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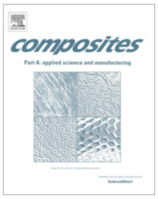

Tough semiconductor polycarbonate/multiwalled carbon nanotubes nanocomposites by rubber modification

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ABSTRACT

Tough polycarbonate (PC)/multiwalled carbon nanotube (MWCNT) nanocomposites (NCs) modified by a maleated styrene/ethylene–butylene/styrene (mSEBS) rubber were obtained in the melt state using a highly dispersed PC/MWCNT master-batch. An electrical percolation threshold (p_c) occurred at only 0.5% MWCNT showing a power law critical exponent of 2.60, which is characteristic of a three-dimensional percolated structure. The presence of MWCNT decreased the rubber particle size due to an increase in matrix viscosity. In addition to high electrical conductivity, the elastic modulus of the NCs was similar to that of the PC, as a result of the combined presence of 0.5% MWCNT and 4% mSEBS; the mSEBS was also able to provide (i) considerable impact strength, (ii) clear ductile behavior and (iii) increased resistance against crack propagation.

1. Introduction

The study of polymer NCs based on carbon nanotubes (CNTs) has attracted significant academic and industrial interest over the last decade [1,2]. Due to the exceptional conductive and mechanical properties of CNTs, thermoplastic/CNT NCs can exhibit drastic improvements in electrical conductivity and significant improvements in mechanical and physical properties. Up to now, the studies based on thermoplastic/CNT NCs aimed to identify either the best performing CNT modification for a particular matrix [3–6], or the influence of the processing conditions [7,8] on dispersion and properties. However, recently, more complex systems where a third component is present [9–12] have warranted attention.

In order to improve electrical conductivity in polymer NCs, the CNTs in the matrix must form a three-dimensional conductive network. The critical concentration at which the sudden change in conductivity occurs is called the percolation threshold (p_c) [13]. The p_c clearly decreases when the aspect ratio of the filler increases [5,13]. In the literature on thermoplastic/non-functionalized CNT NCs, a wide range of p_c values (typically from 0.5% to 5%) can be found depending mainly on the polymer matrix, the nanotube type, and the processing method.

Several processing methods have been employed for the production of thermoplastic/CNT NCs such as melt mixing, in-situ polymerization, solution processing, etc. [14,15]. Among these methods, melt mixing of CNTs with thermoplastic polymers using conventional processing techniques is particularly desirable, because the process is fast, simple, free of solvents and contaminants, and readily available in the plastics industry [14]. Similarly, the use of pre-compounded largely dispersed master-batches (usually containing 10–20% CNTs) produced in "ad hoc" machinery is advantageous for processing, as dispersion is close to optimum and hazardous contact with the nanofiller is reduced to the minimum.

A notable exception to the overall good physical performance of thermoplastic/CNT NCs is toughness. This is because it dramatically decreases upon the addition of CNTs. This is attributed [16] to the mobility restrictions that CNTs impose on the surrounding matrix chains, limiting its plastic deformation. Consequently, ascertaining which nano and micro-structures lead to tough, highly conductive NCs, is an appealing area for research.

Polycarbonate of bisphenol A (PC) is a high performance amorphous polymer, which exhibits high toughness, dimensional stability and good optical clarity. Moreover, electrically conductive NCs based on PC can be obtained at low MWCNT contents (0.1–2%) by direct melt processing of both components [17,18], or by using previously prepared highly dispersed PC master-batches [19,20]. The presence of relatively low MWCNT contents (2–3%) seriously deteriorates the ductility of the PC matrix, which shows a

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dangerous tough/brittle transition at around these contents [21,22]. The impact strength was not measured in these studies.

Rubber modified NCs based on PC [23–27], polyamide 6 [12,28], poly(L-lactide) [29–31] have been extensively studied in the literature. Non elastomeric polymers have been also used to modify PC based NCs [32–36]. In the case of rubber modified PC based NCs, to our knowledge [23–27], only poly(acrylonitrile–butadiene-styrene) (ABS) (butadiene content 5–20%) [23–25] NCs have been studied. In these NCs, the MWCNTs were localized in the PC phase [23–25] when the ABS content was lower than 60% [24] or 70% [25]. Very low p_c values (0.19%) were observed in the NC with 50% ABS [26], due to both the double percolation phenomenon and the co-continuous morphology of the NC [23,26]. The increase in Young's modulus with the MWCNT content was higher at high injection molding temperatures [27], due to the lower melt viscosity and greater homogeneity of the NCs. However, to the best of our knowledge, so far no work has been published concerning the toughening of NCs based on rubber modified PC.

In this study, firstly, the PC was melt mixed with a MWCNT content that varied from 0% to 2.5% in an attempt to obtain a conductive percolated structure. Then, the PC/MWCNT NCs were mixed with 0–10% mSEBS. PC/mSEBS blends were also studied as a reference. This allowed us to examine the reciprocal influence of the presence of MWCNT on toughness, and of rubber on the dispersion and percolation threshold. The morphology of the NCs was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The phase behavior was studied by dynamic mechanical analysis (DMA). The electrical conductivity was measured by means of an impedance analyzer, and toughening was followed by instrumentalized and non-instrumentalized notched Izod tests. Stiffness and ductility, obtained by means of tensile tests, completed the study of the electro–mechanical properties of the NCs.

2. Experimental

The polycarbonate of bisphenol A (PC) used was TARFLON® IV9000, and the styrene/ethylene–butylene/styrene (SEBS) triblock copolymers were Kraton® G 1652 (unmaleated) and G 1901X (maleic anhydride functionalized). The filler (multiwall carbon nanotube (MWCNT)) was embedded in a PC matrix (Plasticyl® PC 1501). The MWCNTs possess a surface area of 250–300 m^2/g, and an average diameter and length of 9.5 nm and 1.5 μm, respectively. This PC/MWCNT master-batch (containing 15% of MWCNT) was diluted to 0.5% for the whole study, and to 0.25–2.5% in the preliminary work to ensure a conductive percolated structure at a minimum MWCNT content. SEBS and maleic anhydride functionalized SEBS were mixed to obtain the desired maleated SEBS (1.0% MAH content) (mSEBS) content. The mSEBS content in the NCs ranged from 0% to 10%. The NCs will be named by their MWCNT and mSEBS content; i.e., 0.5–10% NC indicates a 89.5–0.5/10 PC-MWCNT/mSEBS NC. In the case of blends, the prefix NC will be substituted by blend (0–10% blend indicates a 90/10 PC/mSEBS blend).

Drying before processing was performed at 120 °C in an air-circulation oven for 12 h for the PC and PC/MWCNT masterbatch, and, in the case of the mSEBS at 60 °C, in an air-circulation oven for 6 h. The PC/MWCNT matrices were obtained using a Collin ZK25 co-rotating twin screw extruder–kneader. The diameter and length-to-diameter ratio of the screws were 25 mm and 30, respectively. The barrel temperature was 260 °C and the rotation speed 200 rpm. Subsequently, the PC-MWCNT/mSEBS NCs, and the reference PC/mSEBS blends were obtained using the same equipment at a barrel temperature of 260 °C and at a rotation speed of 100 rpm.

After extrusion, the extrudates were cooled in a water bath and pelletized. Subsequent injection molding was carried out in a Battenfeld BA230E reciprocating screw injection molding machine to obtain tensile (ASTM D638, type IV, thickness 3.2 mm) and impact (ASTM D256, thickness 3.1 mm) specimens. The screw of the plasticization unit had a diameter of 18 mm, L/D ratio of 17.8 and compression ratio of 4. The melt temperature was 265 °C and the mold temperature was held at 20 °C. The injection speed and pressure were 12.5 cm^3/s and 1950 bar, respectively.

The contact angle measurements were carried out on a CAM 100 goniometer (KSV) on injection-molded specimens and pills (in the case of the MWCNT), using water and ethylene glycol. The interfacial tension was calculated by the two-liquid Harmonic Method measuring the contact angle of the two liquids on the surface of the PC, mSEBS, and MWCNT. If the polar and dispersive components, and thus, the surface tension $\gamma = \gamma^d + \gamma^p$ of the liquids are known, then the surface tension of each polymer can be easily obtained by means of the equation:

$$(1 + \cos\theta)\gamma_L = 4\gamma_S^d\gamma_L^d/(\gamma_S^d + \gamma_L^d) + 4\gamma_S^p\gamma_L^p/(\gamma_S^p + \gamma_L^p) \tag{1}$$

that can be written for each liquid, where θ is the contact angle between the solid and the liquid, γ_L the surface tension of the liquid and γ_d and γ_p the dispersive and polar components of the surface tension of the solid and the liquid (subscripts S and L, respectively). The interfacial tension (γ_{12}) between the two polymers can now be obtained by the harmonic mean equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 + \{4\gamma_1^d\gamma_2^d/(\gamma_1^d + \gamma_2^d) + 4\gamma_1^p\gamma_2^p/(\gamma_1^p + \gamma_2^p)\} \tag{2}$$

The phase structure was studied by DMA analysis performed using a TA Q800 that provided the loss tangent ($\tan\delta$) against temperature. The scans were carried out in bending mode at a constant heating rate of 4 °C/min and a frequency of 1 Hz, from −140 °C to roughly 220 °C.

The transmission electron microscopy (TEM) samples were ultrathin-sectioned at 60–100 nm using a cryo-ultramicrotome. The micrographs were obtained in a Philips CM200 apparatus at an accelerating voltage of 200 kV. The surfaces of cryogenically fractured specimens were observed by SEM after gold coating. A Hitachi S-2700 electron microscope was used at an accelerating voltage of 15 kV. The rubber particle size was measured in representative zones of the cryogenically fractured impact specimens. The weight average particle size, $\bar{d}_w$, was calculated from a minimum of 200 particles as follows:

$$\bar{d}_w = \frac{\sum_i n_i d_i^2}{\sum_i n_i d_i}, \tag{3}$$

where n_i is the number of particles with size d_i. The interparticle distance (τ) was calculated by means of

$$\tau = \bar{d}_w\left[\left(\frac{\pi}{6\phi}\right)^{1/3} - 1\right], \tag{4}$$

where ϕ is the volume fraction of the matrix.

The tensile tests were carried out in an Instron 5569 tensile tester at a cross-head speed of 10 mm/min at 23 ± 2 °C and 50% ± 5% relative humidity. Young's modulus was determined by means of an extensometer at a cross-head speed of 1 mm/min. Ductility was measured as the reduction of the transversal area. Izod impact tests were carried out on notched specimens using a Ceast 6548/000 pendulum. The notches (depth 2.54 mm and radius 0.25 mm) were machined after injection molding. A minimum of seven tensile specimens and eight impact specimens were tested for each reported value. Instrumented Izod impact testing was performed on the notched specimens, using a data acquisition system DAS 8000. In the essential work of fracture (EWF) procedure, the total fracture energy (W_f) (calculated from the area under load–displacement curves) is the addition of the surface related essential