In-situ transmission electron microscopy studies of polymer–carbon nanotube composite deformation

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Summary
This paper demonstrates the viability of in-situ transmission electron microscopy for studying the deformation mechanisms of polymer nano-composites. In-situ straining studies are performed on carbon multiwalled nanotube (MWNT)–polystyrene composite films. The experiments show that load transfer across the nanotube–polystyrene interface is operative well into the plastic deformation regime of the composite film. The MWNTs are observed to bridge cracks propagating through the polystyrene, providing closure stresses across the crack wake. Although some MWNTs fracture by either a sword-in-sheath mechanism or transverse shear fracture, most of the MWNTs eventually debond at the MWNT–polymer interface and subsequently pull out of the matrix.

Introduction
Carbon nanotubes (NTs) have exceptionally high Young's moduli on the order of 1 TPa (Treacy et al., 1996; Wong et al., 1997), high fracture strains (~ 10–30%) (Yakobson & Smalley, 1997), flexibility, low density and large aspect ratios. Consequently, they may be ideal reinforcing fibres for structural composites. Because of their novel electronic properties, NT–polymer composites are also promising for functional applications in display, conductive polymer (Coleman et al., 1998; Sandler et al., 1999), electromagnetic interference shielding (Grimes et al., 2000) and opto-electronic devices (Curran et al., 1998; Ago et al., 1999; Shaffer & Windle, 1999). To take advantage of nanotubes in structural composite applications, good interfacial bonding is necessary for achieving effective load transfer across the NT–matrix interface. Both epoxy–MWNT composites (Wagner et al., 1998; Lourie et al., 1998; Schadler et al., 1998; Bower et al., 1999) and epoxy–single walled NT (SWNT) composites (Lourie & Wagner, 1998; Ajayan et al., 2000) have been studied recently. As some of the nanotube Raman modes are sensitive to applied strain, micro-Raman spectroscopy has been employed as an in-situ technique for assessing load transfer to the NTs. Significant shifts of these modes have been observed when MWNT–epoxy composites are loaded in compression (Schadle et al., 1998; Wagner et al., 1998). Shifts in the Raman modes have not, however, been observed in tensile tests of MWNT–epoxy composites, although increases in modulus over the unreinforced polymer were measured (Schadle et al., 1998). These mixed results indicate the need for alternative, complementary techniques to study load transfer mechanisms in these nano-composites. This paper addresses this need by demonstrating in-situ TEM as a viable method for understanding deformation in nano-composite materials.

Recently, we have demonstrated significant load transfer in MWNT–polystyrene composites loaded in tension (Qian et al., 2000). The load transfer was evidenced by an increase in elastic modulus and break stress by 35% and 25%, respectively, with only 1 wt.% MWNTs additions, as shown in Table 1. The experimental Young’s modulus was within 10% of that theoretically predicted for randomly orientated, discontinuous-fibre reinforced composite films assuming perfect interfacial bonding. The obvious enhancement of elastic modulus and break stress as well as the close agreement of experiment and theory indicate that the external tensile loads were transferred to the nanotubes across the MWNT–PS interface.

Table 1 also shows that an addition of only 1 wt.% MWNTs increases the conductivity of the polystyrene by an order of 18 (Andrews et al., 1999a). Due to the extremely high aspect ratios, ~1500, MWNTs easily form a network that introduces continuous conductive paths in the polymer. In fact, the percolation threshold is exceeded with only 1 wt.% (~ 0.5 vol.%) additions of randomly aligned nanotubes. These NT–polymer composites, combining good
Table 1. Tensile properties (Qian et al., 2000) and electrical conductivity (Andrews et al., 1999a) of MWNT–PS composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Break strength (MPa)</th>
<th>Elastic modulus (MPa)</th>
<th>Yield elongation (%)</th>
<th>Electrical conductivity ($\Omega^{-1} \text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank PS</td>
<td>12.8 ± 1</td>
<td>1192 ± 1301.3 ± 0.2</td>
<td>10^{-20} – 10^{-22}</td>
<td></td>
</tr>
<tr>
<td>1% wt. NT – PS</td>
<td>16 ± 0.2</td>
<td>1616 ± 1301.4 ± 0.1</td>
<td>0.071</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. TEM straining holder (JEOL EM-SEH3) and specimen attachment schematic.

Fig. 2. Typical crack nucleation and propagation in MWNT–PS thin films under tensile stress applied by thermal stresses (Qian et al., 2000), which is very similar to the crack induced by the applied tensile stress. The flexible MWNTs tend to align and bridge the crack wake then break or pull out the PS matrix. Arrows point to the fractured MWNTs.

Fig. 3. Real-time TEM observations of MWNT–PS deformation under tension show that MWNTs prevent crack opening. Frames (a)–(c) are captured from video tape in time order. Frame (a) the crack propagates through the composite; (b) a cluster of well-bonded MWNTs obviously retard the crack opening; (c) the MWNTs finally pullout of the polymer matrix or, as indicated by arrows, fracture in the crack wake.

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mechanical properties with good conductivity, have applicability for computer housing, exterior automotive parts, and other electrical apparatus where electrostatic discharge is required.

Although the macroscopic property tests clearly indicate a beneficial effect of nanotube additions on the physical and mechanical properties of polystyrene composites, and indicate good load transfer through the elastic regime well into the plastic deformation regime, the precise deformation mechanisms are not well understood. Here, through in-situ TEM straining studies, we elucidate the operative deformation mechanisms.

Materials and methods

MWNTs with average outer diameters of 33 nm and average lengths of 50 μm, were produced by pyrolysis of a xylene–ferrocene mixture at 700 °C as discussed previously (Andrews et al., 1999b). The MWNTs were used as reinforcing filaments (1 wt.%) in 280 k molecular weight polystyrene (PS) (Aldrich Chemical Company, Inc., Milwaukee, WI, USA).

Uniform MWNT-PS composite films were prepared by a solution-evaporation method assisted by high-energy sonication as described previously (Qian et al., 2000). In short, this procedure includes the following steps: (a) dissolve polystyrene into toluene; (b) disperse MWNTs into toluene with an ultrasonic wand dismembrator at 300 W for ~30 min; and (c) mix the toluene solution and suspension in a bath sonicator to form a suspension solution of (MWNT + PS + toluene). The mixed solution was used to cast thick films (~0.4 mm) for macroscopic tensile tests by evaporating toluene in a culture dish. Very thin films (<500 nm) for in-situ TEM study were prepared by spin coating a few drops of solution onto glass at a spinning rate of 2000 rev min⁻¹. Samples 4 mm × 1 mm in size were cut to fit the straining TEM holder, and a small notch was cut in order to nucleate a crack in the middle of the specimen.

In-situ TEM straining studies of the MWNT–PS composites were conducted on a 200 kV JEOL 2000FX LaB₆ TEM. Schematics of the JEOL EM-SEH3 straining TEM holder and the specimen attachment method used in this study are shown in Fig. 1. The straining rate applied to the specimen could be coarsely adjusted to about 0.1 mm min⁻¹ by a pedal switch that controls the micromotor in the straining holder. Real-time images were captured from a Gatan (Model 622SC, Pleasanton, CA, USA) TV-rate camera and recorded on VHS video with a speed of 30 frames s⁻¹. Periodically, the deformation was suspended and higher resolution images were recorded on photographic film.

Results and discussion

When a tensile stress was applied to the MWNT–PS film, a crack nucleated around the notch (see Fig. 1) due to stress concentration. In-situ TEM observations of the crack propagation through the PS matrix show that the MWNTs
tend to align along the tensile direction and bridge the crack faces in the wake, similar to cracks induced by thermal stresses generated from the electron beam (Fig. 2) (Qian et al., 2000). These bridging nanotubes provide closure stresses across the crack faces and reduce the stress concentration around the crack tip. In Fig. 3, even though the crack opening displacement exceeds 500 nm, locally the well-bonded cluster of nanotubes at the centre of the image retard crack opening in the composite. Eventually, as shown in Fig. 3(c), the nanotubes debond and are pulled out of the matrix.

As the nanotubes are randomly dispersed in the matrix, many MWNTs must be bent at severe angles to align perpendicularly across the crack wake. Once the nanotubes break or pull out of the matrix, however, they elastically spring back their original conformation. For example, the tubes labelled A and B in Fig. 4 are bent by over 45° from their axial direction, but after either breaking or pulling out of the matrix they return to a straight configuration. The high flexibility of MWNTs is important in enhancing the toughness of composites, because the MWNTs can contribute to crack bridging even though they may not be well orientated with respect to the crack faces. Furthermore, the frictional forces generated when pulling the MWNTs out of the matrix also dissipate energy thus increasing toughness.

When the local stress exceeds the critical MWNT–PS interface bonding strength, the nanotubes debond from the PS matrix. Figures 2–4 show examples of nanotubes in the process of debonding and pulling out of the matrix. Although most of the MWNTs were observed to eventually debond and subsequently pull out the PS matrix, ~5% of the NTs were observed to fracture in the crack wake. Examples of fractured nanotubes are identified with arrows in Figs 2 and 3(c).

In the cases where the MWNTs fractured in the crack wake, two kinds of fracture mechanism were observed, either sword-in-sheath (an axial fracture mechanism) or transverse shear fracture, although the former was dominant in this MWNT–PS system. Axial tensile tests on single MWNTs performed in an atomic force microscope show that they tend to rupture by a sword-in-sheath mechanism (Yu et al., 2000). This is consistent with our observation that the sword-in-sheath mechanism (see Figs 5 and 6) dominates when the MWNT axis is aligned closely parallel to the tensile direction. When the MWNT axis is nearly perpendicular to the tensile direction, it tends to rupture by transversal shear fracture (see Fig. 7). The MWNT in Fig. 7 lies parallel to the crack face similar to nanotube A in Fig. 4; however, this NT broke in the crack wake under shear stress since both ends were embedded far into the PS matrix. Tube A in Fig. 4, on the other hand, was pulled out of the matrix because one end was located close to the crack wake. The sword-in-sheath fracture mechanism is attributed to the weak interlayer bonding of MWNTs, whereas the transverse fracture mechanism arises from the relative weak shear strength of MWNTs. Compared with the arc-discharge MWNTs, the chemical vapour deposition (CVD)-derived MWNTs contain a higher density of point defects or volume defects resulting in much lower bending moduli (Poncharal et al., 1999; Gao et al., 2000). Under
tensile stress, these defects initiate the MWNT fracture, and then the sword-in-sheath fracture process of MWNTs can be modulated in a stepwise manner by subsequent graphene layers sliding and rotating. Under a critical external stress, the coaxial graphene layers of MWNT can deform to release stress and absorb energy, thus increasing the toughness of the MWNT–polymer composite.

The effectiveness of load transfer from the matrix to the nanotube reinforcements is determined by the interfacial bonding strength, which depends strongly on the three factors (Schadler et al., 1998): micromechanical interlocking, van der Waals adhesion, and chemical bonding between the filaments and polymer matrix. Molecular mechanics calculations (Lordi & Yao, 2000) show that the sliding friction at the nanotube–polymer interface is much higher than that between neighbouring layers of a MWNT and this frictional force only plays a minor role in determining the interface strength. The van der Waals forces, arising mainly from the hydrogen bond interactions between the π-bonds of the MWNT surface and the hydroxyl side-groups of the polymer.

Fig. 6. Evidence of another nanotube broken by the sword-in-sheath fracture mechanism.

Fig. 7. Transversal fracture mechanism of a single MWNT whose axis is nearly perpendicular to the tensile direction. (a) Schematics of tube before fracture; (b) schematics of tube after fracture; (c) and (d) the fractured ends of MWNT left on both crack surfaces.

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matrix, are determined by the polymer molecular structure, especially its ability to form ordered helices around individual nanotubes (Lordi & Yao, 2000). For our MWNT–PS composite, the average tube diameter is 33 nm, and it is not clear if the polystyrene chains can wrap around the MWNTs. Surface functionalization of NTs, or attachment of certain organic functional groups to the NT ends and wall surfaces (Chen et al., 1998; Gong et al., 2000), could increase the NT–polymer interfacial adhesion and chemical bonding, and further realize effective load transfer to the nanotubes. The selections of matrix polymer and suitable MWNT surface functionalization are the key issues in producing multi-functional NT–polymer advanced composites.

Conclusions

In-situ TEM straining studies of MWNT–polystyrene composites complement previous mechanical properties tests to provide insight into the deformation mechanisms of these composites. The in-situ TEM observations show that the very flexible nanotubes bridge the wakes of propagating matrix cracks regardless of their orientation. Most nanotubes are observed to debond at the NT–matrix interface and subsequently pull out of the PS matrix. The in-situ TEM studies also provide direct evidence of single MWNTs rupturing in a sword-in-sheath mechanism in tensile direction, consistent with previous tests on individual MWNTs. Shear fracture is also observed in tubes that are aligned nearly parallel to the propagating cracks. This in-situ TEM method is a useful technique for understanding load transfer and deformation mechanisms in these nano-composites and could be easily extended to study other NT–polymer systems.

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References


