MICROSCOPIC PROPERTIES AND NUMERICAL SIMULATION OF ALIGNED CNT SHEET COMPOSITES

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1. Introduction

Carbon nanotubes (CNTs) have attracted much attention because they have unique structure and remarkable mechanical, electrical, thermal and chemical properties. In particular, it has been believed that CNTs are ideal fillers for polymers to enhance their mechanical properties. Numerous studies have been devoted for the application of SWNTs and MWNTs to polymers for the last two decades. However, it has been said that mechanical properties of CNT-dispersed polymers are generally inferior to the theoretical predictions.

Nowadays, processing methods to fabricate CNT/polymer composites with high weight fraction and unidirectionally aligned CNT have been attempted and aligned CNT/epoxy prepreg was successfully fabricated using hot-melt technique [1, 2]. This method has some advantages compared with resin infusion and resin transfer molding, which are often applied for CNT composites. A prepreg is easy to handle and enables complex structures or components production. Furthermore, aligned CNT/epoxy prepregs are applicable to press molding because CNTs are not continuous fibers. Our previous experimental studies [2, 3] have reported that higher volume fraction aligned CNT/epoxy composites could be made and they showed higher young’s modulus than previous studies [4]. On the other hand, during the tensile process, some fractures such as interfacial debonding and multiple fracture of CNT were processed, especially “sword-in-the-sheath” fracture of CNT were observed at the fracture surface of the composites, which means that “interfacial debonding or slippage” between outerwall and innerwall of CNT has occurred. Another previous simulation [5] revealed the fracture process of composites, but “sword-in-the-sheath” fracture of CNT could not be reproduced because in the previous simulation CNT was modeled as 1-walled fibers.

In this study we tried to consider the effect of “interfacial debonding or slippage” between outerwall and innerwall of CNT. First, we fabricated an aligned CNT/epoxy composites using hot-melt method and macroscopic and microscopic mechanical properties were evaluated. Next, Continuous damage mechanics (CDM) model and embedded process zone (EPZ) model to permit both interface debonding and matrix cracking were carried out to understand the fracture mechanisms of the composites. Modelling reinforcement mechanism of mechanical properties the carbon nanotube/epoxy composite including interfacial property and fracture property is our objectives.

2. Experiments

2.1 Composite Processing and Characterizations

Horizontally aligned CNT sheets were produced from vertically aligned CNT arrays (forest). Inoue et al. established a simple and efficient synthesis method for producing vertically aligned long MWCNTs using iron chloride powders as precursor of a catalyst [1]. Fig. 1 is SEM images of the CNT
The diameter of CNT are in the range of 30 - 70 nm, and length is about 1 mm.

The procedure to fabricate CNT/epoxy prepreg is presented in Fig. 2(a). The B-stage cured epoxy resin with release paper was obtained from a commercial prepreg company. Detailed procedures and results for the fabrication of CNT composites have been reported by T. Ogasawara et al [2]. The actual composites is shown in Fig.2 (b). Polymers are well impregnated and CNTs are well dispersed. The areal weight of epoxy resin film is well controlled as 30 g/m², and thickness is approximately 25 μm.

Volume fractions of CNTs were calculated by thermogravimetric analysis (TGA) results, following by these equations;

\[ M_f = \frac{\Delta W_{\text{Epoxy}} - \Delta W_{\text{Comp}}}{\Delta W_{\text{Epoxy}} - \Delta W_f} \]  
\[ V_f = \frac{M_f}{M_f + \frac{\rho_{\text{CNT}}}{\rho_{\text{Epoxy}}} (1 - M_f)} \]

where notation \( M, W, V, \rho \) means mass fraction, weight, volume fraction, density and subscript notation \( f, \text{epoxy}, \text{comp} \) means fiber (CNT), epoxy, composites. In this study \( \rho_{\text{CNT}} = 2.0 \, \text{g/cm}^3 \) and \( \rho_{\text{Epoxy}} = 1.2 \, \text{g/cm}^3 \) was applied.

In order to prepare the fracture process observation specimen, tensile tests (Model 5966R; Instron Corp., USA) for various volume fractions were conducted to evaluate the macroscopic mechanical properties of the composites. Geometry and dimensions of tensile test specimen are shown in Fig.3. The longitudinal strain was measured using a non-contacting video extensometer (AVE; Instron Corp., USA).

After tensile loading, samples were carefully cut into a rectangular piece and set on a Transmission Electron Microscope (TEM) tip-on holder (EM-02210, JEOL). Thin samples for TEM observations were prepared using a Focus Ion Beam milling machine (FIB, JEM-9320, JEOL). FIB image for microscopic observation sample is shown in Fig.4. The machined area is approximately 30 μm width, 4 μm depth, and 0.1 μm thickness. In Fig.4, CNTs are aligned from left side to the right side. Nanoscopic observations of CNTs and CNT/epoxy forest, and a horizontally aligned CNT sheet.
interfaces were carried out using an FE-TEM (JEM-2100F, JEOL, Japan) under the accelerated electron voltage of 200 kV.

2.2 Numerical simulation method

A 2-Dimensional finite element model consisting of eight-node elements for CNT and triangle node for matrix was used, as shown in Fig.5. Due to the limitation of our computers, five CNTs (modeled as 2–walled fibers) at 0.05 μm in diameter and 40 μm in length are unidirectionally aligned in the matrix. Model size of the composites is 2.5 μm in width, and 42 μm in length (tensile direction). For simplicity, the matrix is modeled as an isotropic elastic–plastic material and CNT is modeled as an isotropic elastic material.

The shape of 1-walled CNT and 2-walled CNT are depicted in Fig.6(a),(b). Difference of these two models is cohesive elements inserted between CNT walls (interwall). Due to the computational limitation, the distance between outerwall and interwall is set to 10 nm, which is about 30 times larger than that of experimental observation results. Potential CNT break points are positioned at several points along the CNT. Cohesive elements are inserted in the matrix, in the interface between matrix and CNT and in the interface between the walls of CNTs (for 2-walled CNT). The initiation and propagation of matrix cracks, interfacial debonding and fiber break induced by the stress redistribution is permitted through CDMs embedded in matrix elements and EPZs embedded at fiber break points and interface between CNT and polymer and between walls of CNT (interwall for the 2-walled CNT).

For reproducing the matrix cracking, CDM model was applied. In this simulation, we assumed stress-strain relationship of matrix as:
The constitutive model for any EPZ elements represents the cohesive bonding across the surface and relates the cohesive traction \( T \) across the surface to the surface separation \( \Delta \), as shown in Fig. 6(a). In this simulation modified Dugdale model for \( T \) versus \( \Delta \), as illustrated in Fig. 6(b) and (c) was adopted and sufficiently large penalty stiffness \( k_i (> 1.0 \times 10^9 \text{ (N/mm)}^3) \) was assumed. The maximum traction \( T_{\text{max}} \) and the critical energy release rate \( G_{\text{ic}} \) for each mode of separation \( (i = I, II) \) are the parameters characterizing the present EPZ model. For simplicity \( T_{\text{max}} = T_{II,\text{max}} \) and \( G_{\text{ic}} = G_{\text{Ic}} \) were assumed. The complete separation condition is approximately equal to (because \( k_i \) is very large)

\[
d \equiv \left( \frac{\langle \Delta_f \rangle}{\Delta_{Kc}} \right)^2 + \left( \frac{\langle \Delta_m \rangle}{\Delta_{Gc}} \right)^2 = 1
\]

where

\[
\langle \Delta_f \rangle = \begin{cases} \Delta_f (\Delta_f \geq 0) \\ 0 (\Delta_f \leq 0) \end{cases}
\]

It was simply assumed that the interface failure is dominated by Mode II loading, and fiber fracture is dominated by Mode I loading.

The discretized form of virtual work balance including the CDM and EPZ is written as:

\[
(t^* K_f + t^* K_m + t^* K_{\text{epz}}) \Delta U_L = \begin{bmatrix} R_{\text{min}} \end{bmatrix} - \begin{bmatrix} Q_f \quad Q_m \quad Q_{\text{epz}} \end{bmatrix}^T \begin{bmatrix} Q_{\text{dam}} \end{bmatrix}
\]

where \( K_f \) and \( K_{\text{epz}} \) are the tangential stiffness matrices of fiber and matrix elements and the elements in the EPZ, \( Q \) and \( Q_{\text{epz}} \) are the nodal forces corresponding to the element stresses and the tractions, respectively, and \( F \) is the externally applied nodal forces. The effect of matrix cracking is included in the \( K_m \) and \( Q_{\text{dam}} \). In order to properly follow the physical sequence of possibly conflicting damage events, the \( R_{\text{min}} \) method is used to trace the assumed relation between separation and traction of the elements in the CDM and EPZ [6].

The maximum tensile strain of the composites is 1 %, and volume fraction of CNT is about 10 %. Mechanical properties and fitting parameters used in this simulation are summarized in Table 1. Interfacial strength between CNT walls is assumed as 10 MPa, which value is larger than previous reports [7]. This contradiction is due to the limitation of model size, so larger scale modeling will be required for conducting more accurate simulations.

**Fig.6** Schematic modeling of the Embedded Process Zone (EPZ) model. (a) Relationship between \( T \) and \( \Delta \), (b) EPZ model used in this study for mode I (Normal direction) fracture, (c) EPZ model for mode II (tangential direction) fracture [6].

\[
\Delta \sigma = (1 - D) C^\sigma : \Delta e - \frac{\Delta D}{1 - D} \sigma \quad (3)
\]

\[
\Delta D = (1 - D) C \left( \varepsilon_m^p \right) + (B_0 + B_D) \Delta e^p (0 \leq D \leq 1) \quad (4)
\]

\[
C \Delta e^p = A \Delta D \left( \frac{\sigma_m}{\sigma} \right)^2 \quad (5)
\]

where \( D \) is the damage parameter, \( \sigma \) is the hydrostatic pressure and \( A, B_0, B_D \) are fitting parameter. And it was assumed that matrix crack occurs at \( D_e = 0.9 \).

Potential fiber break points are positioned at regular intervals \( \delta \) along the fiber. Each point is assigned failure strength consistent with a weibull distribution such that the cumulative failure probability of a fiber section of length \( \delta \) is

\[
P_i^f (\sigma) = 1 - \exp \left\{ - \frac{\Delta}{L_\sigma} \left( \frac{\sigma}{\sigma_0} \right)^\nu \right\}
\]

The actual strength \( \sigma_i \) for the \( i \)th fiber break point is chosen by selecting a random number \( R_i \) within (0,1) and solving \( R_i = P_i (\sigma) \). During the simulation, if the axial fiber stress at the \( i \)th point reaches the assigned strength \( \sigma \), then a fiber break is introduced at the \( i \)th point by negating the internal nodal force at the fiber break surface.
Table 1. Parameters used for the numerical simulation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus of CNT (GPa, assumption)</td>
<td>400 [5]</td>
</tr>
<tr>
<td>Young’s modulus of polymer (GPa, experimental value)</td>
<td>2.5 [2]</td>
</tr>
<tr>
<td>Representative strength of CNT (GPa, assumption)</td>
<td>3 [5]</td>
</tr>
<tr>
<td>Interfacial strength between CNT and polymer (MPa)</td>
<td>20[8]</td>
</tr>
<tr>
<td>Interfacial strength between CNT walls (MPa, assumption in this paper)</td>
<td>10</td>
</tr>
<tr>
<td>matrix damage fitting parameter A</td>
<td>20</td>
</tr>
<tr>
<td>matrix damage fitting parameter B_0</td>
<td>0</td>
</tr>
<tr>
<td>matrix damage fitting parameter B_1</td>
<td>20</td>
</tr>
<tr>
<td>Initial damage parameter D_{ini}</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 2. Tensile properties of composites (Average value [9]).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Failure strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>2.5</td>
<td>62</td>
<td>3.8</td>
</tr>
<tr>
<td>Comp#1 (V_f=4.5 %)</td>
<td>18.8</td>
<td>97.4</td>
<td>0.50</td>
</tr>
<tr>
<td>Comp#2 (V_f=8.4 %)</td>
<td>32.4</td>
<td>129</td>
<td>0.40</td>
</tr>
<tr>
<td>Comp#3 (V_f=21.4 %)</td>
<td>50.1</td>
<td>181</td>
<td>0.36</td>
</tr>
<tr>
<td>Comp#4 (V_f=29.6 %)</td>
<td>73.4</td>
<td>193</td>
<td>0.27</td>
</tr>
<tr>
<td>Comp#5 (V_f=32.8 %)</td>
<td>89.8</td>
<td>217</td>
<td>0.24</td>
</tr>
</tbody>
</table>

3. Results and discussions

3.1 Tensile properties and microscopic fracture observation results

Young’s modulus and Ultimate tensile strength of the tensile tests are summarized in Fig.7(a),(b) and Table.2. Composites showed much higher Young’s modulus than that of previous studies [2, 9]. Fracture observation results are summarized in Fig.8(a) ~ (d). The fracture surface of CNT/epoxy composite after tensile testing is presented in Fig. 8(a). Many pulled out CNTs are visible, and the length is apparently a few micrometers. Detailed observation revealed the sword-in-sheath fracture of CNTs, as shown in Fig.8(b). The results imply the possibility that the crack which is initiated at the outer wall of CNT propagates into the inner walls and the crack path does not exist in the parallel tensile direction of matrix. Transmission electron microscope (TEM) observations were also carried out for understanding the internal fracture process of the composites.

Typical TEM photograph of broken or interfacial debonded CNTs inside the composites is depicted in Fig. 8(c), (d). Sword-in-sheath breakages are also observed inside the composites, as shown in Fig.8(c), which means that interfacial strength between outerwall and innerwall of CNT is weak. Interfacial debonding is also observed during the tensile
Fig. 8 Pictures of (a) exposed CNTs and (b) sword-in-sheath fracture at fracture surface, (c) internal sword-in-sheath fracture and (d) interfacial debonding during the tensile process.

process, as shown in Fig.8(d), but interfacial debonding has nothing to do with the fracture process of composites [3]. These results suggest the possibility that internal fracture and “sword-in-sheath” fracture of the CNT is an important factor for understanding the fracture process of the composites.

3.2 Numerical simulation results

The numerical simulation results are summarized in Fig. 9 and Fig. 10.

Stress-strain behavior of 2-walled model is depicted in Fig.9, which behavior is similar to that of our previous simulation [5]. Young’s modulus of simulation model is \( E_{\text{comp}} = 34.7 \) GPa, which value is almost same as one of the experimental results of Comp#2 [9].

With increasing the strain, fracture proceeded as follows. First, tensile breakage of CNT occurred. Next, because of the stress concentration matrix crack was propagated from the CNT broken point. And at last, matrix cracks coalesced of and resulted in final fracture, and CNT were exposed at the fracture surface, as shown in Fig.10(a). This fracture process is also same as our previous simulation [5].

Detailed observation at the fracture surface was also conducted. Fig.10(b),(c) are exposed CNTs at fracture surface (Fig.10(b) is at the thick circle in Fig.10(a) and Fig.10(c) is at the thick dotted circle in Fig.10(a)). “Sword-in-sheath” fracture of CNTs, as shown in Fig.10(b), and “interfacial-slipped” CNT were observed at fracture surface, as shown in Fig.10(c).

The mechanism of sword-in-sheath fractures of CNT is considered as below: First, outerwall of CNT has broken (internal fracture occurred) because of stress concentration caused by interfacial slippage and debonding. If the crack path proceeded to interwall, so-called “interwall slippage” has occurred and next stress concentration has taken place around the broken point. Finally, stress concentration resulted in the innerwall fracture, especially near the outerwall broken point, which led to the "sword-in-sheath" fracture, as shown in Fig.10(b), and matrix crack propagation also led the interfacial slippage to the CNT which hasn’t been fractured, as shown in Fig.10(c). Unfortunately we couldn’t experimentally distinguish these two types of sword-in-sheath fracture type of CNT, but these phenomena are in good agreement with experimental results, as shown in Fig. 8(b),(c). And this numerical simulation revealed that outerwall breakage, interwall debonding or slippage, innerwall breakage of CNT are especially important factors to understand the fracture mechanism of the composites.

4. Conclusions

The experimental and numerical simulation results for fracture processes of aligned multi-wall carbon nanotube (MWNT) / epoxy composites were presented in this paper. Aligned multi-walled carbon nanotubes /epoxy composites were fabricated using a hot-melt prepreg method.
Tensile tests of composites and microscopic observations at the fracture surfaces were conducted to evaluate the mechanical properties and microscopic fracture process of the composites. Numerical simulation based on continuous damage mechanics (CDM) model and embedded-process-zone (EPZ) model to permit both interface debonding and matrix/CNT cracking was carried out to understand the fracture process of the composites. Composites showed much higher Young's modulus than that of reported by other researchers. Detailed microscopic observations were conducted which revealed a lot of sword-in-sheath pulled-out CNTs (CNT exposure). Numerical simulation revealed that CNT fracture inside the composite and debonding between CNT walls are important for understanding fracture mechanism of the composites. Our next research is elucidating the effect of toughening by CNTs' three-dimensional alignment, and simulations of large-scale models including more CNT wall effects for reproducing detailed sword-in-sheath breakages.

5. Acknowledgements

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References