Interfacial Damage Effect on the Cryogenic Mechanical Response of Carbon Nanotube-Based Composites under Bending

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Abstract

This article examines the effect of interfacial damage on the cryogenic mechanical response of carbon nanotube (CNT)-based polymer composites under bending through experiments and multiscale simulations. Flexural tests on CNT/polycarbonate composites were performed at cryogenic temperatures, and the fracture surfaces were examined to assess the failure mechanisms. Multiscale analysis was also performed to predict the composite behavior and the stress distributions in the composites at cryogenic temperatures. Three-dimensional finite elements were used to model the representative volume element (RVE) of CNT-based composites, and the effective composite elastic moduli were obtained. Damage parameters were introduced to describe the status of the CNT/matrix interfaces, and the atomistic structure of the CNT was incorporated by determining its elastic properties using an analytical molecular structural mechanics model. The finite element analysis of flexural test specimens was used to predict the specimen response. The variations of the composite behavior and the stress distributions with respect to the interfacial damage state were discussed, and the simulation results were utilized to understand the experimental observations.

Keywords: Cryomechanics, multiscale modeling, bending test, nanocomposite, low temperature deformation
1 Introduction

Nanocomposites have been an area of intense research and have played a significant role in current development of nanotechnology [1]. In particular, composites of carbon nanotubes (CNTs) in polymeric matrices have attracted considerable attention in the research and industrial communities. It has been theoretically and experimentally confirmed that CNTs possess exceptional properties, such as high stiffness and strength, ability to sustain large elastic strain, and high thermal and electrical conductivities [2,3]. These properties as well as their high aspect ratio and low density have stimulated the development of CNT-based polymer composites for both structural and functional applications [4,5].

In many cryogenic systems, polymeric materials have been considered for use as structural and functional parts. This has placed increasing demands on the performance of polymeric materials at cryogenic temperatures, which suggests the potential use of CNT-based polymer composites as alternative materials for cryogenic applications. Therefore, the physical and mechanical properties of CNT-based polymer composites in a cryogenic environment must be explored so that they can be used with confidence and advances can be made in future material development.

Substantial works including the synthesis of different types of CNTs, manufacturing process of CNT-based composites, characterizations of the composites, have been conducted in the past few years, and review articles on these subjects can be found, for example, in Srivastava et al. [6], Lau et al. [7,8] and Paradise and Goswami [9]. However, the potential of using CNTs as reinforcement for polymers has not been fully realized [10]. A morphological characteristic that is of fundamental importance in the understanding of the reinforcing mechanisms in CNT-based composites is the surface area/volume ratio of CNTs [11]. The CNT/matrix interfacial area is much larger than that in traditional fiber-reinforced composites, and the interface region plays a key role in optimizing load transfer between the CNT and the matrix material. In order to take the exceptional properties of CNTs observed at the nanoscale and utilize these properties at the macroscale, basic research on the relationship between the interfacial properties and the composite behavior is necessary.

This paper presents an experimental and numerical study on the mechanical behavior of CNT-based polymer composites under bending at cryogenic temperatures. Cryogenic flexural tests on CNT/polycarbonate composites were performed, and fractographic examination was conducted to assess the failure mechanisms. Also, multiscale analysis was used to predict the composite behavior and the stress distributions in the composites at cryogenic temperatures. The composite was modeled by a representative volume element (RVE) using three-dimensional finite elements, and the effective composite elastic
Interfacial damage effect on the cryogenic mechanical response

moduli were determined. Damage parameters were introduced to represent the CNT/matrix interfacial status, and the CNT properties were determined using the molecular structural mechanics approach. The finite element analysis of flexural test specimens was performed to predict the specimen response. The effect of interfacial damage on the composite behavior and the stress distributions was examined. The numerical findings were then correlated with the experimental results.

2 Experimental Procedure

The materials studied were multi-walled nanotube (MWNT)/polycarbonate composites. The composite samples contained MWNT concentrations of 1.5, 2.5 and 5 wt.%. Neat polycarbonate samples were also prepared. The diameters of the MWNTs ranged from 10 to 40 nm, while their lengths were between 5 and 20 μm. The CNT weight fraction $W^N$ can be converted to the CNT volume fraction $V^N$ using the following equation [12]:

$$V^N = \frac{W^N \rho^M}{W^N \rho^M + (1 - W^N) \rho^N},$$

where $\rho^N$ and $\rho^M$ are the densities of the CNT and matrix, respectively. The superscripts $N$ and $M$ refer to CNT and matrix, respectively. According to the material densities, 1.8 g/cm$^3$ for a MWNT [2] and 1.2 g/cm$^3$ for the polycarbonate (supplier’s data), the $V^N$ values for the 1.5, 2.5 and 5 wt.% MWNT/polycarbonate composites were calculated to be 1.0, 1.7 and 3.4 vol.% respectively.

Flexural tests were performed according to the standard test method ASTM D 790M under a three-point bend configuration utilizing center loading on a simply supported beam [13]. The test specimens were machined from the sample plates to the following dimensions: length $l = 60$ mm and width $b = 13$ mm. The as-received thickness of the plates $d$ was about 2.7 mm for the MWNT/polycarbonate composite samples, and about 3 mm for the neat polycarbonate samples. The support span $s$ was about 16 times the specimen thickness, i.e., 43 mm for the composite samples and 48 mm for the neat polycarbonate samples. The tests were conducted on a 30 kN capacity servo-hydraulic testing machine at a displacement rate of 0.6 mm/min. The specimens were tested at room temperature and liquid nitrogen temperature (77 K). The 77-K testing was conducted with specimens immersed in liquid nitrogen at atmospheric pressure in a dewar. The load $P$ and the load point displacement (deflection) $U$ were measured by the testing machine load cell and transducer, respectively. Due to cost and time constraints, the number of specimens was limited to two or three for each material and condition. Af-
After flexural testing, the fracture surfaces of the specimens were examined by scanning electron microscopy (SEM, JEOL JS-6500F).

3 Multiscale Analysis

3.1 Constituent material properties

The MWNTs were considered to have isotropic elastic properties [14]. The molecular dynamics study has shown that the inner layers of MWNTs do not contribute much to their elastic properties [15]. Hence, the elastic properties of the MWNTs in composites can be estimated by regarding the outermost layer as a single-walled nanotube (SWNT). Based on this finding, the analytical molecular structural mechanics (MSM) model for SWNTs [16] was employed here to determine the Young’s modulus and Poisson’s ratio of the MWNTs. The outermost diameter $2R_N$ of the MWNTs was assumed to be 25 nm, and Young’s modulus $E_N$ and Poisson’s ratio $\nu_N$ were determined to be 1.13 TPa and 0.20, respectively. In the multiscale analysis, the CNT elastic properties were assumed to be independent of temperature [17], and the CNT was treated as an equivalent solid cylinder (effective CNT) with the diameter $2R_E = 2R_N$. The superscript $E$ denotes the effective CNT. The Young’s modulus $E_E$ and Poisson’s ratio $\nu_E$ of the effective CNT can be obtained as

$$E_E = \frac{R_N^2 - (R_N - t_N)^2}{R_N^2} E_N, \quad \nu_E = \nu_N,$$

(2)

where $t_N$ is the tube wall thickness. It should be noted that no established values are available for the tube wall thickness $t_N$ [18]. In this study, the thickness $t_N$ was taken as the interlayer spacing of graphite, 0.34 nm [19], which is the same value used in the analytical MSM model. The shear modulus $G_E$ of the effective CNT was calculated from $G_E = E_E / 2 \{1 + \nu_E\}$. The longitudinal and transverse coefficients of thermal expansion (CTEs) $\alpha_l^E, \alpha_t^E$ of the effective CNT were assumed to be the same as the CTEs of graphite in the in-plane direction ($-1.2 \times 10^{-6}/K$) and in the out-of-plane direction ($25.9 \times 10^{-6}/K$) at room temperature, respectively [20]. The subscripts $l$ and $t$ stand for the longitudinal and transverse directions.

The polycarbonate was considered to be isotropic. The elastic and thermal properties of the polycarbonate were taken to be dependent on temperature $\Phi$. The Young’s modulus $E_M(\Phi)$ and Poisson’s ratio $\nu_M(\Phi)$ of the polycarbonate were determined by tensile tests following ASTM D 638 [21]. The values of $E_M(\Phi)$ and $\nu_M(\Phi)$ at room temperature (293 K) and 77 K are summarized in Table 1, and shear modulus $G_M(\Phi)$ was calculated from $G_M(\Phi) = E_M(\Phi) / 2 \{1 + \nu_M(\Phi)\}$. Also, the CTE of the polycarbonate $\alpha_M(\Phi)$
Table 1 Young’s modulus and Poisson’s ratio of the polycarbonate

<table>
<thead>
<tr>
<th></th>
<th>293 K</th>
<th>77 K</th>
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<tbody>
<tr>
<td>$E^M(\Phi)$ (GPa)</td>
<td>2.35</td>
<td>4.50</td>
</tr>
<tr>
<td>$\nu^M(\Phi)$</td>
<td>0.39</td>
<td>0.38</td>
</tr>
</tbody>
</table>

was approximated by the following exponential function based on the experimental data for its thermal expansion [22]:

$$\alpha^M(\Phi) = 9.378 \exp \left(7.578 \times 10^{-3} \Phi\right) \quad [10^{-6}/K].$$

### 3.2 Finite element analysis of the composite RVE

The RVE of CNT-based composites is shown in Figure 1, where $(x, y, z)$ is the Cartesian coordinate system with origin at the center of the RVE, and $r$ and $\theta$ are, respectively, the radial and circumferential coordinates in the $y$-$z$ plane. In accordance with the figure, $L^E$ represents the length of the effective CNT, and $L^R$ and $L_t^R$ represent the RVE lengths in the longitudinal ($x$-) and transverse ($y$- and $z$-) directions, respectively. The superscript $R$ denotes the RVE. The RVE includes an interfacial layer 1 of thickness $T_{I1} = \frac{L_E}{2} \leq |x| \leq \frac{L_E}{2} + T_{I1}$, $0 \leq r \leq R^E$, $0 \leq \theta \leq 2\pi$) and an interfacial layer 2 of thickness $T_{I2}$ ($|x| \leq \frac{L_E}{2} + T_{I1}$, $R^E \leq r \leq R^E + T_{I2}$, $0 \leq \theta \leq 2\pi$). The superscripts $I1$ and $I2$ represent the interfacial layers 1 and 2, respectively. The interfacial layers 1 and 2 were modeled as isotropic materials with Young’s moduli $E^{I1}(\Phi) = \chi_1 E^M(\Phi) (0 < \chi_1 \leq 1)$ and $E^{I2}(\Phi) = \chi_2 E^M(\Phi) (0 < \chi_2 \leq 1)$, respectively, where $\chi_1$ and $\chi_2$ are damage parameters for representing the status of the CNT/matrix interfaces. The Poisson’s ratios $\nu^{I1}(\Phi)$, $\nu^{I2}(\Phi)$, shear moduli $G^{I1}(\Phi)$, $G^{I2}(\Phi)$ and CTEs $\alpha^{I1}(\Phi)$, $\alpha^{I2}(\Phi)$ of the interfacial layers 1 and 2 were taken to be $\nu^{I1}(\Phi) = \nu^{I2}(\Phi) = \nu^M(\Phi)$, $G^{I1}(\Phi) = E^{I1}(\Phi)/2 \left\{1 + \nu^{I1}(\Phi)\right\}$, $G^{I2}(\Phi) = E^{I2}(\Phi)/2 \left\{1 + \nu^{I2}(\Phi)\right\}$ and $\alpha^{I1}(\Phi) = \alpha^{I2}(\Phi) = \alpha^M(\Phi)$. In the RVE, the effective CNT aspect ratio $L^E/2R^E$ was assumed to be the same as the RVE aspect ratio $L_t^R/L_t^R$ [23], and the interfacial layer thickness was assumed to be $T_{I1} = T_{I2} = 0.05R^E$. The volume fraction of the effective CNT in the RVE $V^E$ can be expressed as:

$$V^E = 2\pi \left(\frac{R^E}{L_t^R}\right)^3.$$  

The effective CNT volume fraction in the RVE $V^E$ corresponds to the CNT volume fraction in the composite $V^N$. 

Figure 1. RVE of CNT-based composites: (a) $y = 0$ plane; (b) $x = 0$ plane.

The RVE was subjected to the mechanical and thermal loads. The thermal load represents the difference between the stress-free temperature $\Phi_s$ and the current temperature $\Phi$, i.e., $\Phi - \Phi_s$. In the finite element analysis, the stress-free temperature $\Phi_s$ was assumed to be the glass transition temperature of the polycarbonate (406 K) [24].

The constitutive equations for the effective CNT, matrix, and interfacial layers 1 and 2 are:

$$
\begin{bmatrix}
\varepsilon^\delta_{xx}(x, y, z) - \varepsilon^\delta_{xxT}(\Phi) \\
\varepsilon^\delta_{yy}(x, y, z) - \varepsilon^\delta_{yyT}(\Phi) \\
\varepsilon^\delta_{zz}(x, y, z) - \varepsilon^\delta_{zzT}(\Phi) \\
2\varepsilon^\delta_{yz}(x, y, z) \\
2\varepsilon^\delta_{xz}(x, y, z) \\
2\varepsilon^\delta_{xy}(x, y, z)
\end{bmatrix}
= 
\begin{bmatrix}
1/E^\delta & -\nu^\delta/E^\delta & -\nu^\delta/E^\delta & 0 & 0 & 0 \\
-\nu^\delta/E^\delta & 1/E^\delta & -\nu^\delta/E^\delta & 0 & 0 & 0 \\
-\nu^\delta/E^\delta & -\nu^\delta/E^\delta & 1/E^\delta & 0 & 0 & 0 \\
0 & 0 & 0 & 1/G^\delta & 0 & 0 \\
0 & 0 & 0 & 0 & 1/G^\delta & 0 \\
0 & 0 & 0 & 0 & 0 & 1/G^\delta
\end{bmatrix}
$$
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\[
\begin{bmatrix}
\sigma^\delta_{xx}(x, y, z) \\
\sigma^\delta_{yy}(x, y, z) \\
\sigma^\delta_{zz}(x, y, z) \\
\sigma^\delta_{yz}(x, y, z) \\
\sigma^\delta_{zx}(x, y, z) \\
\sigma^\delta_{xy}(x, y, z)
\end{bmatrix}, \quad (\delta = E, M, I1, I2), \quad (5)
\]

where \(\varepsilon^\delta_{xx}(x, y, z), \varepsilon^\delta_{yy}(x, y, z), \varepsilon^\delta_{zz}(x, y, z), \varepsilon^\delta_{yz}(x, y, z), \varepsilon^\delta_{zx}(x, y, z), \varepsilon^\delta_{xy}(x, y, z)\) are the strain components, \(\varepsilon^\delta_{xxT}(\Phi), \varepsilon^\delta_{yyT}(\Phi), \varepsilon^\delta_{zzT}(\Phi)\) are the thermal strain components, and \(\sigma^\delta_{xx}(x, y, z), \sigma^\delta_{yy}(x, y, z), \sigma^\delta_{zz}(x, y, z), \sigma^\delta_{yz}(x, y, z), \sigma^\delta_{zx}(x, y, z), \sigma^\delta_{xy}(x, y, z)\) \((\delta = E, M, I1, I2)\) are the stress components. The thermal strain components \(\varepsilon^\delta_{xxT}(\Phi), \varepsilon^\delta_{yyT}(\Phi), \varepsilon^\delta_{zzT}(\Phi)\) \((\delta = E, M, I1, I2)\) are given by

\[
\varepsilon^E_{xxT}(\Phi) = \alpha^E_l (\Phi - \Phi_s), \quad \varepsilon^E_{yyT}(\Phi) = \varepsilon^E_{zzT}(\Phi) = \alpha^E_t (\Phi - \Phi_s), \quad (6)
\]

\[
\varepsilon^\delta_{xxT}(\Phi) = \varepsilon^\delta_{yyT}(\Phi) = \varepsilon^\delta_{zzT}(\Phi) = \int_{\Phi_s}^\Phi \alpha^\delta(\phi)d\phi, \quad (\delta = M, I1, I2). \quad (7)
\]

The RVE of CNT-based composites can be considered as having transversely isotropic symmetry, with the plane of isotropy perpendicular to the \(x\)-axis \([25]\). For the transversely isotropic RVE, there are five independent elastic properties: longitudinal Young’s modulus \(E^R_l\), transverse Young’s modulus \(E^R_t\), longitudinal Poisson’s ratio \(\nu^R_l\), transverse Poisson’s ratio \(\nu^R_t\), and longitudinal shear modulus \(G^R_{lt} = G^R_{tl}\). The Poisson’s ratio \(\nu^R_t\) reflects shrinkage (expansion) in the transverse direction, due to tensile (compressive) stress in the longitudinal direction. In addition, the transverse shear modulus \(G^R_{tt}\) is given by \(G^R_{tt} = E^R_t/2(1 + \nu^R_t)\). The five independent elastic properties can be obtained from the finite element analysis of the RVE under longitudinal normal loading (mechanical mean stress \(\sigma^*_{xx}\)), transverse normal loading (mechanical mean stress \(\sigma^*_{yy}\)) and longitudinal shear loading (mechanical mean stress \(\sigma^*_{zz}\)), see Appendix A \([26]\).

### 3.3 Effective elastic moduli of randomly oriented CNT-based composite

The components of the elastic compliance tensor for the transversely isotropic RVE can be expressed in terms of the five independent elastic properties \(E^R_{lt}, E^R_t, \nu^R_{lt}, \nu^R_t, G^R_{lt} = G^R_{tl}\). The non-zero compliance components, \(S^R_{ijkl}(i, j, k, l = \ldots)\) are...
1, 2, 3), are given by

\[
\begin{align*}
S_{1111}^R &= \frac{1}{E_1^R}, \\
S_{1222}^R &= S_{3333}^R = \frac{1}{E_1^R}, \\
S_{2222}^R &= S_{3333}^R = \frac{1}{E_1^R}, \\
S_{1222}^R &= S_{2233}^R = -\nu_{tt}^R E_t^R, \\
4S_{2323}^R &= 2 \left( S_{2222}^R - S_{2233}^R \right) = \frac{1}{G_{tt}^R} = \frac{2 \left( 1 + \nu_{tt}^R \right) E_t^R}{E_t^R}, \\
4S_{1212}^R &= 4S_{1331}^R = \frac{1}{G_{tt}^R}.
\end{align*}
\]

(8)

The compliance components satisfy the following symmetry relations:

\[
S_{ijkl}^R = S_{klij}^R = S_{jikl}^R = S_{ijlk}^R.
\]

(9)

The effective elastic compliance tensor for the composite with randomly oriented CNTs (denoted by superscript \(C\)) is obtained as [27]

\[
S_{ijkl}^C = \frac{1}{2\pi^2} \int_{-\pi/2}^{\pi/2} \int_{-\pi}^{\pi} \int_{0}^{\pi} a_{ij} a_{jq} a_{kr} a_{ls} S_{pqrs}^R \sin(\gamma) \, d\lambda \, d\gamma \, d\psi,
\]

(10)

where \(\lambda, \gamma\) and \(\psi\) are Euler’s angles, and \(a_{ij}\) are given by

\[
\begin{align*}
a_{11} &= \cos \lambda \cos \psi - \sin \lambda \cos \gamma \sin \psi, \\
a_{12} &= \sin \lambda \cos \psi + \cos \lambda \cos \gamma \sin \psi, \\
a_{13} &= \sin \psi \sin \gamma, \\
a_{21} &= -\cos \lambda \sin \psi - \sin \lambda \cos \gamma \cos \psi, \\
a_{22} &= -\sin \lambda \sin \psi + \cos \lambda \cos \gamma \cos \psi, \\
a_{23} &= \sin \gamma \cos \psi, \\
a_{31} &= \sin \lambda \sin \gamma, \\
a_{32} &= -\cos \lambda \sin \gamma, \\
a_{33} &= \cos \gamma.
\end{align*}
\]

(11)

The resulting effective elastic compliance tensor for the composite is isotropic. Once the composite compliance tensor is determined, then the two independent effective elastic moduli, i.e., Young’s modulus \(E^C\) and Poisson’s ratio \(\nu^C\), of the randomly oriented CNT-based composite can be obtained as follows:

\[
E^C = \frac{1}{S_{1111}^C} = \frac{1}{S_{2222}^C} = \frac{1}{S_{3333}^C}, \quad \nu^C = -\frac{S_{1122}^C}{S_{1111}^C} = -\frac{S_{1133}^C}{S_{1111}^C} = -\frac{S_{2233}^C}{S_{1111}^C}.
\]

(12)

### 3.4 Finite element analysis of flexural test specimens

The finite element models of the flexural tests were developed. The model was three-dimensional and treated the entire test specimen as one homogeneous material with isotropic elastic moduli (i.e., \(E^C, \nu^C\) and \(G^C = E^C/2 \left(1 + \nu^C\right)\)) for the MWNT/polycarbonate composites, and \(E^M, \nu^M\) and \(G^M = E^M/\)}
2 \left\{1 + \nu^M \right\} \) for the polycarbonate. The test specimens were modeled and loaded as shown in Figure 2, in which Cartesian coordinates are used with \(X\)-, \(Y\)- and \(Z\)-axes in the directions of length, width and thickness, respectively. The dimensions correspond to those of the specimens. Eight-noded brick elements were used for meshing the specimens. Owing to symmetry, only a quadrant of the specimen \((0 \leq X \leq l/2, 0 \leq Y \leq b/2, 0 \leq Z \leq d)\) needs to be analyzed. The displacement boundary conditions are:

\[
\begin{align*}
  u_X(0, Y, Z) &= 0, & 0 \leq Y \leq b/2, & 0 \leq Z \leq d, \\
  u_Y(X, 0, Z) &= 0, & 0 \leq X \leq l/2, & 0 \leq Z \leq d, \\
  u_Z(0, Y, 0) &= U^*, & 0 \leq Y \leq b/2, \\
  u_Z(s/2, Y, d) &= 0, & 0 \leq Y \leq b/2,
\end{align*}
\]

(13)

where \(u_X(X, Y, Z), u_Y(X, Y, Z), u_Z(X, Y, Z)\) are the displacement components and \(U^*\) is the prescribed displacement. The total reactions from each node at \(X = 0\) and \(Z = 0\) \((0 \leq Y \leq b/2)\) were summed and quadrupled (on account of the plane of symmetry). The calculated load \(P^*\) corresponds to the load measured by a load cell in the experiments.

![Figure 2. Finite element model of the flexural test.](image)

4 Results and Discussion

Figure 3 shows typical load (\(P\))-deflection (\(U\)) curves for the 1.0, 1.7 and 3.4 vol.% MWNT/polycarbonate composites at room temperature (293 K) and 77 K. The curves are initially linear and then become nonlinear. The neat polycarbonate shows similar behavior (not shown). Table 2 lists the initial slopes of the load-deflection curves for the neat polycarbonate and the MWNT/polycarbonate composites at 293 K and 77 K from the experiments.
and the finite element analysis of specimens \((P^*/U^*)\). In this table, the experimental values of the slope are the average values of two or three data. For the composite specimens, the elastic moduli \(E^C\), \(\nu^C\) and \(G^C\) for the effective

![Figure 3. Load-deflection curves for the MWNT/polycarbonate composites at 293 K and 77 K.](image)

<table>
<thead>
<tr>
<th></th>
<th>Experimental slope</th>
<th>Predicted slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N/mm)</td>
<td>(N/mm)</td>
</tr>
<tr>
<td><strong>293 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>29.9</td>
<td>30.5</td>
</tr>
<tr>
<td>1.0 vol.% MWNT</td>
<td>27.4</td>
<td>32.5</td>
</tr>
<tr>
<td>1.7 vol.% MWNT</td>
<td>32.2</td>
<td>33.2</td>
</tr>
<tr>
<td>3.4 vol.% MWNT</td>
<td>28.4</td>
<td>34.9</td>
</tr>
<tr>
<td><strong>77 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>64.3</td>
<td>58.3</td>
</tr>
<tr>
<td>1.0 vol.% MWNT</td>
<td>56.6</td>
<td>61.4</td>
</tr>
<tr>
<td>1.7 vol.% MWNT</td>
<td>65.0</td>
<td>62.6</td>
</tr>
<tr>
<td>3.4 vol.% MWNT</td>
<td>56.1</td>
<td>65.3</td>
</tr>
</tbody>
</table>

CNT aspect ratio \(L^E/2R^E = 50\) and the damage parameters \(\chi_1 = \chi_2 = 1\) (i.e., perfect CNT/matrix interfacial bonding) were used in the analysis. The slope of the load-deflection curve at 77 K is larger than that at 293 K. There is close agreement between the experimental and predicted slopes for the polycarbonate. The predicted slope for the MWNT/polycarbonate composites increases continuously with increasing nanotube volume fraction, and reasonable agreement between the experimental and predicted slopes is observed for
the 1.0 and 1.7 vol.% MWNT/polycarbonate composites. However, the experimental slope begins to degrade with the addition of 3.4 vol.% MWNTs. Figure 4 shows the SEM micrograph of the fracture surface for the 3.4 vol.% MWNT/polycarbonate composite specimen at 77 K. MWNT/polycarbonate interfacial debonding is found. The interfacial debonding indicates a weak-bonding interface between the MWNTs and the surrounding matrix.

The predicted slope $P^*/U^*$ of the load-deflection curve for the MWNT/polycarbonate composite is shown in Figure 5 as a function of the damage parameter for the effective CNT volume fraction $V^E = 3.4\%$ and the effective CNT aspect ratio $L^E/2R^E = 50$ at 77 K. Here, three cases were considered: $\chi_1, \chi_2 \leq 1$ ($\chi_1 = \chi_2$), $\chi_1 \leq 1$ ($\chi_2 = 1$) and $\chi_2 \leq 1$ ($\chi_1 = 1$). The predicted slope decreases with the decrease in the damage parameter. Also, the slope for $\chi_2 \leq 1$ ($\chi_1 = 1$) is quite close to that for $\chi_1, \chi_2 \leq 1$ ($\chi_1 = \chi_2$). This indicates that the parameter $\chi_2$ has a significant effect on the composite behavior. The numerical results for the variation of the slope with the damage parameter can be interpreted as supporting the experimental results. That is, the imperfect interfacial bonding may be a reason for the small slope for the 3.4 vol.% MWNT/polycarbonate composite. Figure 6 shows the effect of the damage parameter $\chi_2$ ($\chi_1 = 1$) on the distribution of the shear stress $|\sigma^E_{zx}|$ in the effective CNT along an interfacial line ($2L^E/5 \leq x \leq L^E/2$, $y = 0$, $z = R^E$) for $V^E = 3.4\%$ and $L^E/2R^E = 50$ at 77 K. The stress distributions were determined from the finite element analysis of the composite RVE under longitudinal normal loading ($\sigma^*_{xx} = 50$ MPa). The interfacial shear stress decreases as the damage parameter $\chi_2$ decreases. It is well known that the efficiency of load transfer between the reinforcement phase and the matrix.

Figure 4. Fractograph of the 3.4 vol.% MWNT/polycarbonate composite specimen at 77 K.
depends on the interfacial shear stress [28], and, therefore, the stress results imply that load transfer between the MWNT and the polycarbonate is less effective for smaller values of $\chi_2$.

![Figure 5](image1.png)

**Figure 5.** Predicted slope of the load-deflection curve vs. damage parameter for $V^E = 3.4\%$ and $L^E/2R^E = 50$ at 77 K.

![Figure 6](image2.png)

**Figure 6.** Distributions of the shear stress in the effective CNT for $\chi_1 = 1$, $\chi_2 = 0.01, 0.1, 1$, $V^E = 3.4\%$, $L^E/2R^E = 50$ and $\sigma_{xx}^E = 50$ MPa at 77 K ($2L^E/5 \leq x \leq L^E/2, y = 0, z = R^E$).

## 5 Conclusions

In the present work, the cryogenic mechanical response of MWNT/ polycarbonate composites under bending was studied experimentally and numerically. It was found that the composite behavior varied with temperature and nanotube content. At the higher nanotube content, the slope of the load-deflection
curve decreased. Based on the results from the fractographic examination and
the multiscale analysis, the cause of the reduction in the slope may be due
to the imperfect MWNT/polycarbonate interfacial bonding. In addition, the
stress analysis result showed that the interfacial damage led to the limited
load transfer across the interface. Therefore, the interfacial characteristics
are parameters that could affect the mechanical performance of CNT-based
composites.

Appendix A

The finite element analysis was performed using ANSYS. The finite element
models for the RVE were meshed with eight-noded brick elements. For longi-
tudinal and transverse normal loadings, due to the symmetry only one-eighth
of the RVE \(0 \leq x \leq L^R_l/2, 0 \leq y \leq L^R_t/2, 0 \leq z \leq L^R_t/2\) was considered.
Let the displacement components in the \(x\)-, \(y\)- and \(z\)-directions be labeled by
\(u_x^\delta(x, y, z), u_y^\delta(x, y, z)\) and \(u_z^\delta(x, y, z)\) \((\delta = E, M, I1, I2)\), respectively. The
displacement boundary conditions for the RVE under normal load in the lon-
gitudinal \((x-)\) direction are:

\[
\begin{align*}
\{ u_x^E(0, y, z) &= u_x^M(0, y, z) = u_x^{I2}(0, y, z) = 0, \\
&= u_x^*, \\
0 \leq y \leq \frac{L^R_t}{2}, 0 \leq z \leq \frac{L^R_t}{2}, \quad (A.1)
\end{align*}
\]

\[
\begin{align*}
\{ u_y^M(x, 0, z) &= u_y^M(x, 0, z) = u_y^{I1}(x, 0, z) = u_y^{I2}(x, 0, z) = 0, \\
&= u_y^0, \\
0 \leq x \leq \frac{L^R_l}{2}, 0 \leq z \leq \frac{L^R_t}{2}, \quad (A.2)
\end{align*}
\]

\[
\begin{align*}
\{ u_z^E(x, y, 0) &= u_z^M(x, y, 0) = u_z^{I1}(x, y, 0) = u_z^{I2}(x, y, 0) = 0, \\
&= u_z^0, \\
0 \leq x \leq \frac{L^R_l}{2}, 0 \leq y \leq \frac{L^R_t}{2}, \quad (A.3)
\end{align*}
\]

where \(u_x^*\) is the uniform displacement induced by the mechanical and ther-
mal loads, and \(u_y^0\) and \(u_z^0\) are the uniform displacements determined from the
following conditions:

\[
\frac{\int_0^{L_i/2} \int_0^{L_i/2} \sigma_{yy}^M(x, L_i^R/2, z) dxdz}{(L_i^R/2)(L_i^R/2)} = 0, \quad \text{(for } u_y^0),
\]

\[
\frac{\int_0^{L_i/2} \int_0^{L_i/2} \sigma_{zz}^M(x, y, L_i^R/2) dyd y}{(L_i^R/2)(L_i^R/2)} = 0, \quad \text{(for } u_z^0).
\]

The longitudinal Young’s modulus \(E_i^R = E_x^R\) and Poisson’s ratio \(\nu_{it}^R = \nu_{xy} = \nu_{xz}^R\) are given by

\[
E_i^R = E_x^R = \frac{\sigma_{xx}^*}{(u_x^* - u_{xT}) / (L_i^R/2)},
\]

\[
\nu_{it}^R = \begin{cases} 
\nu_{xy}^{R} = -\frac{(u_y^0 - u_{yT})}{(u_x^* - u_{xT})} / (L_i^R/2), \\
\nu_{xz}^{R} = -\frac{(u_z^0 - u_{zT})}{(u_x^* - u_{xT})} / (L_i^R/2). 
\end{cases}
\]

where \(\sigma_{xx}^*\) is the mechanical mean stress acting on the \(x = L_i^R/2\) plane of the RVE, and \(u_x^*, u_y^0, u_{yT}\) and \(u_z^0, u_{zT}\) are the uniform displacements on the \(x = L_i^R/2, y = L_i^R/2\) and \(z = L_i^R/2\) planes of the RVE under pure thermal load, respectively. The mechanical mean stress \(\sigma_{xx}^*\) is obtained as:

\[
\sigma_{xx}^* = \frac{\int_0^{L_i/2} \int_0^{L_i/2} \sigma_{xx}^M(L_i^R/2, y, z) dydz}{(L_i^R/2)^2}.
\]

Transverse normal loading can be simulated by the uniform displacement in the \(y\)-direction applied to the boundary of the RVE. An analysis procedure similar to the case of longitudinal normal loading can be employed for the case of transverse normal loading, and the transverse Young’s modulus \(E_t^R = E_y^R\) and Poisson’s ratio \(\nu_{tt}^R = \nu_{yz}^R\) can be obtained.

For longitudinal shear loading, a whole RVE \((-L_i^R/2 \leq x \leq L_i^R/2, -L_i^R/2 \leq y \leq L_i^R/2, -L_i^R/2 \leq z \leq L_i^R/2\) was considered. The displacement boundary
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Conditions for the RVE under longitudinal shear are as follows:

\[
\begin{align*}
\begin{cases}
    u^M_x(x, y, -L^R_t/2) &= 0, \\
    u^M_y(x, y, -L^R_t/2) &= 0, \\
    u^M_z(x, y, -L^R_t/2) &= 0, \\
    u^M_x(x, y, L^R_t/2) &= u^*_x, \\
    u^M_y(x, y, L^R_t/2) &= 0, \\
    u^M_z(x, y, L^R_t/2) &= 0,
\end{cases}
\end{align*}
\]

\[-L^R_R t/2 \leq x \leq L^R_R t/2, -L^R_R t/2 \leq y \leq L^R_R t/2,
\]

\[
\begin{align*}
\begin{cases}
    u^M_x(-L^R_l/2, y, z) &= u^M_x(L^R_l/2, y, z), \\
    u^M_y(-L^R_l/2, y, z) &= u^M_y(L^R_l/2, y, z), \\
    u^M_z(-L^R_l/2, y, z) &= u^M_z(L^R_l/2, y, z),
\end{cases}
\end{align*}
\]

\[-L^R_l/2 \leq y \leq L^R_l/2, -L^R_l/2 \leq z \leq L^R_l/2.
\]

The longitudinal shear modulus \(G^R_{lt} = G^R_{tl} = G^R_{zx}\) is given by

\[
G^R_{lt} = G^R_{tl} = G^R_{zx} = \frac{\sigma^*_zz}{u^*_x/L^R_t}.
\] (A.10)

The mechanical mean stress \(\sigma^*_zz\) is computed from

\[
\sigma^*_zz = \frac{\int_{-L^R_l/2}^{L^R_l/2} \int_{-L^R_t/2}^{L^R_t/2} \sigma^M_{zx}(x, y, L^R_t/2) dx dy}{L^R_R t L^R_l}.
\] (A.11)

References


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