a value which was lower by ~ 8 cm^{-1} for the PC/SWCNT nanotube composite (Fig. 4 b). Dybal et al [12] reported that the spectral line of crystalline PC shifted from 1775 cm^{-1} to 1765 cm^{-1} in the case of amorphous PC. The present results, when compared to those found in the literature, indicate that considerable structural changes of PC have occurred due to the presence of SWCNTs. Significant differences in the spectral shape and signature were observed in the case of the PC/SWCNT nanotube composites with respect to that of PC (Fig. 4).

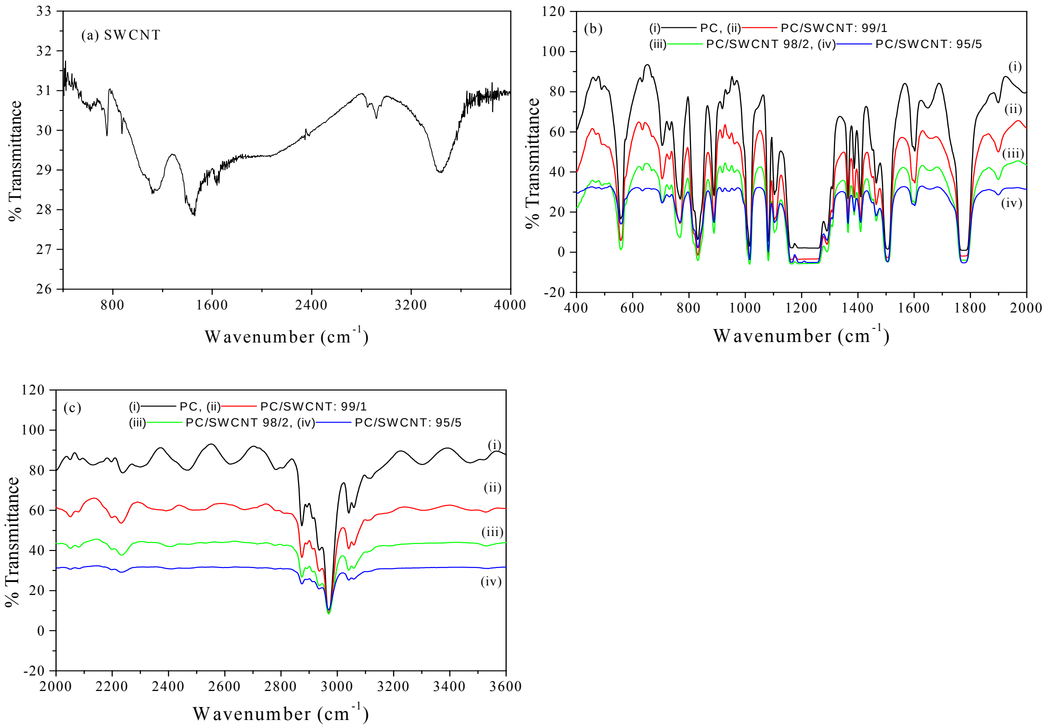

Fig. 4. Fourier transform infrared (FTIR) spectra of (a) SWCNT and (b, c) PC and PC/SWCNT nanotube composite films.

4. Conclusions

From the results of various analyses of the PC/SWCNT samples it is concluded that the SWCNTs incorporated within the polymer matrix cause structural changes which significantly reduce the crystallinity and increase the mechanical strength of the composites. The measured decrease in crystallinity of PC/SWCNT nanotube composites is attributed to the disruption of the regularity of the chain architecture in the crystalline regions of the host matrices by the presence of the SWCNT molecules. The WAXRD and DSC measurements revealed the changes in structural differences due to interactions of the SWCNTs in the PC system. The above conclusions are further substantiated by the observed frequency shift of carbonyl stretching and the intensity differences of the FTIR analysis.

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