Pseudoreinforcement Effect of Multiwalled Carbon Nanotubes in Epoxy Matrix Composites

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ABSTRACT: The carbon nanotube possesses outstanding physical properties. Theoretically, adding carbon nanotubes into a polymer matrix can remarkably improve the mechanical properties of the polymer matrix. In the present work, a series of composites was prepared by incorporating multiwalled carbon nanotubes (MWNTs) into an epoxy resin. The influences of MWNT content and curing temperature on the flexural properties of the epoxy resin were investigated. The results showed that a very low MWNT content should be used to ensure homogeneous dispersion of MWNTs in the epoxy matrix. A higher MWNT content may lead to deteriorated mechanical properties of the composites because of the aggregation of MWNTs. A decline in the flexural properties of the neat epoxy resin with increasing curing temperature was found. However, under the same curing conditions, improvement in flexural properties was observed for the composite with the low MWNT content and a mild curing temperature. The improvement was far beyond the predictions of the traditional short-fiber composite theory. In fact, this improvement should be attributed to the retarding effect of MWNTs on the curing reaction of epoxy matrix. Therefore, the improvement in the flexural properties was only a pseudoreinforcement effect, not a nano-reinforcement effect of the MWNTs on the epoxy resin. Perhaps, it is better for MWNTs to be used as functional fillers, such as electrical or thermal conductive fillers, than as reinforcements. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3664–3672, 2006

Key words: nanocomposites; curing of polymers; mechanical properties; reinforcement

INTRODUCTION

The carbon nanotube (CNT) has a one-dimension tubular structure with a nanometer-scale diameter and a molecular form of carbon that is quite different from graphite and diamond.[1] Theoretically, CNT has several unique physical properties, especially mechanical and electrical properties. Therefore, it possesses a wide range of potential applications, for example, as reinforcement in the construction of supercomposite materials or as conductive filler in the manufacture of functional composite materials.

Several studies have sought to verify the reinforcement effect of CNT on the mechanical properties of polymer matrices.[2–14] Generally, these studies found that the moduli of the CNT/polymer composites were slightly improved by adding CNT into many different types of polymer matrices, but there were conflicting results about improvement in strength. For example, Allaoui et al.[11] reported that considerable improvement in yield strength can be achieved when 0.5–4 wt % MWNTs were incorporated into a rubbery epoxy resin. However, Lau et al.[12] reported a remarkable decrease in flexural strength of an epoxy matrix composite containing 2 wt % MWNTs. These uncertain conclusions about the reinforcement effect of CNT on the mechanical properties of the composites reflected the complexity of the interaction between CNT and polymer matrices. The understanding of this complexity remains inadequate. Therefore, further study of a variety of CNT–polymer systems is necessary.

Good dispersion of CNT was the basic goal in order to maximize the nanoscale effect of CNT on properties of the composites. Because of the fine size and high surface energy of CNT, the as-received CNT was apt to aggregate and entangle together spontaneously. In a CNT/polymer composite, aggregation of CNT may become a defect and cause the mechanical properties of the composite to deteriorate. Therefore, the primary problem in fabricating a nanocomposite is to ensure homogeneous dispersion of CNT in the polymer matrix. By far, only ultrasonic and high-speed mechanical stirring have been verified to be effective methods for the dispersion of CNT. These methods are more appropriate for thermosetting polymer matrices than thermoplastic ones because of their different manufacturing processes. It was found to be essential to ensure good dispersion of CNT that the CNT content be very low, usually less than 1 wt %.
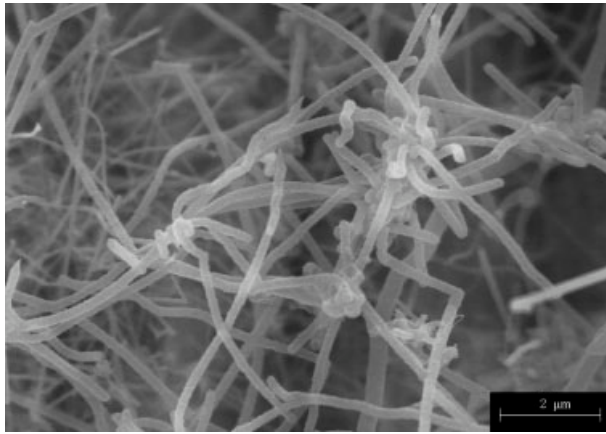
Figure 1 SEM micrograph of as-received MWNTs.

Epoxy resin is an important matrix for high-performance composites. It has perfect adhesive strength with most common materials. In particular, its properties can be easily varied by altering the content or type of hardener or the curing temperature and curing schedule. Several studies have investigated CNT/epoxy composites,[9–13] but none has looked at the effect of the curing process on the mechanical properties of CNT/epoxy composites.

In the present study, a low-viscosity epoxy system was used for cast molding. First, a series of composites with different CNT contents was prepared, and then the mechanical properties of these composites were analyzed. Then another series of composites containing 0.1 wt % CNT was prepared at different curing temperatures, ranging from 80°C to 180°C, with the aim of altering the properties of the epoxy matrix and interface bonding. By comparing the mechanical properties of the composites and neat epoxy resin cured at different temperatures, it was possible to gain a deeper understanding of the influence of CNT on the performance of epoxy matrix.

EXPERIMENTAL

A commercially available grade of novolac epoxy resin (F-51) was used as the matrix, methyl hexahydrophthalic anhydride (MHHPA) was used as the hardener, and 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) was used as the accelerator. The formulation used in this work was 100 parts F-51, 80 parts MHHPA, and 1 part DMP-30 by weight. Catalytically grown multi-walled carbon nanotubes (MWNTs) were kindly provided by the Shenyang Gina New Materials Company. The mean length of the as-received MWNTs was 20 μm, and the mean diameter was 80 nm (Fig. 1). These MWNTs were used directly without any purification.

Following is a description of the process of fabricating the MWNT/epoxy composites.

1. The MWNTs were dispersed in about 30 mL of acetone in a sealed beaker by an ultrasonic process for 10 min. In this step, the MWNT agglomerates obviously were crushed and dispersed, but they could not be suspended stably in the acetone.
2. The mixture of MWNTs and acetone was poured into the prepared mixture of F-51 epoxy and MHHPA and then processed 2 h in an ultrasonic bath in order to disperse the MWNTs into the epoxy resin mixture. Because of a local rise in temperature, the epoxy resin closer to the source of the ultrasonic bath may be cured in an untimely manner. Therefore, mechanical stirring at about 100 rpm was performed along with the ultrasonic process (Fig. 2). The additional gain of performing this additional step is that the mechanical stirring was able to disperse the larger-size MWNT agglomerates, which was difficult to achieve solely with the ultrasonic bath. After this step, the mixture had an average temperature of about 60°C–70°C and possessed lower viscosity. For the epoxy system of F-51 and MHHPA, this temperature range would not cause in gelation and curing prior to adding the accelerator.
3. DMP-30 was added to the mixture as an accelerator. The mixture was then mechanically stirred at about 1000 rpm for 10 min.
4. The prepared mixture was poured into a mold, degassed in a vacuum oven at 80°C for 30 min, and then heated according to the specified curing schedule.

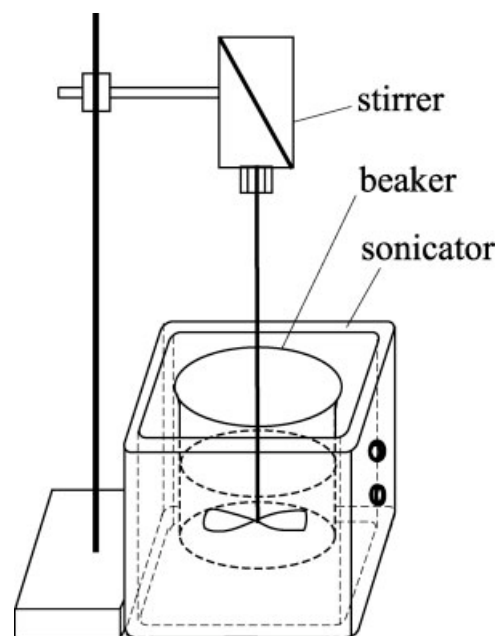Two series of specimens were prepared according to the above fabrication process. One series was

Figure 2 Schematic drawing of dispersion process of MWNTs in epoxy.

TABLE I
Different Curing Conditions for Neat Epoxy and MWNT/Epoxy Composites

No.	Cure process
1	24 h at 80°C
2	3 h at 80°C + 24 h at 100°C
3	3 h at 80°C + 24 h at 120°C
4	3 h at 80°C + 3 h at 120°C + 3 h at 150°C
5	3 h at 80°C + 3 h at 120°C + 3 h at 150°C + 3 h at 180°C

composed of composite specimens in which the MWNT content was varied (0.05%, 0.075%, 0.1%, 0.3%, 0.5%, or 1.0% fraction by weight). These composites were prepared by the same dispersion and compounding procedures and then cured according to the same curing cycle (3 h at 80°C followed by 2 h at 120°C). The composite specimens that made up the other series had the same MWNT content of 0.1 wt %, but were cured at different temperatures and for different durations according to the schedule given in Table I. For purposes of comparison, equal amounts of neat F-51 epoxy resin specimens were prepared in the same curing conditions.

The cured composite bars were ground and finished by 800# abrasive paper to final dimensions of 80 × 10 × 4 mm. Three-point bending tests were conducted according to ISO 178 on a universal testing machine at room temperature. A 2000N load cell and a crosshead speed of 2.0 mm/min were used for the bending tests. At least five samples of each type of composite were tested. The morphologies of the fractured surfaces of the specimens were observed by a JSM-6301F field emission gun scanning electron microscope.

RESULTS AND DISCUSSION

Effect of MWNT content on flexural properties of composites

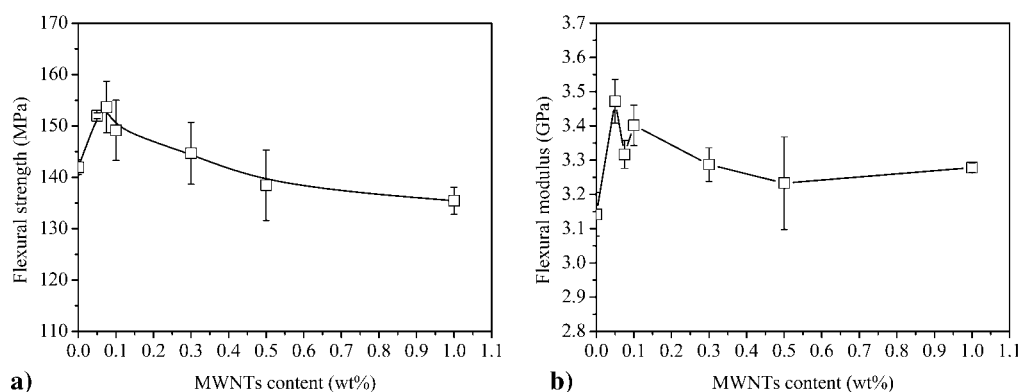The curves of the flexural properties of the MWNT/epoxy composites versus MWNT content are shown in Figure 3. It can be seen that flexural strength increased with increasing MWNT content at very low MWNT contents and then decreased [Fig. 3(a)]. The composites possessed greater strength at MWNT contents ranging from 0.05 to 0.1 wt %. The maximum strength of 154 MPa was achieved at a 0.075 wt % MWNT content, which was 9% higher than that of the neat epoxy resin of 142 MPa. Moniruzzaman et al.[13] reported increased flexural strength of SWNT/epoxy nanocomposites with the nanotubes loading until 0.05 wt % and an increase of 10% in flexural strength with 0.05 wt % nanotubes. Compared with that of traditional fiber composites, this increase in strength is somewhat small. However, given that this increase in strength was obtained by adding only 0.075 wt % MWNTs, this improvement was found very attractive. Unfortunately, flexural strength began to decrease with increasing MWNT content above 0.1 wt %. And flexural strength was even lower than that of neat epoxy resin at MWNT contents of 0.5 and 1.0 wt %.

The aggregation of the MWNTs was primarily responsible for the decrease in flexural strength at higher MWNT contents. Because of their high surface energy and large aspect ratio, MWNTs are apt to aggregate and entangle together. In addition, increasing viscosity as a result of a high nanotube content would also make it more difficult for the nanotubes to disperse in the epoxy resin.[13] In our experiments, use of a combination of ultrasonic vibration and high-speed mechanical stirring successfully dispersed the original conglomerations in the as-received MWNTs. However, because there was a period of low viscosity before the epoxy began to gelate, the MWNTs could have reaggregated after the well-dispersed mixture was poured into a mold and waiting for gelation. This procedure is more crucial to the determination of the final dispersion of the MWNTs in matrix.

The only way to keep MWNTs stably dispersed is to ensure the MWNTs separate from each other with adequate distance. This implies that MWNT content must be limited to a very low value, which means that
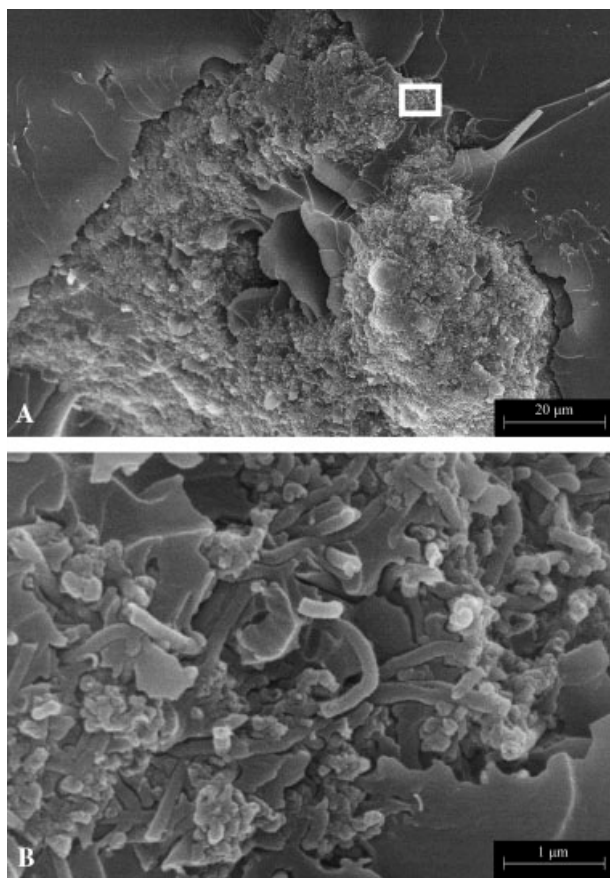

Figure 3 Flexural properties of MWNT/epoxy composites with different MWNT contents: (a) flexural strength, (b) flexural modulus.

Figure 4 SEM micrographs showing (a) aggregation of MWNTs as source of crack and (b) magnification of the rectangle in (a).

for some potential applications, for example, as conductive filler, MWNT content should be small if one needed to ensure the mechanical properties of the matrix not to be compromised. Allaoui et al.[11] reported that the insulator-to-conductor transition took place at 0.5 wt % for MWNT/epoxy composites using MWNTs similar to those used in the present work. Therefore, the prepared MWNT/epoxy composites in the present study can be predicted to serve as conductive functional composites accompanied by a slightly decrease rather than an increase in mechanical properties, which is the opposite of what is commonly anticipated as reinforcement. However, Sandler et al.[15] found a percolation threshold of only 0.04 wt % MWNTs with diameter of about 10 nm. This implies that a coexistence effect of reinforcement and functionality for MWNT composites can be expected when smaller-diameter MWNTs are used.

It is well known that lower performance of nanocomposites than that theoretically predicted is caused by aggregation.[16] The curved morphology of MWNTs exacerbates this problem for MWNT composites. Figure 4 shows SEM micrographs of crack source on the fractured surface of a 0.5 wt % MWNT/epoxy

composite specimen after the 3-point bending test. Aggregates with a diameter of about 100 μm could be found. The MWNTs were entangled together inside the aggregates, which hindered the wetting of epoxy to MWNTs.

Lourie and Wagner[17] applied traditional composite theory to carbon nanotube–based composites and hypothesized that stress transfer occurred between adjacent carbon nanotubes with a distance between them of less than 1–1.5 times the diameter of the carbon nanotubes. This suggested that a very high MWNT content might be acceptable in a MWNT/epoxy composite. However, from Figure 4(b), it can be seen that a high MWNT content would lead to aggregation and the MWNTs could not be wetted very well. Furthermore, aggregated MWNTs possess very different thermal properties from the matrix unlike with dispersed individual MWNTs, so bonding at the interface of the aggregation/epoxy matrix is poor (Fig. 4).

The flexural modulus values of the MWNT/epoxy composites with increasing MWNT content were scattered, as shown in Figure 3(b). However, similar to flexural strength, the composites had higher flexural moduli at very low MWNT content (less than 0.1 wt %). Above that content, the flexural moduli of the composites decreased abnormally but were still higher than that of neat epoxy resin. An improvement of 17% in flexural modulus was reported to be achieved at 0.05 wt % nanotubes in MWNT/epoxy nanocomposites[13]; however, the results with nanotube loadings above 0.05 wt % were not reported.

In summary, as shown in Figure 3, composites containing less than 0.1 wt % MWNTs exhibited higher flexural strength and modulus. We hypothesize that 0.1 wt % is the critical content for ensuring a homogeneous distribution of MWNTs in the epoxy matrix used in this study.

Effect of curing temperature on flexural properties

The results of flexural strength, flexural modulus, and deflections at break tests for neat epoxy resin and 0.1 wt % MWNT/epoxy composite specimens cured according to the different curing procedures given in Table I are shown in Figure 5.

From Figure 5, it can be seen that the flexural properties of the neat epoxy resin decreased with increasing curing temperature. This result was somewhat different from the traditional understanding for epoxy. It is well known that an increase in curing temperature can lead to higher crosslinking density and higher molecule weight and thus a higher heat distortion temperature as well as higher mechanical properties. But in our experiments, the neat epoxy resins showed higher flexural strength and moduli when cured at 80°C and 100°C but lower when cured at 150°C and 180°C. A cur-
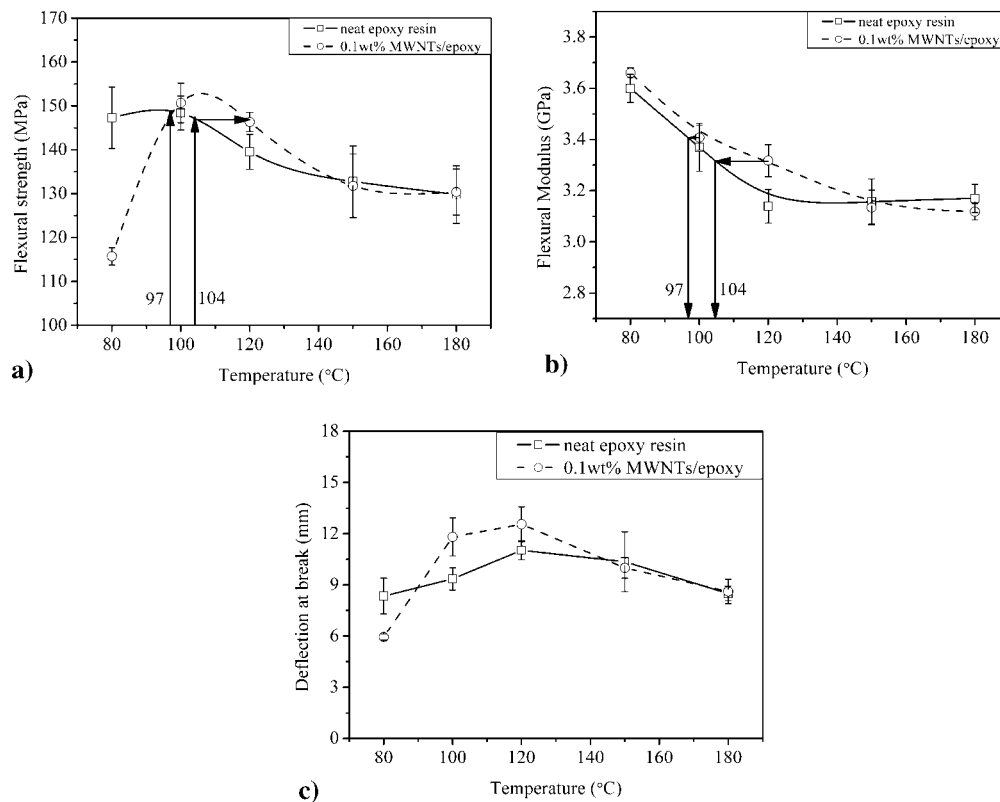
Figure 5 Flexural properties of neat epoxy and 0.1 wt % MWNT/epoxy composite cured at different curing temperatures: (a) flexural strength, (b) flexural modulus, and (c) deflection.

ing temperature of 120°C seemed to be the turning point. As for fracture deflection, a single-peak curve formed, and the maximum occurred at 120°C. This kind of variation in flexural properties with curing temperature was not reported previously. Though the reason for this is not yet clear, a possible explanation for the variation in strength may be internal thermal stress, which increases with increasing curing temperature.

Figure 5(b) shows that the flexural moduli of the neat epoxy resins decreased with increasing curing temperature until 120°C and then were slightly altered above 120°C. This stable state of the modulus at 120°C and above might be explained by the degree of maximum curing achieved under those curing conditions. But we cannot explain why the modulus decreased with increasing curing temperature. It should be emphasized that, although the neat epoxy cured at 80°C had higher strength and modulus at room temperature, its heat distortion temperature was so low that distortion occurred even in the course of grinding the specimens. Therefore, the epoxy cured at 80°C is probably not appropriate as a final application state.

According to the manufacturer, the epoxy system used in this work can cure at 80°C–100°C. To obtain a high heat distortion property, a curing temperature of 120°C –150°C was usually applied. According to our experimental results, if only mechanical properties

were considered, 120°C could be recommended as the optimal curing temperature.

When MWNTs were added into the epoxy resin, composites exhibited trends in flexural properties very similar to those of the neat epoxy resin, except for a sudden drop in flexural strength for the composite cured at 80°C. When the composites were cured at 100°C and 120°C, nominal reinforcement effects were observed, and the maximum occurred at 120°C. But when the curing temperature was increased to 150°C and 180°C, the strength of the composites was the same as that of the neat epoxy resins. It seems that the reinforcement effect of MWNTs could be revealed only when the epoxy composites were cured at 100°C–120°C.

The variations in flexural moduli for 0.1 wt % MWNT/epoxy composites generally were similar to those of the neat epoxy resin. The composite cured at 80°C exhibited maximum modulus in our experiments, which was slightly higher than that of the neat epoxy resin. The flexural moduli of the composites decreased gradually with increasing curing temperature. But compared with the neat epoxy resins, it was found that the composites had higher modulus values. It seems that the MWNTs have a significant stiffening effect at very low content. However, this stiffening effect disappeared when the composites were cured at higher temperatures, as shown in Figure 5(b).
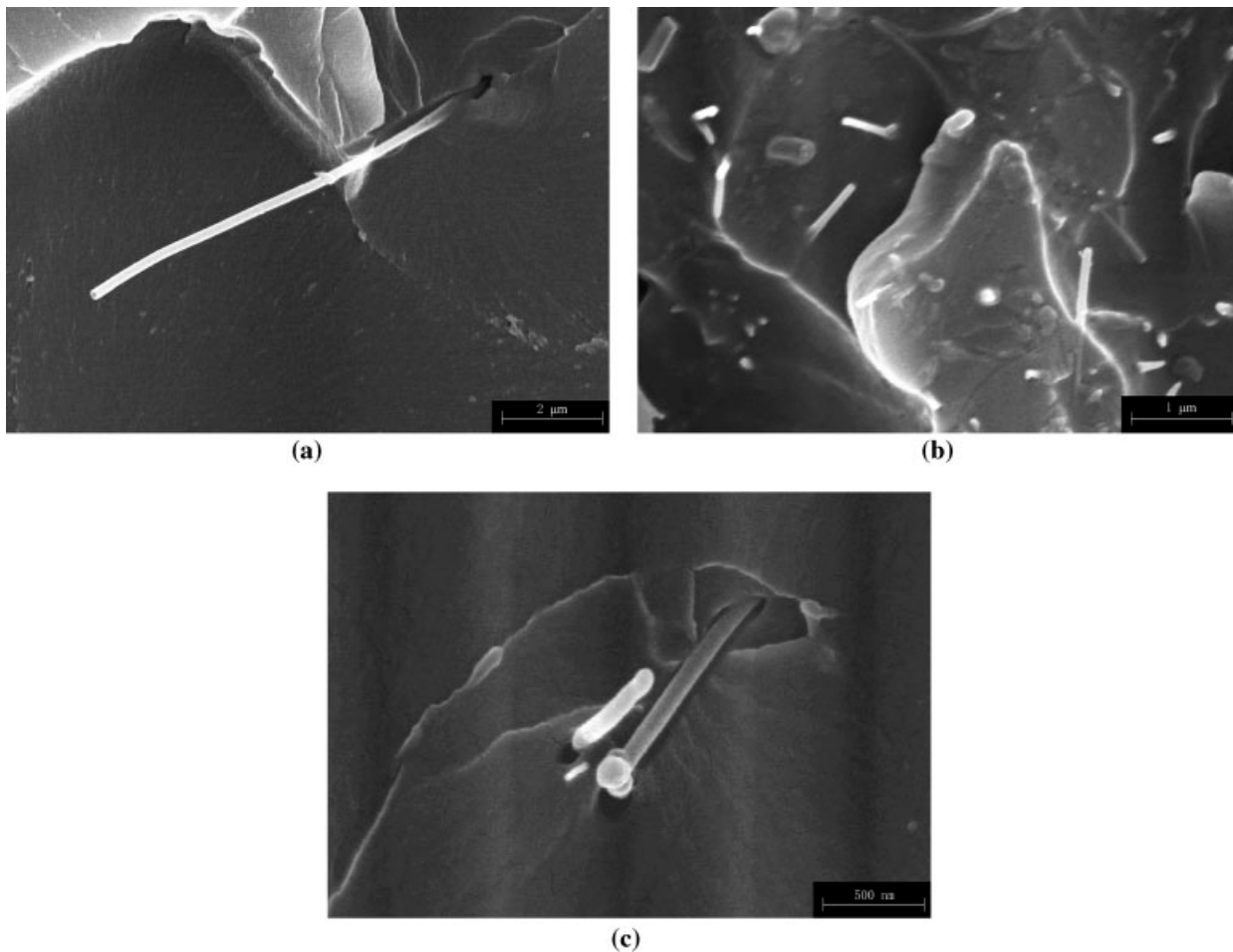
Figure 6 SEM micrographs of fracture surfaces of 0.1 wt % MWNT/epoxy composites cured at different temperatures: (a) 80°C, (b) 120°C, and (c) 180°C.

Fracture deflection can reflect the ductility of materials. Variation in fracture deflection is illustrated in Figure 5(c). When the composites were cured at temperatures below 120°C, fracture deflection increased with increasing curing temperature. But when they were cured at temperatures above 120°C, fracture deflection decreased with increasing curing temperature. The decrease in deflection when cured above 120°C can be attributed to the influence of internal thermal stress, which is a common problem in an epoxy system in which MHHPA is used as the hardener. The smaller deflections in the neat epoxy resins cured at 80°C and 100°C imply that they have higher brittleness. The 0.1 wt % MWNT/epoxy composites showed a relationship of average fracture deflection versus curing temperature similar to that of the neat epoxy resins, as shown in Figure 5(c). However, it can be seen that the composites cured at 100°C and 120°C had higher fracture deflection than did the neat epoxy resin.

The fracture surfaces of the 0.1 wt % MWNT/epoxy composites showed that bonding at the MWNT/epoxy interfaces varied with curing temperature. Figure 6a shows that the interface bonding in the composite cured at 80°C did not seem good because of the insufficient curing reaction, although a good-bonding interface can be found for the composites cured at 100°C and 120°C [Fig. 6(b)] because a sufficient curing reaction was achieved at this temperature. When the composites were cured at 150°C and 180°C, most nanotubes were observed to have bonded well with the epoxy matrix. However, some poor bonding was still observed, especially for the relatively thick nanotubes [Fig. 6(c)]. This poor bonding at higher curing temperatures might be caused by the difference in the thermal expansion coefficient between MWNT and epoxy resin. The variation in interface bonding can partially interpret the variations in flexural properties of the MWNT/epoxy composites varying with the curing temperature.

Predictions based on traditional short-fiber composite theories

The composite cured at 120°C seemed to have a reinforcement effect. To evaluate the reinforcement effect

of MWNTs on epoxy matrix, traditional composite theory was applied to predict the strengths of the composites and to compare these predictions with the experimental results.

According to the theory of short-fiber composites,[18,19] the critical aspect ratio of the fiber, $(l/d)_c$, for short-fiber-reinforced polymer composites can be calculated by

$$(l/d)_C = \frac{\sigma_f}{2\tau} \qquad (1)$$

where σ_f is the tensile strength of the fiber and τ is the interface shear strength or matrix shear strength.

If the actual aspect ratio is larger than the critical aspect ratio, the fibers will fracture at the point of composite failure. Otherwise, the fibers will be pulled out from the matrix. In this case, individual fibers with a maximum length equal to half the critical fiber length will be observed on the fractured surfaces of the composites.

Assuming that a perfect bonding exists at the MWNT/epoxy interface, the values of interface shear strength should be equal to the matrix shear strength. For the used epoxy system, the matrix shear strength is about 18 MPa. The exact strength value of as-received MWNTs is not clear. However, from literatures, the strength of MWNTs can be from 10^{20} to 150 GPa.[21] Even a lower value of 10 GPa is used, the critical length of MWNTs can be calculated from eq. (1) as 22.2 μm. This value is larger than the average length of MWNTs of 20 μm. If this is correct, most MWNTs should have been pulled out from the matrix when the composites failed. This means many MWNTs of about 10 μm in length should be observed on the fractured surfaces.

In fact, however, it was observed that the MWNTs pulled out from the matrix were all less than 2 μm in length for the composite cured at 120°C [Fig. 6(b)], indicating the actual critical fiber length of MWNTs should be less than 4 μm. On the one hand, this may have occurred because MWNTs may have been broken during processing; however, on the other hand, the critical fiber length might have been dramatically reduced as a result of friction at the point where fibers and matrix cross on the fracture surface of the composite when misaligned short fibers were pulled from the polymer matrix.[18,19] In their study of VGCF-filled rubbery epoxy and SBR nanocomposites,[14] Gauthier et al. found that after sonication the fiber length distribution was narrower and the average length was shorter, reduced from 11 to 4 μm. Therefore, eq. (1) could be employed to evaluate fiber strength, and MWNT strength was estimated to be only about 1.8 GPa, a value at least 2 orders of magnitude lower than the result of Demczyk et al.,[21] 0.15 TPa in strength and 0.9 TPa in Young's modulus. But it was approximately the same as the experiment result of

Pan et al.,[22] 1.72 GPa in strength and 0.45 TPa in modulus. This lower strength of the as-received MWNTs may be attrbuted to the structural defect on the walls of the MWNTs. Sammalkorpi et al.[23] found that the concentration of defects in the nanotubes had little effect on the Young's modulus but a stronger effect on the tensile strength. On the other hand, because of the big diameter of as-received MWNTs, it is more accurate to call them carbon nanofibers instead of carbon nanotubes. And a strength of 1.8 GPa is also consistent with the results reported by Endo et al.[24] for vapor-grown carbon fibers.

The Kelly model is widely used for short-fiber composites and was used in the present study to predict the strength of the fabricated MWNT/epoxy composites. It can be expressed as

$$\sigma_C = \eta\phi\sigma'_{NT}V_{NT} + \sigma_m(1 - V_{NT}) \qquad (2)$$

where σ_c is the composite strength, η is the orientation factor (for randomly distributed short fibers in three dimensions, $\eta = 1/5^{25}$), ϕ is the reinforcement effective factor, taking a value of about 0.85 in the present study,[26] V_{NT} is the volume fraction of MWNTs, and σ'_{NT} is the average stress of the MWNTs at composite failure. For $l > l_c$,

$$\sigma'_{NT} = \left(1 - \frac{l_C}{2l}\right)\sigma_{NT} \qquad (3)$$

where l is the effective average length of the MWNTs and l_c is the critical length.

For the 0.075 wt % (0.06 vol %) MWNT/epoxy composite, strength was calculated from eq. (2) as about 142.08 MPa, an increase of only 0.08 MPa over the epoxy resin. Therefore, theoretically, the reinforcement effect in strength of composites at low MWNT content is small and can be neglected. However, the experimental result showed an obvious improvement in strength at 0.075 wt % MWNT loadings, as shown in Figure 3(a). If the reinforcement effect of MWNTs can be neglected, what caused the improvement in strength remains unanswered.

Effect of MWNTs on cure reaction of epoxy resin

From the above discussion, it was found that the composite cured at 120°C possessed much greater strength than that predicted from the traditional composite theory. However, this reinforcement effect cannot be called a nanoeffect because the influence of MWNTs on the curing reaction of the epoxy matrix must be considered.

Representative load-deflection curves for the neat epoxy resin and the 0.1 wt % MWNT/epoxy composite cured at 120°C for 2 and 24 h are plotted in Figure 7. It can be seen that the flexural strength and modulus of
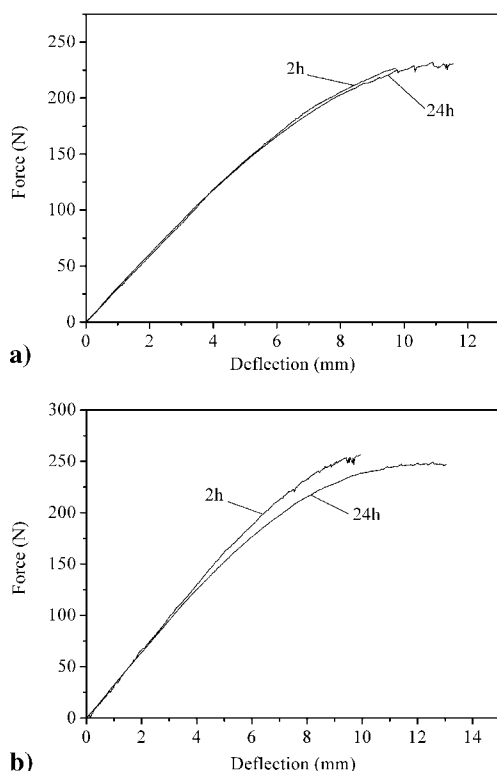
Figure 7 Load-deflection curves of (a) neat epoxy and (b) 0.1 wt % MWNT/epoxy composites cured at 120°C for 2 and 24 h.

the neat epoxy resin were almost the same when cured at 120°C for 2 or 24 h [Fig. 7(a)]. For the 0.1 wt % MWNT/epoxy composite, however, obvious differences in load-deflection curves were observed. Remarkably lower flexural strength was seen for the composite cured at 120°C for 24 h [Fig. 7(b)]. It can be seen from a comparison of the variations in flexural strength and modulus of the neat epoxy resin and its composites with increasing curing temperature, shown in Figure 5(a,b), that the variations in the mechanical properties corresponded to the increasing extent of the curing reaction. This result verifies that MWNTs can retard the crosslinking reaction of epoxy matrix. A similar result was reported by Bae et al.[27] in a study on the effects of the carbon nanotube and carbon black on the curing behavior of liquid-crystalline epoxy using differential scanning calorimetry. They reported the retarding effect of fillers on epoxy matrix, attributing this retarding effect to steric hindrance.[27]

On the basis of the experimental results, we believe the increases in strength and modulus for the 0.1 wt % MWNT/epoxy composite cured at 120°C should be attributed to the retarding effect of MWNTs on the cure reaction of the epoxy matrix. To verify this, we deduced the strength and modulus of the corresponding neat epoxy resin according to the properties of the composite. The process is illustrated by arrows in Figure 5(a,b). First, the curing temperature of the neat

epoxy resin that possessed the same modulus as the 0.1 wt % MWNT/epoxy composite cured at 120°C was determined. As shown in Figure 5(b), that temperature was 104°C. Then, as Figure 5(a) shows, the strength of the neat epoxy resin cured at 104°C was determined. By comparing that with the curve of the corresponding composite cured at 120°C, the strength of the composite could be determined. The deduced composite strength was in very good agreement with the experimental results, as shown in Figure 5(a). This suggests that for the composite cured at 120°C, the apparent improvement in mechanical properties was not evidence of a real reinforcement effect of the MWNTs but was a pseudoreinforcement effect. In fact, it reflected the retarding effect of MWNTs on the curing reaction of the epoxy matrix.

Following the same procedure, the retarding effect was also determined for the composite cured at 100°C, as shown in Figure 5(a,b). The result showed that the corresponding curing temperature of the neat epoxy was about 97°C, which means there was less retarding effect at 100°C than at 120°C. This suggests that the retarding effect of MWNTs on the curing reaction of the epoxy matrix is temperature dependent.

It is known that during the curing process of a novolac epoxy system, a stronger steric hindrance effect arises from groups and advanced cured structures. This steric hindrance effect can retard the process of the curing reaction but can be weakened by elevating the curing temperature. When adding MWNTs into epoxy matrix, the steric hindrance effect was contributed from two parts, MWNTs and the matrix itself. Therefore, three main factors greatly influenced the mechanical properties of the MWNT/epoxy composites: the steric hindrance effect of the epoxy matrix, the retarding effect of MWNTs, and the reinforcement effect of MWNTs on epoxy matrix. Both the steric hindrance effect from matrix and the retarding effect of MWNTs are relative to the curing temperature. At the same MWNT content, the difference in reinforcement effect for composites cured at different temperatures can be neglected. The less retarding effect that MWNTs had on the composite cured at 100°C should be attributed to the lower degree of curing and the larger steric hindrance effect from the matrix. At a higher curing temperature, 150°C or above, the maximum degree of cure can be achieved, and the energy is high enough to overcome the diffusion barrier from MWNTs. Therefore, both the steric hindrance effect of the matrix and the retarding effect of MWNTs vanish at high curing temperatures.

It should be noted that for the composites with different MWNT contents cured at 120°C, the mechanical properties of the epoxy matrix were different from the neat epoxy resin under the same curing temperature because of the retarding effect. In this

case, the traditional fiber composite theories are not applicable. Further investigations should be carried out at a higher curing temperature of 150°C and above to minimize the influence of the retarding effect of MWNTs.

CONCLUSIONS

A series of nanocomposites was prepared by incorporating multiwalled carbon nanotubes (MWNTs) into an epoxy resin. The influences of MWNT content and curing temperature on the flexural properties of the epoxy resin were investigated. Some conclusions can be drawn as follows.

1. To prevent MWNTs from aggregating and to ensure good dispersion of the MWNTs in the epoxy matrix, the MWNT content has to be limited to a very small amount. Therefore, it is hard to fabricate a MWNT/epoxy composite that shows remarkable improvement in mechanical properties because of the very low reinforcement loadings, based on the traditional short-fiber composite theory.
2. The mechanical properties of a novolac epoxy/MHHPA system were found to decrease with increasing curing temperature. A retarding effect of the MWNTs on curing reaction of the epoxy system was found.
3. An improvement in the flexural properties was found only when 0.05–0.1 wt % MWNTs were incorporated into the epoxy system. However, the increase in flexural properties of the composite with low MWNT content was a pseudoreinforcement effect that in fact should be attributed to the retarding effect of MWNTs on the curing reaction of the epoxy matrix. A nanoreinforcement effect of MWNTs was not found.
4. Because the mechanical properties of the MWNT composites did not improve a lot at higher MWNT contents, as anticipated, it is perhaps better for MWNTs to be used as a functional filler in functional composites, such as electrical or thermal conductive filler, but not as a reinforcement fiber.

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