Interface-Dependent Mechanical Properties in MWNT-Filled Polycarbonate

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Static tensile tests, dynamic mechanical analysis as well as electron microscopy were used to characterize the macromechanical properties of MWNT-filled polycarbonate composites. Meanwhile the behavior of the nanotube/polymer interfaces was examined by changing nanotube contents and measuring electrical conductivity and dielectric spectroscopy. When the interface achieved the state of percolation (2 mass% MWNT), strain of fracture of MWNT-filled polycarbonate composites reached a peak of 9.3%, elastic modulus increased 30% comparing to pure polycarbonate and damping ratio bottomed out. [doi:10.2320/matertrans.MRA2008450]

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1. Introduction

Carbon nanotubes filled polymer composites have attracted considerable attention in the research and industrial communities due to their astonishing mechanical properties, low mass density, especially the large interfacial contact area. In traditional fiber-filled composites the interfacial region is critical to control the load transfer from the matrix to the fiber and thus critically influences both the modulus and fracture behavior of the composites. However, in nanotube filled polymers, the interfacial region can be quite significant. A number of researchers have taken composite interface as a medium phase (interphase). Polymer within this interfacial region has a structure and properties altered from the bulk polymer matrix due to interactions with the embedded nanotubes.

There have been few studies related to macromechanical properties of the nanotube-polymer interface. Bhabani K and co-workers observed a tough-to-brittle transition caused by nanotube bridging phenomenon; they also found the resistance against crack initiation (J0.5, EWF) was correlated with the matrix behavior (state of percolation). The formation of the interphase region, the dispersion state of the interphase and the effect of the interphase structure on the macromechanical properties of nanotube-filled polymers is so far not clear.

Experimental results also demonstrated that the improvement of material properties relies on nanotube dispersion and polymer/nanotube interfacial bonding. Although we can achieve good dispersion of the SWNTs in the polymer matrix by solution mixing, dispersion down to the single tube level is not possible for SWNTs. The SWNTs are held together with relatively weak van der Waals forces and this may have effect on investigating the behavior of the interphase region. Therefore, we choose MWNTs as preferred fillers rather than SWNTs.

This paper presents a detailed study of the impact of MWNT weight percentage on the interphase and macromechanical properties for MWNT–polycarbonate composites. The correlation between the macromechanical properties and behavior of the interphase region offers the ability to realize of optimal effective mechanical properties for nanotube-polymer systems.

2. Experimental

The MWNTs were produced in a Fluidized Bed CVD Reactor, with an average diameter of 30 nm. PC 2805 (Bayer) was chosen for the polymer matrix with a melt flow index of 10.0, tensile strength of 2400 Mpa and an elongation to break of 60%.

The as-received MWNTs were refluxed in 5 M HCl solution for 6 h at 80°C. After acid treatment, the samples were calcined in static air at 510°C with the reaction time of 30 min, and the pure MWNTs were obtained. The temperature of air oxidation of acid-treated MWNTs was determined by thermo gravimetric analysis (TGA 2050) with a rate of 10°C/min from room temperature to 700°C.

A solution mixing process was used to prepare MWNT-filled polycarbonate composites. The MWCNTs were first sonicated for 3 h in tetrahydrofuran. PC pellets were dried at 125°C for 2 h, followed by dissolution in tetrahydrofuran. The MWCNT dispersion and the PC solution were then mixed together and ultrasonicated for 1 more hour. Anhydrous methanol was then dropped into the mixture causing precipitation of the composite material. The composite material was dried at 70°C under vacuum for 14 h. A compressive mold (pre-heated to 225°C) was used to prepare test specimens. The dimensions of the test specimens for DMA were 40.0 mm × 5.0 mm × 0.2 mm (length × width × thickness). The composite material was compression molded into plates with a diameter of 1.23 cm and a thickness of about 1.35 mm for electrical testing and dielectric testing. The weight fraction of MWCNT in the composite samples was varied between 0.5 and 10%.

Tensile tests were conducted on an Instron 3042 equipped with an extensometer. Samples were run at an extension rate of 2 mm/min. Examination of the samples by electron microscopy was conducted on the fracture surfaces that were obtained from the tensile-tested samples. Temperature dependent tests were completed on a DMTA 2980 in tensile mode. Storage (E′) and loss moduli (E″) were measured as a function of temperature. In these tests the samples were measured.
subjected to a sinusoidal strain of 0.1% at a frequency of 1 Hz. The temperature scan rate for these tests was 2°C/min. The damping ratio curve is defined as the ratio of the loss modulus to the storage modulus.

3. Results

3.1 Mechanical properties

The quality of MWNTs dispersion in the polycarbonate was examined by scanning electron microscopy (SEM) in a S-450 instrument operated at 20 kV of the fracture surface broken in liquid nitrogen. Figure 1(d) shows an example of the fracture surface for MWCNT-PC composite with 6% weight fraction of MWCNTs. MWCNTs are well dispersed in the polymer matrix. From the inset of Fig. 1(d), the uniform distribution of nanotubes on the fracture surface shows excellent dispersion. The good dispersion insures maximum surface area for nanotube/polymer interaction. Apparently each nanotube is about 100 nm in diameter and become fatter than the oringin, which is only 30 nm. It seems that the nanotube was coated with a polymer layer known as “polymer wrapping”.\textsuperscript{7} The morphology of the carbon nanotube/polymer composites powder with 4% weight fraction of MWCNTs was examined by TEM (Hitachi H-800). The inset of Fig. 1(c) proved that some nanotubes were wrapped well and some were partly wrapped. Figure 2 shows typical stress-strain curves for the MWCNT/PC composites at several concentrations. Table 1 summarizes the modulus, yield stress, and strain-to-failure for each composite sample. It is clearly seen that elastic modulus has been constantly on the rise with the increase of MWCNT content. The sample with 2 mass% MWNT has an increase of 16.9% in elastic modulus compared to pure PC.

There is a tough-to-brittle transition at 2 mass% MWNTs in Table 1. Below 2 mass% MWNT strain to failure (%) increases with the increase in the MWNT content demonstrating toughening characters. At 2 mass% MWNT strain to failure (%) reaches the highest point and has a 33% increase compared to pure PC. However, at higher MWNT contents there is no obvious yield process and deformation is transformed from tough failure to brittle failure.
3.2 Morphology of the nanocomposites

Morphology character of multiwalled carbon nanotubes (MWNT)/polycarbonate (PC) composites of the tensile-tested specimens are shown in Fig. 1(a), (b) and (c). We also observed a tough-to-brittle transition just like the results of the room temperature tensile tests. The fracture surface for pure polycarbonate shows river pattern; between 0.5 mass%–2 mass% MWNT contents dimples were visible on the fracture surfaces. The fracture morphology below 2 mass% was of cleavage character. For the sample with contents higher than 2 mass% MWNT, the fracture surface is plane-like possibly due to the crack propagates directly perpendicular to interface region. Both from stress-strain curves and morphology of the fracture surfaces, a tough-to-brittle transition takes place at 2 mass% MWNT.

3.3 Electrical conductivity and dielectric spectroscopy

Characterization and quantification of the state of nanotube dispersion is a difficult task. Electrical measurements can serve as a good indicator of the state of dispersion. In order to examine the state of percolation in these nanocomposites electrical volume conductivity measurements have been carried out and are presented in Fig. 3. The result reveal that the electrical conductivity increases with the filler volume fraction first slowly and then dramatically changes by several orders of magnitudes when filler volume fraction approaches a critical volume fraction (percolation threshold). The results show that percolation threshold was found at about 2 mass% MWNT content, when the formation of a network structure of nanotubes surrounded by the immobilized polymer formed.

Dielectric spectroscopy has been successfully applied to investigate the percolation structure of other conductive fillers, e.g. carbon black (CB). The dielectric measurements were performed using a HP4194A impedance analyzer at room temperature. Figure 4(a) and 4(b) shows the dielectric constant and dielectric loss of nanocomposites as a function of the frequency in the range of 1 to 1 MHz, respectively. The samples with MWNT contents below 2 mass% exhibited negligible dependence on frequency and the dielectric constant and dielectric loss remains almost constant in the whole test range. However, at 2 mass% MWNT-PC composites dielectric constant and dielectric loss decrease with increasing the frequency. At higher MWNT contents the change in dielectric constant and dielectric loss is more obvious. Dielectric spectroscopy convinced that the percolation threshold was at about 2 mass% MWNT content. It is interesting that a tough-to-brittle transition takes place at 2 mass% MWNT-PC composites when the interface achieved the state of percolation by coincidence.

3.4 Viscoelastic properties

Having characterized the static mechanical properties, we proceeded to study the effect of interface structure on the dynamic mechanical behavior. The DMTA results of the temperature sweeps for the nanocomposite and baseline polycarbonate samples are shown in Fig. 5. Figure 5(a) indicates that the storage modulus ($E'$) shows a gradual

<table>
<thead>
<tr>
<th>MWNT content (mass%)</th>
<th>Young's modulus (GPa)</th>
<th>Yield stress (MPa)</th>
<th>Yield strain (%)</th>
<th>Strain to failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate</td>
<td>1.42 ± 0.1</td>
<td>55</td>
<td>6.6</td>
<td>7.0</td>
</tr>
<tr>
<td>0.5 mass% MWNT</td>
<td>1.55 ± 0.1</td>
<td>55</td>
<td>6.3</td>
<td>7.9</td>
</tr>
<tr>
<td>1 mass% MWNT</td>
<td>1.57 ± 0.1</td>
<td>59</td>
<td>6.6</td>
<td>8.0</td>
</tr>
<tr>
<td>2 mass% MWNT</td>
<td>1.65 ± 0.1</td>
<td>65</td>
<td>7.6</td>
<td>9.3</td>
</tr>
<tr>
<td>4 mass% MWNT</td>
<td>1.73 ± 0.1</td>
<td>/</td>
<td>/</td>
<td>4.9</td>
</tr>
<tr>
<td>6 mass% MWNT</td>
<td>1.89 ± 0.1</td>
<td>/</td>
<td>/</td>
<td>2.3</td>
</tr>
<tr>
<td>8 mass% MWNT</td>
<td>1.95 ± 0.1</td>
<td>/</td>
<td>/</td>
<td>2.8</td>
</tr>
<tr>
<td>10 mass% MWNT</td>
<td>2.13 ± 0.1</td>
<td>/</td>
<td>/</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 1 Comparison of mechanical properties for MWNT-filled polycarbonate composites and pure PC.

![Fig. 3 Electrical conductivity of the PC/MWNT composites with MWNT content.](image)

![Fig. 4 (a) The dielectric constant and (b) the dielectric loss as a function of the frequency applied.](image)
increase in the glassy state region as a function of the MWCNT concentration due to the confinement of the PC chain mobility. From Fig. 5(b), the broadening of the loss modulus ($E''$) curve as the concentration of MWCNTs increases, also suggesting confinement of the PC chain mobility. The damping ratio curve is defined as the ratio of the loss modulus to the storage modulus. From Fig. 5(c), the damping ratio curves basically decrease as the concentration of MWCNTs increases.

The peak of the loss modulus curve was defined as the glass transition temperature ($T_g$). The values of $T_g$ as a function of nanotube concentration are presented graphically in Fig. 5(d). $T_g$ seems to shift slightly to higher temperatures upon further loading of MWCNTs. However, we notice that $T_g$ at 2 mass% MWNT is lower than the sample with 0.5 mass% MWNT and the sample with 1 mass% MWNT. The peak of the damping ratio curve as a function of nanotube concentration are also presented graphically in Fig. 5(d). The damping ratio of the composites decreases with MWCNT loading below 2 mass% MWNT. At 2 mass% MWNT damping ratio reaches the bottom and has a 51% decrease compared to pure PC. However, at higher MWNT contents damping ratio begins to climb.

4. Discussion

The diameter of the carbon nanotubes are on the same size scale as the the radius of polymer chains and thus supports the formation of large diameter helices around the nanotubes known as “polymer wrapping”. This immobilized polymer leads to the strengthening of the polymer-nanotube interface. With the increase of loading of MWNT, the volume fraction of the interface increases and much more polymer chains at the surface of the nanotubes were immobilized. Below 2 mass% MWNT the interphase zone is on the rise with increasing nanotube weight fraction. At 2 mass% MWNT the interphase zone forms network structure. Above the percolation threshold, interphase zone overlaps. The affects of interphase structure on macromechanical properties of MWNT-filled polycarbonate composites as follows:

(1) Elastic modulus shows a gradual increase as a function of the MWCNT concentration both from the stress-strain curves and the storage modulus ($E'$) curves because the interface region restrains the PC chain mobility and provides a reinforcement mechanism for nanotube-filled composites.

(2) Below 2 mass% MWNT strain to failure (%) increases with the increase in the MWNT content. At 2 mass% MWNT the interphase zone forms network structure and fracture toughness reaches the highest point. Above 2 mass% MWNT interphase zone overlap cause high stress or strain localization. Thus, the cracks propagate through the intensively strain localized zones in PC–MWNT composite systems causing brittle failure, and hence a tough-to-brittle transition takes place in the composites at 2 mass% MWNT.

(3) Interfacial reinforcement mechanism was not the only mechanism during the glass transition progress. The state of percolation maybe beneficial to diffusion motion and
polymer chains movement from one position to another position. Therefore $T_g$ at 2 mass% MWNT is lower than the sample with 0.5 mass% MWNT and the sample with 1 mass% MWNT.

(4) The peak of damping ratio of the composites decreases with MWCNT loading, which reflects the reduction in the damping for samples with greater MWCNT concentrations. However above 2 mass% MWNT, damping ratio begins to increase. During the dynamic deformation, energy dissipation is consisted of interfacial slip energy and energy release of high strain localization due to interphase zone overlap. Therefore loss modulus is larger than without considering strain localization, and hence damping ratio of the sample with 4 mass% MWNT is larger than the sample with 2 mass% MWNT.

5. Conclusion

The present study focuses on the correlation between the macromechanical properties and the properties of the interphase region. We find that when the interphase achieves the state of percolation, strain of fracture (%) of MWNT-filled polycarbonate composites reaches a peak of 9.3%, elastic modulus increases 30% comparing to pure polycarbonate and damping ratio hits a trough. The results present new insights to realize optimal effective mechanical properties for nanotube-polymer systems by tailoring the interphase within the material.

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