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Dispersion and its relation to carbon nanotube concentration in polyimide nanocomposites

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ABSTRACT

Characterization of Carbon Nanotube (CNT) dispersion in a polyimide matrix and its effect on nanocomposite mechanical properties is presented in this paper. CNT bundle aspect ratio, measured by voltage-contrast scanning electron microscopy, is determined to be the quantitative measurement of dispersion and is found to decrease with increase in nanotube concentration. The reduction of CNT bundle aspect ratio with concentration is shown to explain the less effective reinforcement observed in composites as CNT concentration is increased beyond the electrical percolation concentration. It is shown that increase in CNT concentration beyond percolation concentration does not yield proportional improvement in elastic modulus because CNT aspect ratio systematically decreases as concentration increases. A modified Cox micromechanical model that accounts for the actual nanotube bundle aspect ratio as a function of concentration, nanotube waviness and orientation is shown to predict the observed nanocomposite elastic modulus dependence upon concentration.

1. Introduction

In the past three decades, CNTs have generated significant interest in the scientific community due to their outstanding mechanical, thermal and electrical properties [1]. Owing to their high stiffness, one potential application of CNTs is the mechanical reinforcement of polymer matrices [2]. Even though moderate success has been achieved, the effective polymer reinforcement due to CNTs has exhibited large variability. For instance, for polyimide (PI)–CNT nanocomposites containing 1% CNTs, improvements in elastic modulus lower than 10% [3–5], between 10% and 40% [5–9] and greater than 40% [10–13] have all been reported.

It is well known that mechanical properties of polymer–CNT composites are strongly influenced by the quality of CNT dispersion [14]. Nanotube bundles, agglomerates or non-uniform distribution of polymer and CNTs are characteristics of non-ideal dispersion of CNTs in polymer matrices [15]. CNT bundles or ropes are arrays of aligned nanotubes, while CNT agglomerates refer to the disordered arrangement of CNTs resembling a nest-like structure.

Dispersion of nanotubes and other nanofillers in polymer matrices has been widely studied by imaging methods such as optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) [16]. OM allows macro-scale imaging of nanocomposites, making possible to identify macroscopic agglomeration, but no information on nano-scale dispersion is gathered [11,17]. Some information regarding nano-dispersion can be obtained from SEM [4,11], TEM [6,7,10] or AFM [18], but in most cases nanocomposite images are limited to surface features and render limited information on overall nanofiller dispersion. An alternative technique for dispersion assessment is the voltage-contrast SEM method [19–24]. This method provides sub-surface images of the CNT network embedded in the polymer matrix, significantly increasing the number of nanotubes analyzed per scan and thereby facilitating the characterization of CNT dispersion.

In the present paper, a systematic approach to characterize dispersion of CNTs in a PI matrix using voltage-contrast SEM, and its effect on nanocomposite mechanical properties is presented.

2. Synthesis and characterization

2.1. Synthesis of PI-CNT nanocomposites

PI-CNT nanocomposites were synthesized by *in situ* polymerization under sonication. Single-walled carbon nanotubes (SWNTs,

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Carbon Nanotechnologies Inc.) were first dispersed in anhydrous dimethylacetamide (DMAc, Acros organics) for 2 h under bath sonication. 4-4′Oxydianiline (Chriskrev) and sodiumdodecylbenzene sulfonate surfactant (Aldrich, 0.2 wt% with respect to polymer) were added to the SWNT dispersion and sonicated for 30 min before adding an equimolar amount of 3-3′,4-4′benzophenone tetracarboxylic dianhydride (Acros Organics). After 3 h of polymerization under sonication, films were cast on glass plates, DMAc was removed at 80 °C under vacuum and the polymer was thermally imidized by a series of isothermal steps at 150, 250, 300 and 350 °C, thereby obtaining PI-SWNT films of 25–35 μm in thickness.

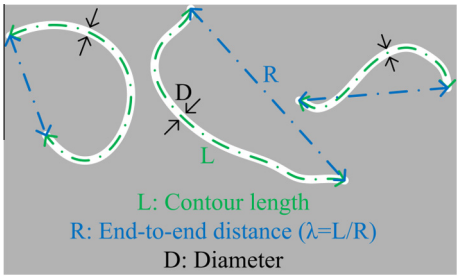

Fig. 2. Parameters used to characterize CNT dispersion from SEM images.

2.2. Dispersion characterization: voltage-contrast SEM

The characteristics of CNT dispersion in the PI matrix were assessed by voltage-contrast Scanning Electron Microscopy [19]. SEM voltage contrast is due to potential differences between insulating polymer and conductive CNTs. For low accelerating voltage, the nanocomposite is charged positively and as a result CNTs are observed as dark features surrounded by bright polymer. CNT imaging is challenging in these conditions due to significant charge accumulation in the polymer matrix. As the accelerating voltage increases, the sample undergoes a transition from positive to negative charge, modifying the contrast difference between polymer and CNTs. Therefore, for high accelerating voltages, CNTs appear as bright (conductive) features embedded in a dark (not conductive) polymer matrix and sub-surface features become evident [20–24] (Fig. 1).

Sub-surface images of the CNT network embedded in the non-conductive polymer were obtained from uncoated conductive nanocomposites with a FEI NOVA nano SEM using the through-the-lens detector and operating at 10–15 kV accelerating voltage.

As shown in Fig. 2, CNT dispersion was quantified from voltage-contrast SEM images by measuring bundle diameter (D), bundle contour length (L) and end-to-end distance (R, straight-line distance between the ends of a CNT bundle). Six images from each nanocomposite were used for dimension characterization. Average and standard deviations of bundle dimensions were determined by measuring CNT bundle diameter from high magnification images (50,000×) and contour length and end-to-end distance from lower magnification images (10,000×), using a minimum of 40 or 10 measurements, respectively. The voltage-contrast method allows sub-surface imaging of the CNT network, up to approximately 250 nm [20–24]. Therefore, determination of L and R is not trivial, since bundle orientation with respect to the image plane is not known. To minimize this artifact, L and R were measured carefully choosing CNT bundles with ends that could be clearly identified and that were approximately in the same plane (i.e. with no significant brightness change across their length).

For the voltage-contrast SEM method, image quality strongly depends on nanocomposite conductivity; therefore, it was not possible to obtain quality images of nanocomposites containing 0.05 and 0.1 vol% SWNTs due to the lower composite conductivity.

One disadvantage of the voltage-contrast SEM method is that the observed CNT dimensions are influenced by local charging of polymer surrounding the CNT, and therefore, the diameter of CNT bundles is likely overestimated [21]. To remove this artifact,

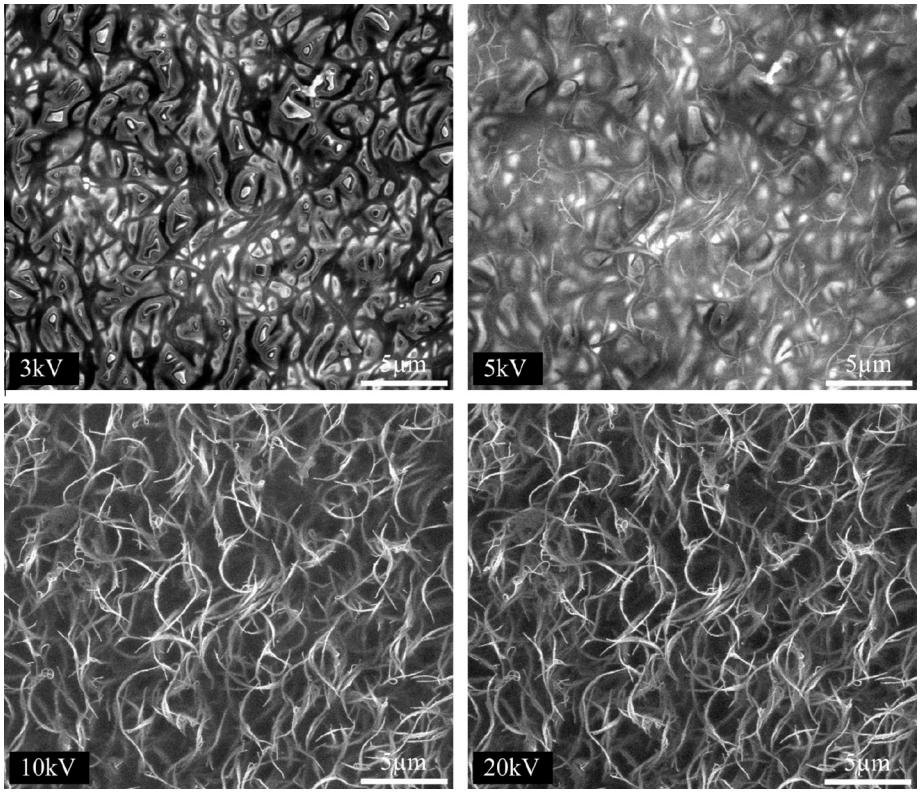

Fig. 1. Voltage contrast SEM images obtained at 3, 5, 10 and 20 kV accelerating voltages.