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Effective separation and alignment of long entangled carbon nanotubes in epoxy

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This paper investigated the microstructural change of long entangled carbon nanotubes in an epoxy matrix under continuous shear. It was found that a critical composite viscosity is required to effectively separate the entangled nanotubes and align them along the shear direction. The major nanotube separation-alignment in composite processing is reflected by the plateaus on the viscosity variation curve. An improvement of the nanotube dispersion and composite flexural modulus was obtained in aligned MWNTs-epoxy. It was also found that the addition of MWNTs decreases the crosslinking rate of the epoxy.

1. Introduction

Carbon nanotubes have attracted considerable interest in making composite materials [1, 2]. It has been found that randomly oriented nanotube-polymer composites possess noticeable improvement of both electrical and mechanical properties [3–5]. However, the superior properties of nanotubes were not fully utilized due to their entangling nature [4–6]. It is expected that if carbon nanotubes can be well aligned and dispersed in a matrix, tailored properties of composites can be achieved.

Currently, the dispersion of entangled nanotubes is ineffective, usually by sonication in a solvent such as acetone. Fig. 1 shows an example of some multi-walled carbon nanotubes (MWNTs) sonicated in acetone over an hour. It can be seen easily that they are still highly entangled with each other. Although a prolonged sonication can separate nanotubes by breaking them into short pieces [7], it produces defects and causes thermal degradation of the nanotubes at the same time [8]. On the other hand, short nanotubes are not desirable because they cannot maximize the stress transfer ability [9] which is an important factor for making a composite of strong reinforcement.

To align carbon nanotubes in polymer matrices, some methods have been proposed, including the melt-processing [10], mechanical stretching [11], slicing [12], spin coating [13], extruding [14, 15] and magnetic field oriented processing [16]. Viscosity of matrix should have an important influence on the unentanglement of nanotube aggregates and alignment of tubes. However, this issue has not been addressed yet in previous work. Here we report an effective mechanical method to simultaneously separate and align long entangled carbon nanotubes in epoxy matrices with emphases on the effect of matrix viscosity on the microstructures of the composites using a shear flow theory.

2. Experiment

The MWNTs used in our experiment were prepared by chemical vapor deposition (provided by Nanolab) with diameters ranging from 10 to 20 nm and lengths varying from 10 to 20 μm. To properly mix them with the epoxy matrix (QC epoxide resin, Leco, USA), the nanotubes were ultrasonicated for 1 h in high purity acetone (0.1 mg/ml) and then for another hour after the addition of epoxy. The acetone was then removed by heating the mixture to 70°C while stirring, followed by evaporation under high vacuum at 50°C for 24 h. The MWNT content in all composites is 0.1% by weight.

To effectively disperse and align the MWNTs, the matrix viscosity must be sufficiently high so that high mechanical stresses can be transferred to separate and orientate the nanotubes. Hence, matrix hardener was added to the MWNTs-epoxy composite with a weight ratio of 100:25. The mixture was then placed between two parallel steel disks (40 mm in diameter) of a strain-driven rheometer. A continuous steady shear at the rate of 0.22 s^{-1} at 40°C was applied until the viscosity of the composite increased to above 6×10^4 Pa s. The composite was further cured in situ to ensure that the nanotubes remained along their aligned direction.

For comparison, a randomly distributed MWNTs-epoxy composite was prepared, following the same procedure stated above but without the application of shear. For the same purpose, the viscosity variations

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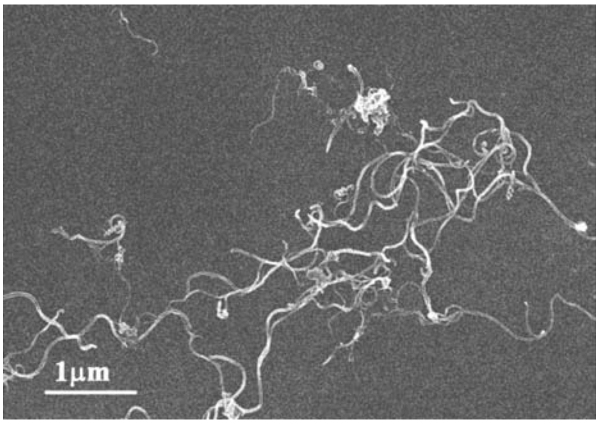

Figure 1 Entangled long MWNTs after pre-sonication of 1 h in acetone. MWNTs were deposited on a silicon wafer.

of the pure epoxy and the MWNTs-epoxy composite without hardener were also measured at room temperature using a spindle-type rheometer (Brookfield) with a cone plate (4°) of 20 mm in diameter. The dynamic mechanical spectra were obtained at the frequency of 1 Hz on a DMA 2980 Dynamic Mechanical Analyzer (TA instruments). The micro structural analysis using SEM was conducted on a FEGSEM6000 with the voltage of 15 kV. TEM specimens were microtomed into thin sections (60–100 nm) at 90° to shear direction, using a diamond knife and a Reichert-Jung Ultracut microtome at –80°C and viewed by a Philips CM12 TEM.

3. Results and discussion

3.1. Alignment and separation

Fig. 2 illustrates the expected alignment direction of the nanotubes in a composite disk after continuous shear between two steel disks. It also shows the cutting orientation of the specimens for our micro structural examination and flexural strength tests. The TEM image in Fig. 3 shows that the nanotubes were aligned in the shear direction, as expected. The orientation distribution of the MWNTs is displayed in Fig. 4, which shows that about 75% of nanotubes are aligned within ±30° along shear direction. The A-A cross-section of the specimen in Fig. 5, which is perpendicular to the nanotube alignment direction as indicated in Fig. 2, also clearly show that the nanotubes, while accurately aligned, were uniformed dispersed in the epoxy matrix. The effectiveness of alignment and dispersion of the method becomes much clearer if we compare the above with the same composite but prepared without the application of shear (Fig. 6). In the latter, the nanotubes remain random and entangled.

In making the cross-sectional view of a specimen shown in Figs 5 and 6, a fracture method was used to break it along the A-A section illustrated in Fig. 2. Even though, no nanotubes were pulled out in the

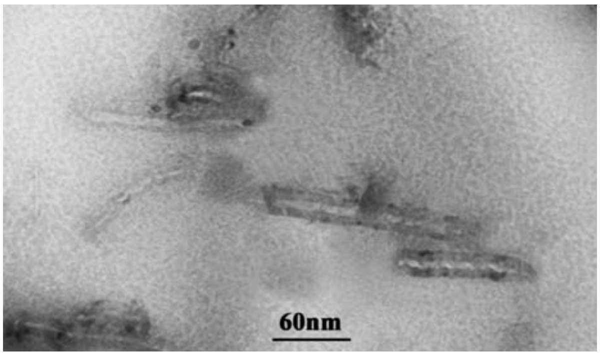

Figure 3 Nanotubes aligned in the shear direction (from left to right).

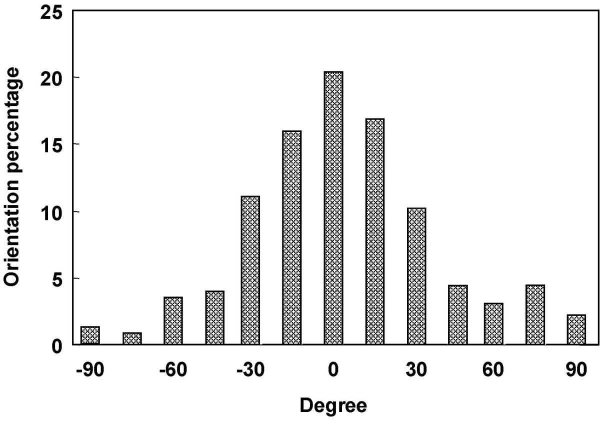

Figure 4 Orientation distribution histograms for the composite after alignment.

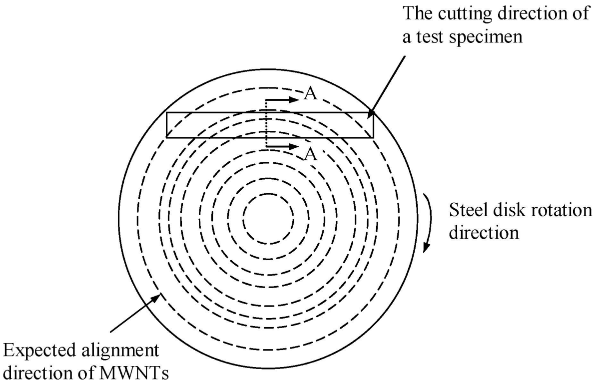

Figure 2 A schematic illustration of the expected nanotube alignment in matrix after continuous shear. The rectangle indicates the cutting location and shape of the specimen for our flexural strength tests using three-point bending, where A-A is the cross-section for observing nanotube dispersion shown in Fig. 5.

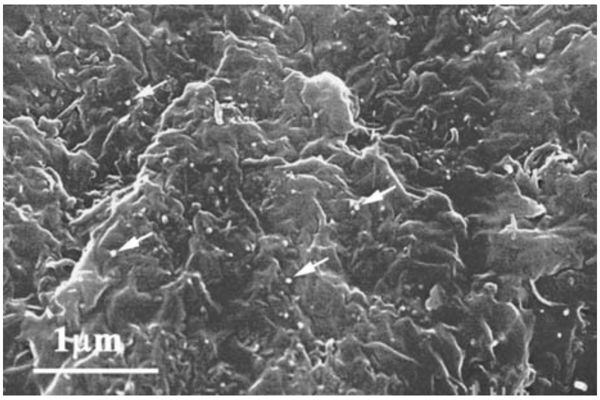

Figure 5 A cross-sectional view (at A-A in Fig. 2) of MWNTs in matrix. The cross-sections of the broken nanotubes are clearly shown (some are indicated by white arrows). Note that the nanotubes were well dispersed in the epoxy matrix and that nanotube pull-out and interfacial debonding are not seen.

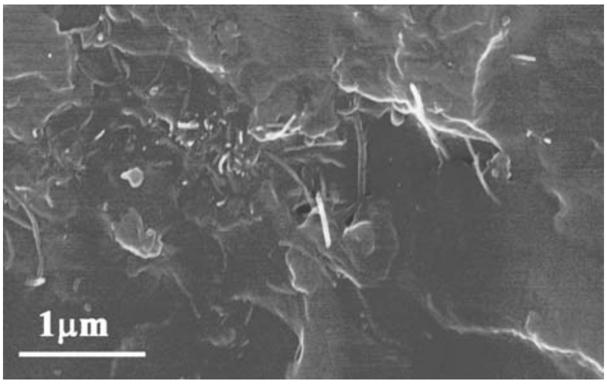

Figure 6 Randomly distributed nanotubes in the epoxy. Note that the nanotubes remain entangled.

breaking process and no interfacial debonding was seen. This seems to indicate that a strong interface bonding between the nanotubes and matrix has formed in the composites with either aligned or randomly distributed MWNTs. This is further demonstrated by our flexural strength tests (Fig. 7) which are considered sensitive to interface bonding and a weak bonding failed to offer any improvement on the bending strength [17]. Comparing with pure epoxy, both composites offer a clear increase in storage modulus (especially in the glass transition region) even with a very small quantity of nanotube addition (0.1% by weight). For instance, the moduli of aligned and random composites increase by 720 and 640%, respective, at 60°C. Glass transition temperature of aligned MWNT-epoxy increases by 13.8°C over pure epoxy and 2.1°C over random distributed MWNT counterpart, respectively. The observed T_g increases in the aligned and random composite samples were attributed to the decrease in mobility of epoxy molecular chains due to hindrance of MWNTs and bonding between nanotubes and epoxy matrix.

3.2. Effect of matrix viscosity

The process of the above nanotube separation and alignment is reflected by the viscosity changes of the MWNTs-epoxy composite. As shown in Fig. 8, the viscosity of the pure epoxy without hardener remains constant during shear. However, the viscosity of the MWNTs-epoxy composite decreases with the time of the continuous shear, a typical thixotropic behavior. This demonstrates that the contribution of nanotubes to the composite viscosity varies due to their gradual aligning and weakening of entanglement.

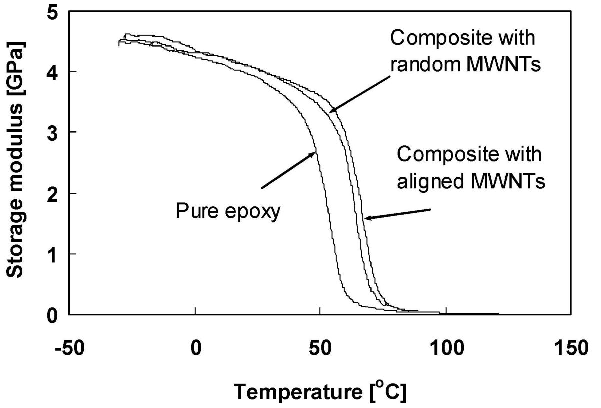

Figure 7 The dynamic mechanical spectra of storage modulii of pure epoxy and MWNTs-epoxy composites. The tests were under the three-point bending configuration.

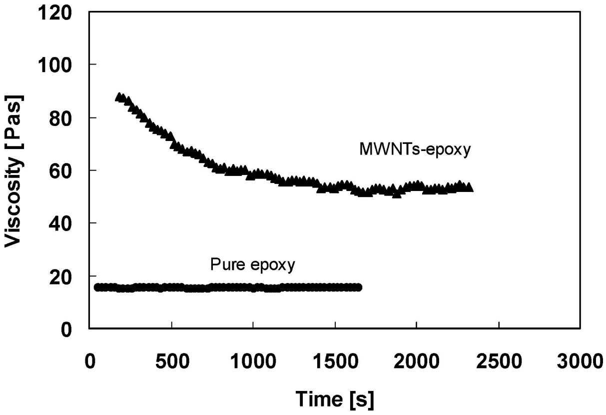

Figure 8 A comparison of viscosity variation between the pure epoxy resin and the MWNTs-epoxy composite (Shear rate = 0.1 s^{-1}).

The ability to orientate nanotubes along the shear direction can be evaluated from the Peclet number [18] of the MWNTs-epoxy composite, P_e, which is the ratio of timescale for Brownian motion to that for convection motion, i.e.,

$$P_e = \frac{\dot{\gamma}}{D_r} = \dot{\gamma}\frac{8\pi\eta a^3}{3kT(\text{In}2r_p - 0.5)} \tag{1}$$

where $\dot{\gamma}$ is the shear rate applied, η is the viscosity, D_r is the rotary Brownian diffusion coefficient, k is the Boltzman's constant, T is temperature, r_p is the aspect ratio of the nanotubes and a is the length of the nanotubes. To obtain an effective alignment of nanotubes, hydrodynamic forces by convection motion should dominate over Brownian motion, i.e., a large P_e value. Equation (1) shows that to obtain a large P_e, viscosity η must be high enough when other parameters are constants. This can be realised by adding an epoxy hardener.

Fig. 9 shows the viscosity variations of both the pure epoxy and the MWNTs-epoxy composite with

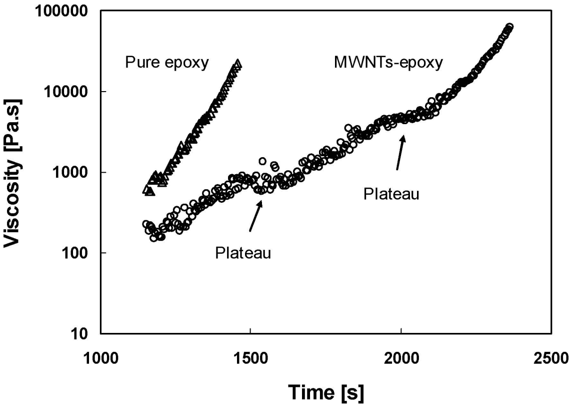

Figure 9 A comparison of viscosity variation between the pure epoxy and the MWNTs-epoxy composite with added hardener (Shear rate = 0.22 s^{-1}).

hardener. The viscosity of the pure epoxy increases quite smoothly with shear time because of the curing of epoxy by the added hardener. In the case of the MWNTs-epoxy composite with hardener, however, the viscosity variation reflects the coupled effect of matrix curing (viscosity increase) and separation-alignment of nanotubes (viscosity decrease as shown in Fig. 8). The micro structural change of the MWNTs-epoxy composite during shear can experience two stages. When the viscosity is low, the alignment and separation of the nanotubes are gradual. When the viscosity reaches a critical value, the entanglement of the MWNTs is broken down by strong shear forces from the matrix, resulting in a major separation and alignment. If this happens in a short period of time, then a viscosity decrease will dominate according to what Fig. 8 shows. We therefore believe that the two plateaus on the viscosity variation curve of the MWNTs-epoxy composite in Fig. 9 are the result of the viscosity decrease due to the nanotube separation-alignment and the viscosity increase of the matrix curing. The plateaus appeared at different stages of shear also indicate that major separation-alignment of entangled nanotubes can only occur when viscosity becomes high enough. In present case, a critical composite viscosity of 10^4 Pa·s seems to be needed to allow complete development of separation-alignment process. Our successful separation and alignment of MWNTs shown in Figs 3 and 5 are the direct evidence of the above analysis. The plateaus can be viewed as the indicators of major separation and alignment of nanotubes in composite processing.

In contrast to the result in Fig. 8 without hardener, the viscosity of the composite with hardener in Fig. 9 is lower than that of the pure epoxy. This indicates that the nanotubes contribute to the rate of matrix curing. It is known that the relationship between viscosity, η, and the degree of matrix cure, α, can be described as [19]

$$\ln \eta = A + K_1\alpha + K_2\alpha^2 \tag{2}$$

where A, K_1 and K_2 are constants depending on temperature. Fig. 9 clearly shows that when compared with the pure epoxy, α of the composite increases more slowly with time because in this case η increases more slowly. Such slower curing rate of epoxy in the composite can be ascribed to the fact that the addition of MWNTs and their movement during shear reduces the probability of collision among epoxy molecules and results in a lower cross-linking rate of the epoxy.

4. Conclusions

In summary, this paper proposed and investigated an efficient method for separating and aligning long entangled nanotubes in epoxy using continuous shear. The study found that the effectiveness of shear flow depends strongly on the matrix viscosity, that the continuous shear improves nanotubes' dispersion, and that the curing rate of epoxy in the composite was retarded by the addition of MWNTs. The plateaus on the viscosity variation curve can be regarded as the indicators of major separation and alignment of nanotubes in composite processing.

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