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Research Article

Effects of CNT Diameter on the Uniaxial Stress-Strain Behavior of CNT/Epoxy Composites

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The present work studies the effects of the diameter of carbon nanotube (CNT) as well as CNT weight fraction on the uniaxial stress-strain behavior, stiffness, and strength of CNT-reinforced epoxy-matrix composites. The experimental results show that average Young's moduli of 5 wt%-CNT/epoxy composites with a CNT diameter $D < 20$ nm and $D = 40{\sim}60$ nm are 4.56 GPa and 4.36 GPa, and the average tensile strengths are 52.89 MPa and 46.80 MPa, respectively, which corresponds to a percentage increase of 61.1%, 54.1%, 106%, and 82.3%, respectively. Two micromechanics models are employed and the predicted Young's moduli are benchmarked with the experimental data of MWCNT-reinforced epoxy-matrix composites.

1. INTRODUCTION

In view of its excellent stiffness and strength, the carbon nanotube (CNT) is considered as an ideal candidate for the reinforcement in composites. Andrews et al. [1] added 5 wt% single-walled carbon nanotubes (SWCNTs) in isotropic petroleum pitch. The elastic modulus of SWCNT/petroleum increased from 34 GPa to 78 GPa, whereas the tensile strength increased from 490 MPa to 850 MPa. Jia et al. [2] used AIBN, a free radical initiator, and Gong et al. [3] used the surfactant dodecylether ($C_{12}EO_8$) as a processing aid to improve the interfacial bonding between multiwalled carbon nanotubes (MWCNTs) and the matrix. The tensile test results of Allaoui et al. [4] reported that Young's modulus and the yield strength were doubled and quadrupled for MWCNT/epoxy composites with 1 and 4 wt% CNTs, respectively, in comparison with those of pure epoxy samples. However, the three-point bending test results by Lau et al. [5] indicated that the flexural strengths of all CNT composites were relatively lower than the pure epoxy sample. The nanoindentation results by Li et al. [6] using an atomic force microscope showed an increase in elastic modulus by 75% and hardness by 30% in the epoxy reinforced by 5 wt% SWCNTs in comparison with those of neat epoxy. Song and Youn [7] reported that the tensile strength of epoxy filled with well-dispersed CNTs increased as the CNT weight fraction increased, yet that of the composite filled with poorly-dispersed CNTs decreased. Thostenson and Chou [8] used a microscale twin-screw extruder to align MWCNTs in polystyrene composite films. The interface between CNT and matrix was studied by Schadler et al. [9], Ajayan et al. [10], and Cooper et al. [11]. CNTs were also used as reinforcements in ceramic- or metal-matrix composites [12–15].

In the present work, MWCNTs with a variety of weight fractions and diameters are added into epoxy and the composites are subjected to uniaxial tensions. The mechanical properties of composites containing CNTs at the same weight fraction, yet different CNT diameters, are compared and, therefore, the effects of CNT diameter on Young's modulus and tensile strength of MWCNT/epoxy composites are characterized.

2. EXPERIMENTS

As received MWCNTs purchased from Desunnano Co. in specific weight fraction (1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt%) are mixed with 7.5 mL epoxy resin E-120 together with 2.5 mL associated hardener H-100. It is noted that the

Figure 1: MWCNT/epoxy specimen.

resin-to-hardener volume ratio is kept at 3 : 1. The mixture is first sonicated for 10 minutes and then stirred amply for 5 minutes. The sonication-stirring step is repeated three times in order to ensure the uniform distribution and the separation of the entangled MWCNTs. The nanotube/epoxy mixtures are then poured into an aluminum mold, vacuumed in an oven for 30 minutes, and then released to the atmosphere for 10 minutes. This step is repeated two times in order to remove air bubbles from the mixtures. The mixture is then cured in atmosphere. After simple machining, the specimen is ready for test; see Figure 1. The dimensions of the specimen follow ASTM D638 Type IV. In the present work, there are pure epoxy and composites with 1 wt%-, 2 wt%-, 3 wt%-, 4 wt%-, and 5 wt%-MWCNTs with their diameters being less then 20 nm or between 40 to 60 nm. The weight fraction $W_t\%$ of CNTs is given by

$$W_t\% = \frac{W_{\text{CNT}}}{W_{\text{CNT}} + W_e + W_h} \times 100\%, \tag{1}$$

where W_{CNT}, W_e, and W_h are the weight of the carbon nanotubes, epoxy resin, and hardener in grams, respectively. Three specimens for each of the group-neat epoxy, 1 wt%-, 3 wt%-, and 5 wt%-MWCNT/epoxy, and only one specimen for the group 2 wt%- and 4 wt%-MWCNT/epoxy is prepared. The total number of samples is twenty five. If the dispersion of MWCNTs is uniform in the epoxy resin, the composite specimen can be regarded as isotropic. The testing of the composites follows the ASTM D638 standard tensile test. The grip of the microcomputer tensile tester (Model No. H-10KS, Hounsfield Test Equipment Co.) can be controlled in such a manner that the relative displacement rate of the grips is 1.0 mm/min so that the test can be regarded as quasistatic.

At the time of measurement, a resistance-type (120 ohms) strain gage is pasted on the surface of the specimen in the axial direction. The elastic modulus of MWCNT/epoxy composite is determined by calculating the slope of the linear portion of the stress-strain curve.

3. THE MODELS

In the present work, two micromechanics models, Eshelby [16] and Mori-Tanaka [17], are employed to predict Young's modulus of epoxy reinforced by randomly distributed MWCNTs. The former ignores the interaction between CNTs and gives the effective elastic constants $[\overline{C}]$ of the composite as follows:

$$[\overline{C}] = [C^M] + V_I([C^I] - [C^M])[X], \tag{2}$$

where $[C^M]$ is the stiffness matrix of the matrix, $[C^I]$ is the stiffness matrix of CNT, V_I is the CNT volume fraction, and $[X]$ is given by [18]

$$\begin{aligned}[X] = \frac{1}{2\pi}\int_0^{\pi} d\phi \int_0^{\pi} &[\Phi]^{-1}\left([C^M] - [C^I]\right)^{-1}[C^M] \\ &\times \left(\left([C^M] - [C^I]\right)^{-1}[C^M] - [S]\right)^{-1} \\ &\times [\Phi]\sin\theta \, d\theta\end{aligned} \tag{3}$$

with $[S]$ being the Eshelby tensor, which is a function of the geometry of CNT and the elastic properties of the matrix, and $[\Phi]$ being given by

$$[\Phi]=\begin{bmatrix} \cos^2\theta & \sin^2\theta\cos^2\phi & \sin^2\theta\sin^2\phi & \sin^2\theta\sin\phi\cos\phi & \sin\theta\cos\theta\sin\phi & \sin\theta\cos\theta\cos\phi \\ \sin^2\theta & \cos^2\theta\cos^2\phi & \cos^2\theta\sin^2\phi & \cos^2\theta\sin\phi\cos\phi & -\sin\theta\cos\theta\sin\phi & -\sin\theta\cos\theta\cos\phi \\ 0 & \sin^2\phi & \cos^2\phi & -\sin\phi\cos\phi & 0 & 0 \\ 0 & -2\cos\theta\sin\phi\cos\phi & 2\cos\theta\sin\phi\cos\phi & \cos\theta(\cos^2\phi - \sin^2\phi) & -\sin\theta\cos\phi & \sin\theta\sin\phi \\ 0 & -2\sin\theta\sin\phi\cos\phi & 2\sin\theta\sin\phi\cos\phi & \sin\theta(\cos^2\phi - \sin^2\phi) & \cos\theta\cos\phi & -\cos\theta\sin\phi \\ -2\sin\theta\cos\theta & 2\sin\theta\cos\theta\cos^2\phi & 2\sin\theta\cos\phi\sin^2\phi & 2\sin\theta\cos\theta\sin\phi\cos\phi & \sin\phi(\cos^2\theta - \sin^2\theta) & \cos\phi(\cos^2\theta - \sin^2\theta) \end{bmatrix}. \tag{4}$$

Moreover, the Mori-Tanaka model considering the interaction between CNTs to a certain extent gives

$$[\overline{C}] = [C^M] + V_I([C^I] - [C^M])\left(V_I[\mathrm{I}] + (1 - V_I)[X]^{-1}\right)^{-1}. \tag{5}$$

4. RESULTS

In the present work, neat epoxy, 1 wt%-, 2 wt%-, 3 wt%-, 4 wt%-, and 5 wt%-MWCNT/epoxy composite specimens where MWCNTs exhibit two groups of diameters, D: (i)

Table 1: Tensile strength, Young's modulus, and fracture strain of CNT/epoxy composites.

Average tensile strength of CNT/epoxy composites (percentage increase)		
CNT weight percentage	CNT diameter	
	D < 20 nm (MPa)	D = 40~60 nm (MPa)
0 (neat epoxy)	25.67 ± 0.28	
1 wt%	42.64 ± 1.47 (66.1%)	36.63 ± 1.06 (42.7%)
2 wt%	46.03 (79.3%)	38.97 (51.8%)
3 wt%	48.02 ± 1.46 (87.1%)	42.52 ± 1.47 (65.6%)
4 wt%	51.10 (99.1%)	45.78 (78.3%)
5 wt%	52.89 ± 0.79 (106%)	46.80 ± 0.51 (82.3%)
Average Young's modulus of CNT/epoxy composites (percentage increase)		
CNT weight percentage	CNT diameter	
	D < 20 nm (GPa)	D = 40~60 nm (GPa)
0 (neat epoxy)	2.83 ± 0.22	
1 wt%	3.64 ± 0.20 (28.6%)	3.47 ± 0.15 (22.6%)
2 wt%	4.18 (47.7%)	3.74 (32.2%)
3 wt%	4.31 ± 0.21 (52.3%)	4.10 ± 0.17 (44.9%)
4 wt%	4.39 (55.1%)	4.26 (50.5%)
5 wt%	4.56 ± 0.21 (61.1%)	4.36 ± 0.20 (54.1%)
Average fracture strain of CNT/epoxy composites (percentage increase)		
CNT weight percentage	CNT diameter	
	D < 20 nm	D = 40~60 nm
0 (neat epoxy)	0.87 ± 0.09	
1 wt%	1.19 ± 0.11 (36.8%)	1.16 ± 0.06 (33.3%)
2 wt%	1.11 (27.6%)	1.05 (20.7%)
3 wt%	1.15 ± 0.01 (32.2%)	1.05 ± 0.11 (20.7%)
4 wt%	1.20 (37.9%)	1.08 (24.1%)
5 wt%	1.18 ± 0.11 (35.6%)	1.10 ± 0.03 (26.4%)

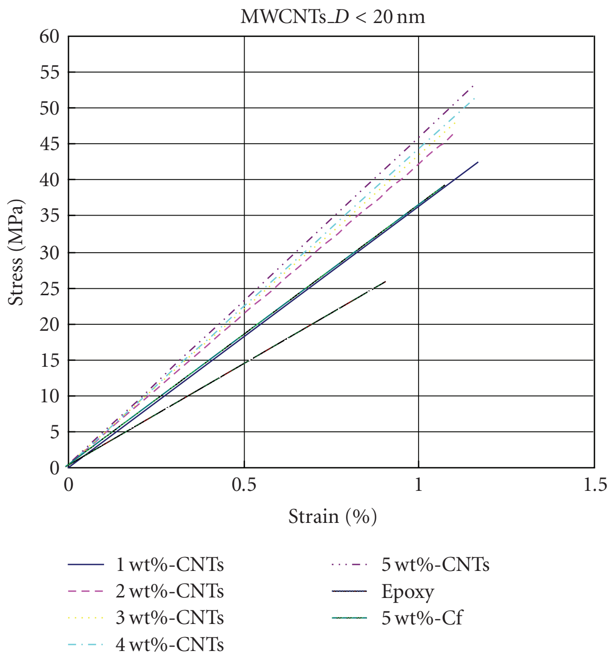

Figure 2: Stress-strain curve of MWCNT/epoxy with CNT diameter $D < 20$ nm.

less than 20 nm and (ii) between 40 and 60 nm, are used. Typical stress-strain curves of MWCNT/epoxy composites, where CNT diameter $D < 20$ nm is shown in Figure 2 while those of MWCNT/epoxy composites with CNT diameter D being 40~60 nm could be seen in Figure 3. The composite strength, modulus of elasticity, and fracture strain data are listed in Table 1. The relationship between composite tensile strength and CNT weight fraction is shown in Figure 4 and that between Young's modulus and CNT weight fraction is shown in Figure 5. The experimental results show that the average tensile strength of 1 wt%-, 2 wt%-, 3 wt%-, 4 wt%-, and 5 wt%-MWCNTs/epoxy with a CNT diameter $D < 20$ nm increases 66.1%, 79.3%, 87.1%, 99.1%, and 106.0%, and average Young's modulus increases 28.6%, 47.7%, 52.3%, 55.1%, and 61.1%, respectively. By adding MWCNTs of the same weight fraction with a larger diameter (D = 40~60 nm), the average tensile strength of 1 wt%-, 2 wt%-, 3 wt%-, 4 wt%-, and 5 wt%-MWCNTs/epoxy increases 42.7%, 51.8%, 65.6%, 78.3%, and 82.3%, and average Young's moduli increase 22.6%, 32.2%, 44.9%, 50.5%, and 54.1%, respectively, compared with average Young's modulus (2.83 GPa) and the average tensile strength (25.67 MPa) of the neat epoxy specimens. Adding MWCNTs into epoxy does increase the mechanical

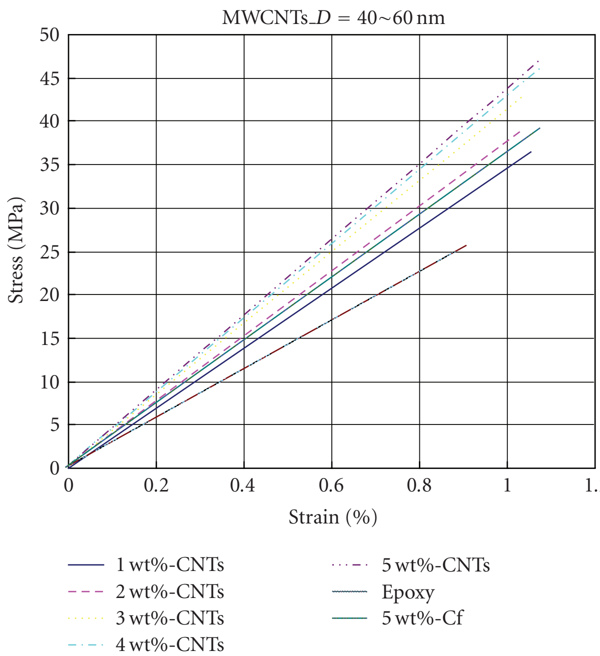

FIGURE 3: Stress-strain curve of MWCNT/epoxy with CNT diameter $D = 40\sim60$ nm.

properties of the composites, and the smaller the CNT diameter is the higher the composite stiffness and strength are.

The fracture surface of a 5 wt%-CNT/epoxy specimen, where the diameter of CNTs is less than 20 nm is examined using field-emission scanning electron microscopy and is shown in Figure 6. The dispersion of the CNTs is uniform, which contributes to the improved mechanical properties of CNT-based composites [8].

The following elastic properties of a single-crystal graphite sheet (i.e., a graphene) are used in the micro-structure-based double-inclusion model developed by Yu et al. [19] to determine Young's modulus of MWCNT as follows:

$$[C] = \begin{bmatrix} 1060 & 15 & 180 & 0 & 0 & 0 \\ 15 & 36.5 & 15 & 0 & 0 & 0 \\ 180 & 15 & 1060 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4.5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 440 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.5 \end{bmatrix} \text{GPa}, \quad (6)$$

where the x_1-x_3 plane is the plane of isotropy of a graphene. Poisson's ratios of the graphene are $\nu_{12} = 0.01$, $\nu_{23} = 0.2$, and $\nu_{13} = 0.2$ [20]. Since two ranges of CNT diameters ($D = 40\sim60$ nm and $D < 20$ nm) are used in our specimens, the diameters of two groups of MWCNTs are taken as 50 nm and 15 nm, respectively, in the present models. The double-inclusion model [19] gives Young's modulus of an MWCNT with a diameter of 50 nm as 770 GPa, and 1015 GPa for MWCNT with a diameter 15 nm, which is consistent with the available experimental data [21]. Young's modulus of

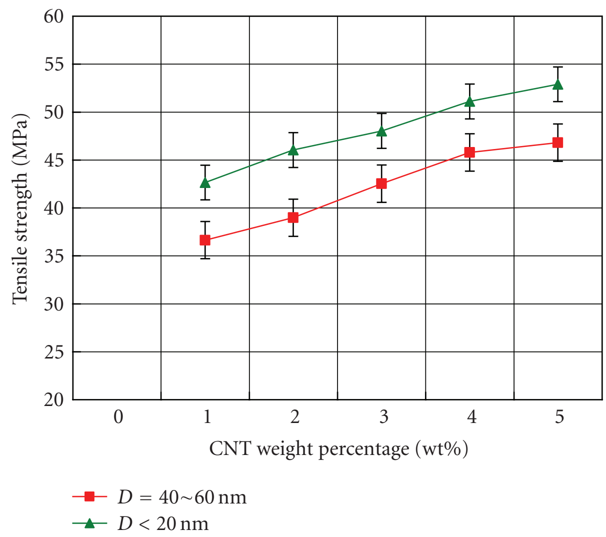

FIGURE 4: Relationship between composites tensile strength and CNT weight percentage.

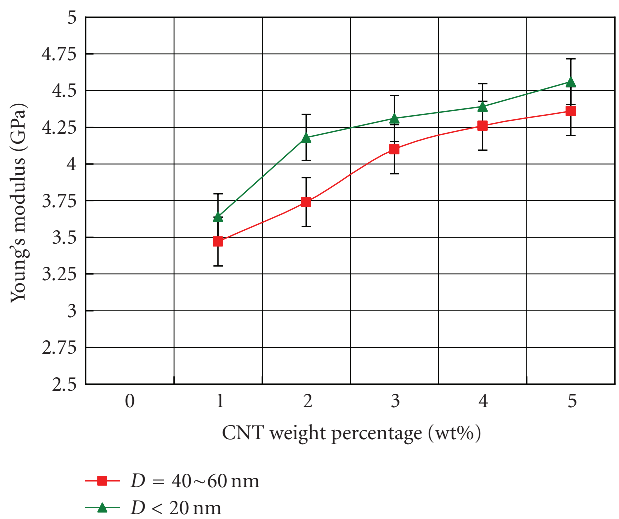

FIGURE 5: Relationship between the composites of Young's modulus and CNT weight percentage.

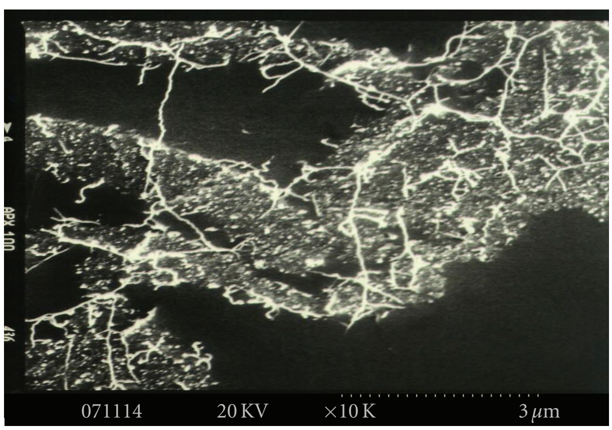

FIGURE 6: The fracture surface of 5 wt%-MWCNT/epoxy specimen ($D_{CNT} < 20$ nm).

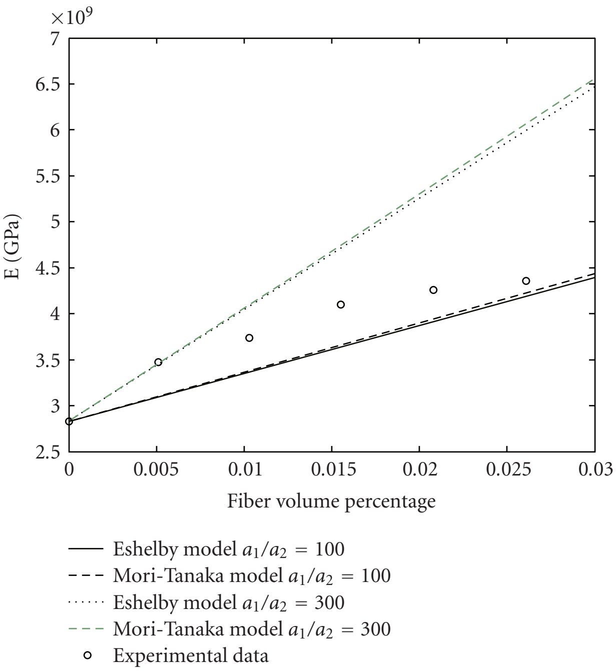

Figure 7: Predicted Young's modulus compared with the experimental data of the MWCNT/epoxy composite D_{CNT} = 40∼60 nm.

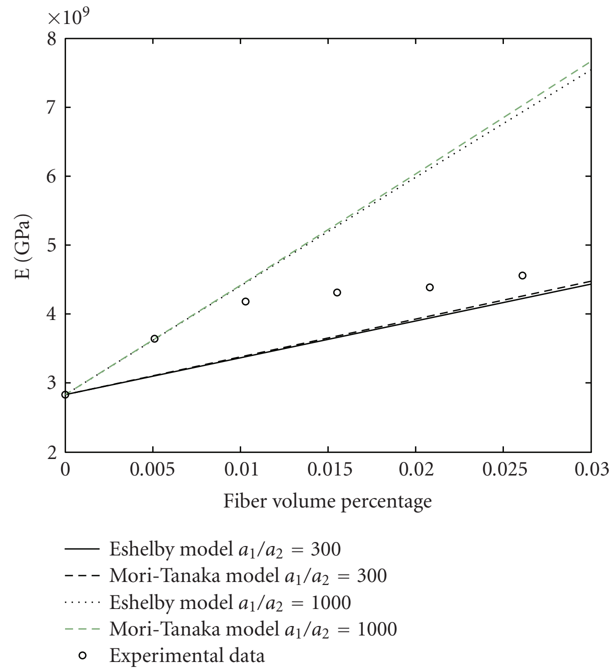

Figure 8: Predicted Young's modulus compared with the experimental data of the MWCNT/epoxy composite D_{CNT} < 20 nm.

epoxy E_m is 2.83 GPa and the Poisson's ratio, ν_f, of the CNT is assumed to be 0.2 and that of epoxy, ν_m, is 0.32. Since the density of MWCNT and that of epoxy are 2.1 g/cm^3 and 1.07 g/cm^3, respectively; the CNT volume fractions are 0.51% (1 wt%), 1.03% (2 wt%), 1.55% (3 wt%), 2.08% (4 wt%), and 2.61% (5 wt%). The lengths of the as received MWCNTs range between 5 and 15 μm, thus the lower and upper bounds on the aspect ratio a_1/a_2 of MWCNT are roughly estimated as 100∼300 and 300∼1000 for the two groups of MWCNTs in our calculations. The predicted values are compared with the experimental data in Figures 7 and 8 for the two groups of CNT diameters D = 40∼60 nm and D < 20 nm, respectively. The curves in Figures 7 and 8 give the prediction on Young's moduli of the composites reinforced by CNTs with a constant aspect ratio. The experimental data are from specimens reinforced by CNTs with aspect ratios varying in a certain range and, therefore, are not expected to follow the trend of any specific curve in Figures 7 and 8. However, the experimental data indeed fall within the curves corresponding to the predictions based on the lower and upper bounds on CNT aspect ratio.

5. CONCLUSION

In the present work, six groups of specimens—neat epoxy, 1 wt%-, 2 wt%-, 3 wt%-, 4 wt%-, and 5 wt%-MWCNT/epoxy composites—are prepared and tested. Furthermore, MWCNTs with a diameter D (i) less than 20 nm and (ii) between 40 and 60 nm are used in each of the five groups of composites. The tensile test results show that the average tensile strength of 5 wt%-MWCNT/epoxy with a diameter D < 20 nm increases 106.0%, and average Young's modulus increases 61.1%. When the same weight fraction of MWCNT with a larger diameter D = 40∼60 nm is added into epoxy, the average tensile strength of 5 wt%-MWCNT/epoxy increases 82.3%, and average Young's modulus increases 54.1%, compared with those of neat epoxy, of which the tensile strength is 25.67 MPa, and Young's modulus is 2.83 GPa. The FESEM observation shows the uniform dispersion of MWCNTs in epoxy resulting in improved mechanical properties of MWCNTs/epoxy composites. Despite the fact that it is not easy to characterize CNT aspect ratio, which are roughly estimated in our models, the experimental data indeed fall within the curves corresponding to the predictions given by Eshelby and Mori-Tanaka models based on the lower and upper bounds on CNT aspect ratio.

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