Effect of multiwalled carbon nanotube diameter on mechanical behavior and fracture toughness of epoxy nanocomposites

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Abstract

Epoxy nanocomposites reinforced by multiwalled carbon nanotubes (MWCNT) with different diameters were prepared. The effect of MWCNT diameter on mechanical and fracture properties of epoxy nanocomposites were investigated. The results show that the MWCNT diameter has an important influence on its dispersion performance. As the MWCNT diameter increases, the dispersion performance becomes better. The reinforcing effect of MWCNTs on epoxy resins (EP) is affected by the combination of factors including the diameter and the additive amount of MWCNTs as well as its dispersion. At low additive amount of MWCNTs (≤0.3 wt%), the reinforcing effect of MWCNTs with smaller diameter is better. However, as the additive amount of MWCNTs increases (≥0.5 wt%), the reinforcing effect of MWCNTs with larger diameters becomes more significant. MWCNTs with diameter of 25 nm (MWCNT-25) have the best reinforcing effect when the additive amount is 0.5 wt%, and the tensile strength and elastic modulus of the MWCNT-25/EP composites are increased by 11.5% and 8.3% than those of EP, respectively. The fracture toughness of the composites shows a tendency to increase first and then decrease with the increase of MWCNT diameter. The main reason of this tendency is that the main failure mode of MWCNTs gradually changes from fracture to pull-out with the increase of MWCNT diameter. The optimal MWCNT diameter is 25 nm, reaching the best toughening effect (KIC and GIC are increased by 38.8% and 80.9% than those of EP, respectively) at the additive amount of 0.7 wt%.

1. Introduction

Epoxy resins (EP), which have a series of excellent performance such as good mechanical properties, high adhesion and chemical stability, are widely used as adhesives, coatings and composite matrix materials [1–6]. However, due to the tight crosslinking structure, there are some shortages such as high internal stress, inherent brittleness, and poor cracking resistance limiting their further application. Therefore, improving the toughness of EP and enhancing their mechanical properties become a research hotspot in this field.

Carbon nanotubes (CNTs) are the tubes curved by graphite sheets around the central axis according to a certain degree of helicity, with a unique quasi-one-dimensional structure. In recent years, research works have shown that CNTs possess excellent thermal conductivity [7, 8], electrical conductivity [9, 10], and mechanical strength [11–14], which make CNTs one of the most potential reinforcing materials. Meanwhile, numerous research works have focused on the reinforcing and toughening effect of CNTs, but the results have shown a great disparity [15–19] and some studies even have shown an undesirable toughening effect [20, 21]. Thus it is necessary to further investigate the influencing factors of CNTs reinforcing and toughening effect.

In particular, the diameter of CNTs has a significant effect on its mechanical properties. Poncharal et al [22] reported that the modulus of MWNTs decreased sharply from 1 TPa to 0.1 TPa when the diameter of MWCNTs increased from 8 nm to 40 nm. The severe degradation in mechanical properties of CNTs could affect the failure
In this study, EP was a bisphenol A epoxy resin (WSR618) with an epoxy equivalent of 185–192 g/eq, which was provided by Bluestar Wuxi Petrochemical Co., Ltd., China. The curing agent was the mixture of modified aromatic amine (QS-1622) and modified phenolic amine (QS-1635), which were provided by Beijing Qingda-QS Materials Co., Ltd., China. The mixing ratio of QS-1622, QS-1635 and WSR618 was 1: 1: 4. Three types of MWCNTs with different diameters were supplied by Nanjing XFNANO Materials Tech Co., Ltd., China. They were all prepared by CVD method. In order to control variables, three types of MWCNTs were all not functionalized and assumed to have similar interfacial properties. Their dimensions are shown in table 1.

To investigate the effect of CNT diameter on reinforcement and toughening effect, some researchers focused on theoretical and numerical studies [27, 28]. Chen et al [27] proposed a three-level failure analysis model to study the effect of CNT diameter on toughening effect. They found that the failure mode of carbon nanotubes was changed with the decrease of CNT diameter which led to a different toughening effect. However, these studies inevitably ignore some key factors, such as the dispersibility and/or morphological characteristics of CNTs in the process of simplifying the model. Besides, most experimental works focused on the effect of CNT diameter on the reinforcing effect [29, 30], but the effect of CNT diameter on the toughening effect has not been reported. The effect of CNT diameters on the failure mode remains to be further studied. So it is necessary to further investigate the effect of CNT diameters on the toughening effect and the failure mode.

In this study, MWCNTs reinforced epoxy composites (MWCNT/EP) were prepared using three types of MWCNTs with different diameters by the same process conditions. The morphology, structure and dispersibility of MWCNTs with different diameters were analyzed. The effect of MWCNT diameter on the tensile properties and fracture toughness of MWCNT/EP composites was investigated. Then the effect of MWCNT diameters on the failure mode was studied. The main aim of this study was to provide detailed experimental data and theoretical guidance for choosing the MWCNTs with optimal diameter to achieve the best reinforcing and toughening effect.

### 2. Materials and methods

#### 2.1. Materials

In this study, EP was a bisphenol A epoxy resin (WSR618) with an epoxy equivalent of 185–192 g/eq, which was provided by Bluestar Wuxi Petrochemical Co., Ltd., China. The curing agent was the mixture of modified aromatic amine (QS-1622) and modified phenolic amine (QS-1635), which were provided by Beijing Qingda-QS Materials Co., Ltd., China. The mixing ratio of QS-1622, QS-1635 and WSR618 was 1: 1: 4. Three types of MWCNTs with different diameters were supplied by Nanjing XFNANO Materials Tech Co., Ltd., China. They were all prepared by CVD method. In order to control variables, three types of MWCNTs were all not functionalized and assumed to have similar interfacial properties. Their dimensions are shown in table 1.

| Types     | Outer diameter (nm) | Inner diameter (nm) | Length (μm) | SSA (m² g⁻¹) | Purity |
|-----------|---------------------|---------------------|-------------|--------------|--------|
| MWCNT-8   | <8                  | 2–5                 | 0.5–2       | >500         | >95%   |
| MWCNT-25  | 20–30               | 5–10                | 0.5–2       | >110         | >95%   |
| MWCNT-50  | >50                 | 5–15                | 0.5–2       | >40          | >95%   |

#### 2.2. Manufacturing process

In general, the addition of MWCNTs increases the viscosity of epoxy system, especially at high additive amount. However, the epoxy system with high viscosity is not conducive to the dispersion of MWCNTs using ultrasonication, which requires the epoxy system to be diluted using a solvent to reduce the viscosity. In this study, MWCNTs were dispersed in the epoxy matrix in two steps, in which the MWCNTs were firstly pre-dispersed in tetrahydrofuran (THF) solution and then the THF solution of dispersed MWCNTs was dispersed in the epoxy system. The specific steps for the fabrication of MWNT/EP composites were as follows:

1. Firstly, MWCNTs were dispersed in THF solution at 40 °C via a high speed mechanical stirrer (JJ-1 type). After stirring for 1 h at the speed of 1000 rpm, the THF solution of dispersed MWCNTs was obtained.
2. In order to achieve a better dispersing condition, the THF solution of dispersed MWCNTs was mixed with the epoxy matrix using ultrasonic treatment and high-speed mechanical stirring (2000 rpm) at 60 °C for 4 h.
3. The dispersed blend was degassed in vacuum for 2 h to remove air bubbles. Then the curing agent was mixed with the dispersed blend and stirred for 5 min. Finally, the blend was casted into the PTFE mold for curing. The whole schematic description of the fabrication of MWCNT/EP composites was shown in figure 1 and the compositions of MWCNT/EP composites were listed in table 2.
2.3. Characterization

For characterizing the structure of MWCNTs, the Raman spectra of MWCNTs were measured by a Renishaw (inVia) laser confocal microscopic Raman spectrometer. The wavelength of the He-Ne laser used is 532 nm, and the laser output power is 5 mV. Using a 50× objective lens to focus the laser beam on sample surface, the laser spot was 20 μm. The dispersion of MWCNTs and the fracture surfaces of the specimens were investigated by the transmission electron microscopy (TEM; JEM-2100, Japan) and the scanning electron microscopy (SEM; Hitachi S4800, Japan).

The tensile and fracture properties of the composites were tested by SANS CMT5105 electronic universal testing machine. According to ASTM D638-2010 standard, dumbbell shaped specimens were used for tensile properties test, the loading rate was 5 mm min⁻¹, and the test temperature was at room temperature. According to ASTM D 5045-99, the fracture toughness of the composite was obtained using single edge notched bend (SENB) specimens. The size of the rectangular specimen was 50 mm × 10 mm × 5 mm. The pre-crack was introduced by machining a notch firstly and then tapping a razor blade into each specimen. The loading rate was

Table 2. Composition of MWCNT/EP composites.

| Series       | Mass fraction of MWCNT (wt%) | Matrix (g) | MWCNT-8 (g) | MWCNT-25 (g) | MWCNT-50 (g) |
|--------------|-----------------------------|------------|-------------|---------------|---------------|
| EP-Reference | —                           | 100        | —           | —             | —             |
| MWCNT-8/EP   | 0.1                         | 99.9       | 0.1         | —             | —             |
|              | 0.3                         | 99.7       | 0.3         | —             | —             |
|              | 0.5                         | 99.5       | 0.5         | —             | —             |
|              | 0.7                         | 99.3       | 0.7         | —             | —             |
| MWCNT-25/EP  | 0.1                         | 99.9       | —           | 0.1           | —             |
|              | 0.3                         | 99.7       | —           | 0.3           | —             |
|              | 0.5                         | 99.5       | —           | 0.5           | —             |
|              | 0.7                         | 99.3       | —           | 0.7           | —             |
| MWCNT-50/EP  | 0.1                         | 99.9       | —           | —             | 0.1           |
|              | 0.3                         | 99.7       | —           | —             | 0.3           |
|              | 0.5                         | 99.5       | —           | —             | 0.5           |
|              | 0.7                         | 99.3       | —           | —             | 0.7           |
1 mm min$^{-1}$, and the test temperature was at room temperature. In order to ensure the repeatability and accuracy of the data, at least five samples were tested for each category.

The fracture toughness ($K_{IC}$) and the critical energy release rate ($G_{IC}$) were calculated by the following formula [31]:

\[ K_{IC} = G \cdot \frac{P_0 S}{4BW^{3/2}} \]  

\[ G_{IC} = \frac{(1 - \nu^2)}{E} K_{IC} \]  

where, $G$ is the crack shape factor, $S$ represents the support span of the three-point bend, $B$ is the specimen thickness, $W$ represents the specimen width, and $E$ is the elastic modulus. The Poisson's ratio of the materials studied was 0.35 [32].

3. Results and discussion

3.1. Morphology and structure of MWCNTs

Figure 2 shows the Raman spectra of MWCNT-8, MWCNT-25 and MWCNT-50. It can be seen from the spectra that the defect mode (D band) and the tangential mode (G band) of MWCNTs with different diameters are found at 1337 cm$^{-1}$ and 1569 cm$^{-1}$, respectively. The ratio of the integrated intensity of D band ($I_D$) to the integrated intensity of G band ($I_G$) can be used to characterize the defect density of MWCNTs. The larger the $I_D/I_G$ value, the greater the defect density [33]. By quantitative analysis, the $I_D/I_G$ values of MWCNT-8, MWCNT-25 and MWCNT-50 are 1.04, 0.8 and 0.61 respectively, which indicates that MWCNT-8 has the highest defect density, followed by MWCNT-25 and MWCNT-50.

The SEM and TEM photographs of MWCNT-8, MWCNT-25 and MWCNT-50 are shown in figure 3. To ensure the accuracy of the experiment, the mean value of all sample diameter is measured. As shown in figures 3(a) and (b), the mean value of MWCNT-8 diameter is 10 nm. And the mean value of MWCNT-25 diameter is 25 nm (figures 3(c) and (d)). MWCNT-50 possess the largest diameter which is around 50 nm (figures 3(e) and (f)). Meanwhile, it also can be found from the spectra (figure 2) that the relative intensities of G modes of MWCNT-8, MWCNT-25 and MWCNT-50 are 38.98, 65.05 and 124.25 respectively, indicating that the intensity of G band has evident positive correlation with the diameter of MWCNTs. This phenomenon is identical with the literature by Jorio [34].

3.2. Effect of MWCNT diameter on the dispersibility

To reduce the viscosity of the epoxy system, MWCNTs are firstly pre-dispersed in THF solution. Figure 4 shows the TEM images of the dispersion of MWCNT-8, MWCNT-25 and MWCNT-50 in THF. It can be seen from figure 4(a) that MWCNT-8s exhibit a curved shape and generate a large amount of entanglements in THF solution. A small amount of entanglements can also be observed in the THF solution of MWCNT-25 (figure 4(b)). Compared with the entanglement of MWCNT-8s and MWCNT-25s, many individual MWCNT-50s are observed in figure 4(c). So, it shows that MWCNTs with smaller diameters are more prone to hold...
together in entanglements. This phenomenon is mainly due to their large SSA, which results in strong Van der Waals forces among MWCNTs. Also, the entanglements will affect the further dispersion of MWCNTs in epoxy matrix.

Figures 5 and 6 shows the TEM and SEM images of MWCNT (MWCNT–8, MWCNT–25 and MWCNT–50) dispersed in epoxy matrix, respectively. For MWCNT–8, it can be seen from figure 5(a) that the dispersion of MWCNT–8s is not uniform in the epoxy matrix, showing a large number of entanglements and some agglomerations caused by severe entangled MWCNT–8s, as marked by the white dotted circles. Meanwhile, figure 5(b) shows that the areas near entangled MWCNT–8s are interspersed with many gaps (the white bright spots). The main reason for the formation of gaps is that the original severe entangled MWCNTs are pulled and deformed under the shear force during the process of ultra-microtome cutting. Moreover, the severe entangled MWCNT–8 may lead to the decrease of the interface area between the MWCNT–8 and the epoxy matrix. From the low magnification SEM images (figures 6(a) and (b)), it is found that the dispersion condition of MWCNTs become worse with the increase of the additive amount. Figure 6(a) shows many individual MWCNT–8s (indicated by arrows), indicating a relatively well dispersion condition achieved at low additive amount (0.3 wt%). However, the dispersion of MWCNT–8s becomes worse and numerous agglomerations (indicated by arrows, with the size less than 1 μm) are observed at high additive amount (0.7 wt%) as shown in figure 6(b).
Figure 4. TEM images of achieved state of dispersion in THF for: (a) MWCNT-8; (b) MWCNT-20; (c) MWCNT-50.

Figure 5. TEM images of the dispersion of MWCNT in epoxy matrix: (a) is the TEM image of MWCNT-8/EP composites at 0.7 wt%; (b) is the magnification of (a); (c) and (d) are the TEM images of MWCNT-25/EP and MWCNT-50/EP composites, respectively, at 0.7 wt%.
Compared with MWCNT-8s, MWCNT-25s show a more uniform dispersion except a small amount of entanglements (indicated by the white dotted circles in figure 5(c)). As shown in figure 6(c) (the low magnification SEM image), agglomerations are observed at high additive amount (0.7 wt%), indicated by a white rectangle. However, the high magnification SEM image (figure 6(d)) shows that most MWCNT-25s are still separated and disperse uniformly within the agglomeration, indicating a favorable dispersion condition. This indicates that MWCNT-25 has good dispersion performance in epoxy matrix.

From figure 5(d), it can be seen that MWCNT-50s are uniformly distributed in epoxy matrix and MWCNT-50s do not entangle with each other. Compared with the agglomeration of MWCNT-8s (figure 6(b)) and MWCNT-25s (figure 6(c)), MWCNT-50s show the most uniform dispersion condition with individual MWCNTs as shown in figure 6(e) (indicated by arrows).

### 3.3. Tensile properties

Figure 7 shows the stress–strain curves, tensile strength, elastic modulus and elongation at break of materials in table 2. Compared with the pure epoxy resin (EP), the tensile strength, elastic modulus and elongation at break of MWCNT/EP composites are improved. In particular, the improvement of tensile strength, elastic modulus
and elongation at break is more remarkable when the additive amount of MWCNTs is more than 0.1 wt%.
Meanwhile, the reinforcing effect of MWCNTs on EP depends on the diameter of MWCNTs and the additive
amount of MWCNTs. This means that the reinforcing effect is affected by the combined effect of factors
including the diameter of MWCNTs, the amount of MWCNTs and their dispersion in epoxy matrix. For
example, when the additive amount of MWCNTs is low (≤ 0.3 wt%), the reinforcing effect of MWCNTs with
smaller diameter is better. However, as the additive amount of MWCNTs increases (≥0.5 wt%), the reinforcing
effect of MWCNTs with larger diameter is more significant.

When the additive amount of MWCNTs is less than 0.3 wt%, MWCNT/EP composites exhibit that the
smaller the diameter of MWCNTs, the higher the tensile strength and elastic modulus of MWCNT/EP as shown
in figures 7b and c. Thus MWCNT-8/EP composites show the highest tensile strength and elastic modulus. For
example, when the additive amount is 0.3 wt%, the tensile strength and elastic modulus of MWCNT-8/EP
composites increase by 5.0% and 7.8% respectively, compared with EP. At the low additive amount, the SSA of
MWCNTs is fully utilized due to the favorable dispersion condition with individual MWCNTs (figure 6(a)) and
thereby the MWCNTs with the smaller diameter would obtain a larger effective interface area. For MWCNT-8,
although it has the highest defect density which may weaken its reinforcing effect, it still possesses the larger
effective interface area which contributes to improving the stress transfer efficiency. Therefore, MWCNT-8/EP
has the best tensile properties when the additive amount of MWCNTs is low (≤ 0.3 wt%).

However, as the additive amount of MWCNTs increases to 0.5 wt%, the reinforcing effect of the three types
of MWCNTs is all improved compared with that of the low additive amount (≤ 0.3 wt%), but the reinforcing
effect of MWCNTs with different diameters is different. With the increase of additive amount, the reinforcing
effect of MWCNT-8s becomes weak (figures 7(b), (c)). This is because that MWCNT-8s exhibit a relatively poor
dispersion and the entangled MWCNT-8s reduce the effective interface areas. But MWCNT-25s and MWCNT-
50s have good reinforcing effects because they can be still well dispersed in epoxy matrix. Meanwhile, since the
MWCNT-25s have better reinforcing effect than MWCNT-50s, it is reasonable to assume a more prominent
role of the MWCNTs with smaller diameter when dispersed well. For example, MWCNT-25s reach the best
reinforcing effect, enhancing the tensile strength of MWCNT-25/EP to 67.9 MPa and the elastic modulus to
3110 MPa (increased by 11.5% and 8.3% than EP, respectively). Furthermore, it can be seen from figure 7(a) that
MWCNT-25/EP composites show the highest elongation at break, resulting in the largest area under the stress-
strain curve, which reflects that the composites can dissipate much more energy in the fracture process.
At high additive amount (0.7 wt%), the further agglomeration of MWCNT-8s as shown in figures 5(a) and (b) makes MWCNT-8/EP composites failure early and decrease the elongation at break drastically compared with MWCNT-25/EP and MWCNT-50/EP composites (figure 7(d)), which weakens the reinforcing effect seriously (figures 7(b) and (c)). Meanwhile, MWCNT-25s also have an undesirable reinforcing effect due to some agglomerations (figure 6(d)). By contrast, MWCNT-50s show the better reinforcing effect (figures 7(b) and (c)) owing to its good dispersibility (figures 5(d) and 6(e)), which makes the tensile strength and the elastic modulus of composites increase by 11.0% and 8.9% than EP, respectively.

According to the Halpin-Tsai equation [35], the elastic modulus of MWCNT/EP composites with different MWCNT diameters can be predicted. In the prediction model, it is assumed that MWCNTs are uniformly dispersed with random orientation, and impregnate well with matrix. Then the equations for calculating the modulus of MWCNT/EP composites is given below.

\[
E_C = \left[ \frac{3}{8} \left( \frac{l_{\text{MWCNT}}}{d_{\text{MWCNT}}} \right)^2 \frac{1 - \eta_L V_{\text{MWCNT}}}{\eta_L} + \frac{5}{8} \left( \frac{l_{\text{MWCNT}}}{d_{\text{MWCNT}}} \right)^2 \frac{1 - \eta_T V_{\text{MWCNT}}}{\eta_T} \right] E_M
\]

(3)

\[
\eta_L = \frac{(E_{\text{MWCNT}}/E_M) - 1}{(E_{\text{MWCNT}}/E_M) + 2(l_{\text{MWCNT}}/d_{\text{MWCNT}})}
\]

(4)

\[
\eta_T = \frac{(E_{\text{MWCNT}}/E_M) - 1}{(E_{\text{MWCNT}}/E_M) + 2}
\]

(5)

Where, \(E_C\), \(E_M\) and \(E_{\text{MWCNT}}\) represent the elastic modulus of the composite, the matrix and the MWCNTs in GPa, respectively. \(l_{\text{MWCNT}}\) and \(d_{\text{MWCNT}}\) represent the length and the diameter of the MWCNTs, respectively. \(V_{\text{MWCNT}}\) is the volume fraction of the MWCNTs.

For the analysis, it is assumed that the three types of the MWCNTs have diameters of 10 nm, 25 nm and 50 nm respectively, and their lengths are assumed to be 0.5 μm (from microscopy, figure 3). The elastic modulus of the MWCNTs and the epoxy matrix is 1TPa [36], and 2.9 GPa (from the tensile test data in this paper), respectively.

Figure 8 shows that the predicted elastic modulus of MWCNT/EP is dependent on the diameter of the MWCNTs, especially at the high additive amount, indicating that the smaller diameter MWCNTs has more potential to enhance the elastic modulus. Meanwhile, it is found that the predicted values first fits well with the experimental values (the maximum deviation is less than 4.6%) when the MWCNTs content is low (0.1 ~ 0.3 wt%). However, the deviation between predicted values and experimental values increases with the increase of the additive amount, especially for the smaller diameter MWCNTs. For example, MWCNT-8s show a poor fitting (the deviation is higher than 11%) when the additive amount is more than 0.5 wt%. The main reason of the poor fitting is considered to be the poor dispersion condition of MWCNT-8s at high additive amount, as shown in figure 5(b) and 6(b).
Figure 9 shows the KIC and GIC test results for the samples in Table 2. The KIC and GIC of pure epoxy is 3.4 MPa m$^{1/2}$ and 0.157 KJ m$^{-2}$, respectively. After adding MWCNTs, the KIC and GIC of MWCNT/EP are bigger than those of EP, and both of them increase with additive amount of MWCNTs. But the toughening effects of three different types of MWCNTs are different, in which MWCNT-25 shows the best toughening effect.

The KIC and GIC of MWCNT-8/EP composites increase slowly with the addition amount of MWCNT-8s, reaching the maximum values at 0.7 wt% (0.81 MPa m$^{1/2}$ and 0.217 KJ m$^{-2}$), which are increased by 20.9% and 38.2% than those of EP, respectively. By contrast, MWCNT-25 and MWCNT-50 exhibit the better reinforcing effects, and the KIC and GIC of the MWCNT-25/EP and MWCNT-50/EP composites with only a small additive amount of MWCNT-25s and MWCNT-50s (0.3 wt%) can reach the same value as the maximum values of MWCNT-8/EP at the high additive amount of MWCNT-8s (0.7 wt%). This means that MWCNT-8s with the smallest diameter do not exhibit the best toughening effect due to the largest SSA (larger than 500 m$^2$ g$^{-1}$). This phenomenon can be explained from two aspects: (a) MWCNT-8s are easy to entangle with each other (Figure 9 (a)), leading to the reduction of effective interface areas, and thus exhibit an undesirable toughening effect. (b) Because of the smaller values of KIC and GIC of MWCNT-8/EP than those of MWCNT-25/EP and MWCNT-50/EP as shown in Figure 9, it is implied that MWCNT-8s have a different failure mode from MWCNT-25s and MWCNT-50s, which leads to the undesirable toughening effect. The further discussion on this is explained as the following part of 3.6.

The KIC and GIC of MWCNT-25/EP composites show the same increase tendency as MWCNT-50/EP composites, but the toughening effect is more excellent. For example, MWCNT-25/EP composites achieve the best toughening effect when the additive amount is 0.7 wt%, enhancing the KIC and GIC of pure epoxy resin to 0.93 MPa m$^{1/2}$ (+38.8%) and 0.284 KJ m$^{-2}$ (+80.9%), respectively. Compared with MWCNT-50, it is found that the smaller diameter MWCNTs (MWCNT-25) improve the fracture toughness more effectively, because the smaller diameter MWCNTs have a larger SSA, which provides a larger interface areas and contributes to the energy dissipation during the fracture process.

For MWCNT-50/EP composites, the KIC and GIC increase with the addition amount of MWCNT-50s. When the additive amount is 0.1 wt%, the KIC and GIC of the composites are increased by 6% and 8.9% than EP. As the additive amount increases to 0.3 wt%, the KIC and GIC are further increased by 11.3% and 22.8%, respectively. However, the increase tendency of KIC and GIC becomes slow when the additive amount changes from 0.5 wt% to 0.7 wt%.

3.5. Fractography
The fracture surface micrograph of SENB samples of MWCNT-8/EP composites is shown in Figure 10. A large amount of plastic deformation accompanied by shear band (indicated by arrows) is found around the agglomeration (about 1 μm in diameter). The plastic deformation of the matrix and the generation of shear bands can dissipate more energy, contributing to the enhancement of fracture toughness. These make the fracture toughness of MWCNT-8/EP composites does not decrease due to the further agglomeration but still increase slightly when the additive amount changes from 0.5 wt% to 0.7 wt%.

Figure 11 shows the fracture surface micrographs of SENB samples of MWCNT-8/EP, MWCNT-25/EP and MWCNT-50/EP composites, respectively. As shown in Figure 11 (a), a large number of MWCNT-8s with short head shape (indicated by arrows) are distributed symmetrically on both sides of the crack tip (about 0.2 μm in width). According to the micrograph of the crack initiation region as shown in Figure 11 (a’), it can be seen more clearly that the fractured MWCNT-8s are in short head shape. This phenomenon indicates that the load-bearing
capacity of MWCNT-8s is less than the load-bearing capacity of the interface between MWCNT-8 and matrix when the crack tip is extended to the MWCNT-8s, resulting in the fracture of MWCNT-8s. Therefore, it is implied that the main failure mode of MWCNT-8s is the fracture of MWCNTs, and the improvement in fracture toughness of MWCNT-8/EP composites is mainly attributed to the fracture energy dissipation by the fractured MWCNTs.

As is shown in figure 11(b), the crack (also about 0.2 μm in width) is bridged by plenty of MWCNT-25s (shown by black arrows) and some of MWCNT-25s have been pulled out from the matrix (indicated by white arrows). Moreover, by comparing figure 11(a)' and figure 11(b)', it can be found that the length of the MWCNT-25s pulled out from the matrix (about 0.3 μm) is much larger than the length of the fractured MWCNT-8s (about 0.06 μm). Thus it indicates that MWCNT-25s can first bridge the crack and then are pulled out due to the early failure of the interface between MWCNT-25 and matrix. The main failure mode of MWCNT-25s is the pull-out from matrix. So, in the pull-out process of MWCNTs, the sum of the friction energy dissipation of the MWCNTs with the matrix and the energy dissipation caused by the plastic deformation of the matrix can improve the fracture toughness greatly. Meanwhile, it can be seen from figures 11(c) and 11(c)' that MWCNT-50s have the similar morphology, such as crack bridge of MWCNTs and the pull-out of MWCNTs, so the main failure mode of MWCNT-50s is also the pull-out of MWCNTs from matrix.

From the above analysis on fracture morphologies, it is obvious that with the increase of the MWCNT diameter, the main failure mode of MWCNTs gradually changes from the fracture of MWCNTs to the pull-out of MWCNTs, leading to a significant increase in the toughening effect (figure 9). Based on the theoretical study of Yuli Chen [28], the load-bearing capacity of the fiber and the interface are both positively related to the fiber diameter under tensile stress. However the load-bearing capacity of the fiber changes faster with the fiber diameter. Therefore, when the fiber diameter is small enough, the failure mode turns to be fiber fracture due to the lower load-bearing capacity of the fiber than that of the interface. Furthermore, it is found in this paper that the transition of the failure mode is also closely related to the structure and the morphological characteristics of MWCNTs. On the one hand, the MWCNTs with small diameter (MWCNT-8s) are easier to entangle with each other (figure 4(a)). So the entanglements may hinder the pull-out of individual MWCNTs, and then MWCNTs may be fractured in weak regions due to the stress concentration. On the other hand, because MWCNT-8s have a high defect density ($I_D/I_G$) according to the Raman spectra (figure 2) and the defects on MWCNTs can significantly decrease the mechanical properties of MWCNTs [37], so this will cause the much lower actual load-bearing capacity of MWCNT-8s than its theoretical load-bearing capacity. Thus the fracture failure of MWCNT-8s precedes the interface failure between MWCNT-8 and the epoxy matrix.

4. Conclusions

(1) The method of high speed mechanical stirring combined with ultrasonic treatment was adopted to disperse MWCNTs in epoxy matrix. The diameter of MWCNTs has important influence on its dispersion performance. The dispersion performance of MWCNTs was improved with the increase of MWCNT diameter. MWCNT-50 had the best dispersibility, followed by MWCNT-25 and MWCNT-8.
The mechanical properties of MWCNT/EP composites were improved by adding a small amount of MWCNTs (maximum additive amount of 0.7 wt%). The reinforcing effect of MWCNTs on EP is affected by the combination of factors including the diameter of MWCNTs, the additive amount of MWCNTs and its dispersion. At low additive amount of MWCNTs (<0.3 wt%), the reinforcing effect of MWCNTs with smaller diameter is more obvious. However, as the additive amount of MWCNTs increases (>0.5 wt%), the reinforcing effect of MWCNTs with larger diameter is more significant. In particular, MWCNT-25 reached the best reinforcing effect with the great increase in tensile strength and elastic modulus of MWCNT-25/EP composites when the additive amount was 0.5 wt%, which was increased by 11.5% and 8.3% than those of EP, respectively.

Based on the Halpin-Tsai equation, the elastic modulus of MWCNT/EP composites was predicted. By comparing the experimental and predicted values, it shows the Halpin-Tsai equation predicted results are relatively accurate and the maximum deviation is less than 4.6% in the case that the dispersion condition of MWCNTs was well in epoxy matrix at the low additive amount of MWCNTs (0.1 ~ 0.3 wt%).

Figure 11. SEM micrographs of surface crack of SENB specimens. Figures (a), (b) and (c) are the crack tip profile of MWCNT-8/EP, MWCNT-25/EP and MWCNT-50/EP composites, while figures (a’), (b’) and (c’) are near the crack initiation region of MWCNT-8/EP, MWCNT-25/EP and MWCNT-50/EP composites.
(4) The fracture toughness of MWCNT/EP composites increased first and then decreased with the increase of MWCNT diameter. The main reason for this trend is attributed to the transition of the main failure mode of MWCNTs from fracture to pull-out, which is closely related to the structure and the morphological characteristics of MWCNTs. The optimal MWCNT diameter was 25 nm (MWCNT-25), reaching the best toughening effect ($K_{IC}$ and $G_{IC}$ were increased by 38.8% and 80.9% than those of EP, respectively) at the additive amount of 0.7 wt%.

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