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Shear Modulated Percolation in Carbon Nanotube Composites

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A novel time-dependent percolation transition has been observed in sheared carbon nanotube (CNT) composites. At a fixed CNT filler loading, the electrical conductivities of CNT composites can change abruptly as much as 8 orders of magnitude as the shear processing time increases. Microstructure characterization shows that the CNTs have aligned along the shear flow direction, which leads to the dramatic increase of the percolation threshold and thereby the dramatic decreases of the electrical conductivities. Our results highlight the great importance of understanding the response of CNT dispersion states to the processing conditions.

Introduction

Carbon nanotubes (CNTs) exhibit superior thermal,[1,2] mechanical,[3] and electrical properties,[4−7] and are considered the most promising building block for manufacturing low-cost, high-performance nanostructured composite materials. As compared to the polymer matrixes, CNT composites show significant improvements in tensile modulus,[8−10] thermal conductivities,[11−13] dielectric properties,[14,15] and electrical properties.[16−19] Of particular interest is the electrical properties of CNT composites. Because of the high aspect ratio one-dimensional structure and the extraordinary carrier mobilities,[7] a small loading of CNTs can make an insulating matrix conductive, and the resulting composites can be used for antistatic, electromagnetic interference shielding (EMI) applications,[16,17] electrically conductive composites,[18,19] etc.

The electrical properties of CNT composites depend on the final microstructure or the dispersion state of CNTs in the composites, which in turn is affected by the processing conditions. However, the effect of bulk processing conditions on the dispersion state of CNTs has rarely been studied and the correlation of processing conditions with the electrical properties is yet to be established. CNT composites are usually processed in suspensions or melts, therefore the major factor that determines the dispersion state of CNTs is the shear force that CNTs have encountered during the processing. In light of this consideration, we have focused our studies on the effect of shear flow processing on the microstructure and properties of CNT composites. We have observed a novel time-dependent percolation transition in sheared carbon nanotube composites. At a fixed CNT filler loading, the electrical conductivities of CNT composites can change abruptly as much as 8 orders of magnitude as the shear time increases. Microstructure studies show that the CNTs have aligned along the shear flow direction, which leads to the dramatic increase of the percolation threshold from 1.05 vol % for unsheared composites to 2.08 vol % for sheared composites and thereby the decreases of the electrical conductivities at the fixed filler loading. Our results suggest the great importance of understanding the response of CNT dispersion states to the processing conditions.

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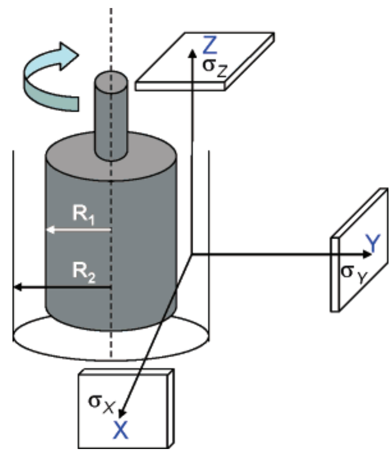

Figure 1. Schematic showing a disposable shear flow setup consisting of two coaxial cylinders. In the coordinate, the *X* axis is the shear flow direction, the *Y* axis is the velocity gradient direction, and the *Z* axis is the vorticity direction. The sheared composites were cut into a rectangular shape, about 10 mm long, 10 mm wide, and 1 mm thick, with the thickness directions along the *X*, *Y*, and *Z* axes, respectively. R_1 and R_2 are the radii of the inner and the outer cylinder, respectively.

Experimental Section

Sample Preparation. The multiwalled CNTs (MWNTs) grown via the chemical vapor deposition (CVD) method were obtained commercially (from Sun Nanotech Co Ltd). A liquid diglycidyl ether of bishpenol A-type (DGEBA, from Shell Chemicals Company) epoxy resin and a tetraethylenepentaamine (TEPA, from Sigma-Aldrich Inc.) hardener with a stoichiometry ratio of 8.13:1 were used as the polymer matrix for CNT/epoxy composites. The CNTs were first dispersed in the liquid TEPA hardener by ultrasonication for 2 h, and then DGEBA epoxy resin was mixed with the dispersed CNT/TEPA mixture. Subsequently, the whole formulation of CNT/epoxy was transferred into the shear flow setup, which follows the structure of a coaxial cylinder viscometer consisting of two coaxial cylinders with different diameters (Figure 1). The liquid CNT/epoxy composites were sheared in the gap by rotating the inner cylinder at a constant angular velocity of about 34 rad/s. The shear rate can be calculated from $\gamma_x = 2\omega R_1^2 R_2^2 / R_x^2 (R_2^2 - R_1^2)$, where R_1 and R_2 is the radius of inner and outer cylinder, respectively, and R_x is the arbitrary radius between R_1 and R_2. Nearly constant shear rate throughout the entire volume of fluid

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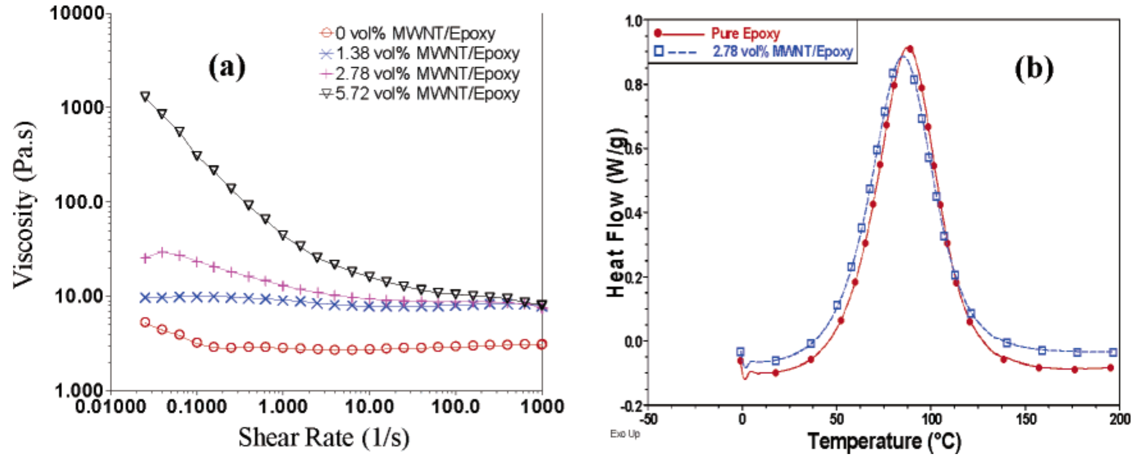

Figure 2. (a) Shear viscosity vs shear rate in the CNT/epoxy composites. (b) Differential Scanning Calorimeter (DSC) thermograph of pure epoxy (DGEBA/TEPA) and 2.78 vol % MWNT/epoxy composite.

can be obtained if the space between cylinders is small.[20] In our setup, the shear rate was estimated to be about 50 s^{-1}. At this high shear rate, the viscosities of CNT composites with various CNT loadings were already leveled off and very close according to our rheology measurement (Figure 2a). As such, at this shear rate one may expect the dispersion state of CNTs is similar for composites with different CNT loadings. Because of the high reactivity of aliphatic amine and the exothermic curing reaction of DGEBA with TEPA, the CNT composite formulations can be cured at room temperature (Figure 2b). After being sheared for a specific period of time and cured at room temperature for 12 h, the CNT/epoxy composites, together with the whole setup were cut accordingly in three directions. The sheared composites were cut into rectangular shape, about 1 mm thick, 10 mm long, and 10 mm wide with the thickness directions along the X, Y, and Z axes, respectively. The X axis is the shear flow direction, the Y axis is the velocity gradient direction, and the Z axis is the vorticity direction, as shown in Figure 1. We measured the electrical conductivities along the X, Y, and Z axes, respectively, and found the electrical conductivities along the Y and Z axes were almost the same but different from those along the X axis. Therefore, we denote the conductivities along the X axis as σ_X and the average of conductivities along the Y (σ_Y) and Z (σ_Z) axes σ_{YZ}.

Characterization. The viscosity of epoxy and its CNT composites was investigated by an AR Rheometer (Model AR1000-N, from TA Instruments), under steady-state flow procedure with parallel plate geometry at room temperature of 25 °C. A LEO thermally assisted field emission (TFE) scanning electron microscope (SEM) was used to study the dispersion state of CNTs in the composites. A relatively low voltage of 1.5 kV was used in the observations and no gold coating was applied on the top of the observation plane. The volume condcutivities of unsheared and sheared MWNT/epoxy composites were characterized by a Keithley High Resistance Electrometer (Model 6517), which is capable of measuring high resistance up to $10^{17}\Omega$. Both sides of the samples were coated with a 300 nm thick gold layer, acting as the electrodes. For samples with resistance above 200 GΩ, a high voltage of 400 V was used in the resistivity measurement, otherwise, a low voltage of 40 V was used to prevent an electric short of the low resistivity samples.

Results and Discussion

The 1.38 vol % CNT/epoxy composites were sheared in the coaxial cylinder setup for various durations of time, to study the effect of processing time on the dispersion state of CNTs (Figure 3). We observed very interesting behaviors in the sheared CNT composites. First, we found that 3 min of shear flow processing at the shear rate of 50 s^{-1} leads to the increase of electrical conductivities, as shown in Figure 3. This increase is not in line with the overall decreasing trend of the sheared composites, but this discrepancy is attributable to the hydrodynamic tube−tube interactions. Due to the high specific surface area of CNTs, hydrodynamic tube−tube interactions are significant.[21] Application of suitable shear force could lower the repulsive barrier between conductive particles and lead to agglomeration and formation of a conductive network at lower filler loadings.[22] Moreover, the CNTs are flexible enough to deform in modest flows and they can readily form interlocked coherent structures under suitable shear forces.[23] Therefore, a proper shear flow for short time resulted in the agglomeration of CNTs and thereby the increase of conductivities in the CNT/epoxy composites. Second, we found a distinctive transition behavior in the sheared composites with a filler loading of 1.38 vol %. Longer than 3 min of shear flow time results in the decrease of electrical conductivities, and specifically from 9 to 12 min, the electrical conductivities drop dramatically. Overall in the whole period of shear time up to 18 min, the electrical conductivities change as many as 8 orders of magnitude. This transition behavior is similar to the typical percolation transition, although here the transition is a function of shear time instead of a function of CNT filler loading as in a typical percolation transition. The third interesting finding is the anisotropic properties of the shear processed composites. After 18 min of shear flow, the electrical conductivity along the X axis (σ_X) is

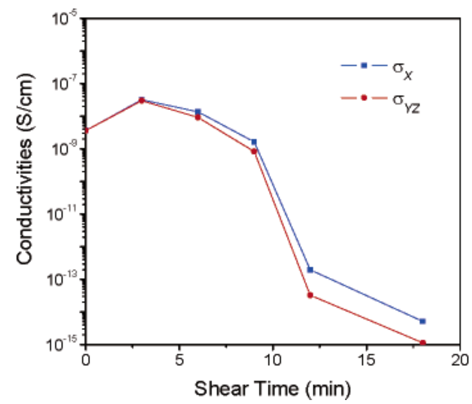

Figure 3. Shear time-dependent transition and anisotropic electrical conductivities of shear processed CNT/epoxy composites.

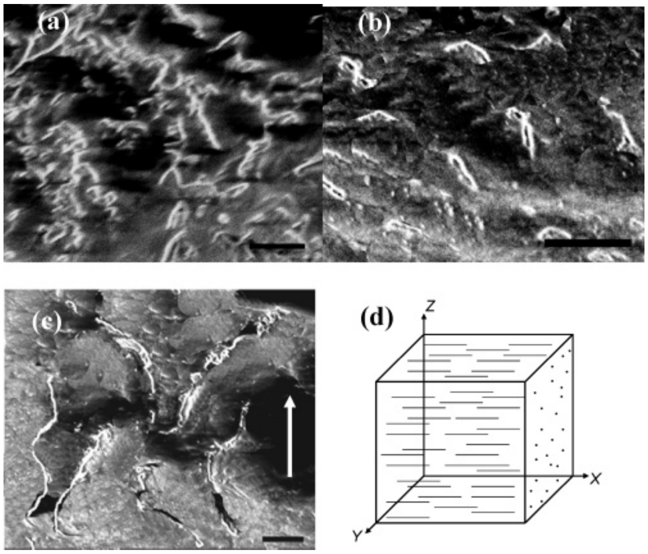

Figure 4. SEM images of unsheared and sheared 0.17 vol % CNT/epoxy composites. (a) SEM image of unsheared CNT/epoxy composite. (b) SEM image on the *YZ* plane of the sheared CNT/epoxy composite. (c) SEM image on the *XZ* or *XY* plane of the sheared CNT/epoxy composite. CNTs on these planes were aligned along a specific direction. The white arrow shows the shear flow direction. (d) Schematic showing the alignment of CNTs along the *X* direction (shear flow direction). Scale bar, 1 μm.

almost 5 times higher than those along the *Y* or the *Z* axis (σ_{YZ}). Both the time-dependent transition and the anisotropic properties of the shear processed CNT composites suggest that the shear flow processing has significantly changed the dispersion state of the CNTs.

To study the dispersion state of the CNTs in the shear processed composites, the shear processed samples were examined by a scanning electron microscope (SEM). We used a lower filler concentration composite (0.17 vol % CNT/epoxy composite) to demonstrate the dispersion state of CNTs, because we found it was difficult to compare the microstructures at very high filler loading. Actually our recent reports[24,25] show that even for nicely grown vertically aligned CNTs, one can see that at high magnifications the CNTs are always bent and kinked, not to mention in the composites the CNT alignment is not as good as that in the directly grown aligned CNTs. Both the unsheared and sheared composites (at the rate of 50 s^{-1} for 18 min) were studied. As can be seen in Figure 4a, in the unsheared sample the CNTs were coiled and randomly dispersed. The SEM observation on the *YZ* plane (see the coordinate in Figure 1) of sheared CNT/epoxy composite sample reveals that the CNTs were much shorter than the full length of CNTs, indicating the CNTs on this plane were heads/tails of shear aligned CNTs (Figure 4b). In contrast, the SEM images on the *XZ* or *XY* planes of sheared CNT/epoxy composite samples show that CNTs were extended and aligned along a specific direction (Figure 4c). And a schematic showing the alignment of CNTs along the *X* axis (shear flow direction) is given in Figure 4d. A comparison of the schematic and its projections on the *YZ*, *XZ*, and *XY* planes (not shown) with the SEM images in Figure 4b,c suggests that CNTs in the sheared composites were aligned along the shear flow direction.

Now the novel and interesting behavior found in Figure 3 can be explained by the microstructures in Figure 4. Due to the alignment of the CNTs with shear flow, after a specific period of shear processing time the conductive CNT network was broken down and thus aligned CNTs were formed in the CNT/epoxy composites. The electrical conductivities of CNT/epoxy composites thus dramatically decrease, showing the abrupt time-dependent transition. Also because of the alignment of the CNTs along the shear flow direction, the electrical conductivities along the *X* axis are always higher than those along the *Y* or the *Z* axis, as conductive paths can be more easily formed along the CNT length direction. Because the shear flow can affect the formation and breakdown of the percolative network, the percolation transition (as a function of filler loading) should be affected by the processing conditions such as the shear flow time.

The unsheared CNT/epoxy composites show a sharp transition in the percolation region (Figure 5a). The electrical conductivities dramatically increase about 10 orders of magnitude when the CNT concentration increases in the percolation region. According to scaling theory, the effective conductivities ($\bar{\sigma}$) of insulator−conductor composites near the percolation threshold f_c can be predicted by power laws:[26]

$$\bar{\sigma} = \sigma_m(f_c - f)^{-s} \qquad \text{for } f < f_c \tag{1}$$

$$\bar{\sigma} = \sigma_f(f - f_c)^{t} \qquad \text{for } f > f_c \tag{2}$$

where σ_m and σ_f are the electrical conductivities of insulating matrix and conductive filler, respectively; f is the concentration of the conductive filler within the insulating matrix; and s and t are scaling constants. The electrical conductivity data of unsheared CNT/epoxy composites were fitted to eq 1 for $f < f_c$ (Figure 4a inset). The best fit gives a percolation threshold of 1.05 vol %. The scaling component of unsheared CNT

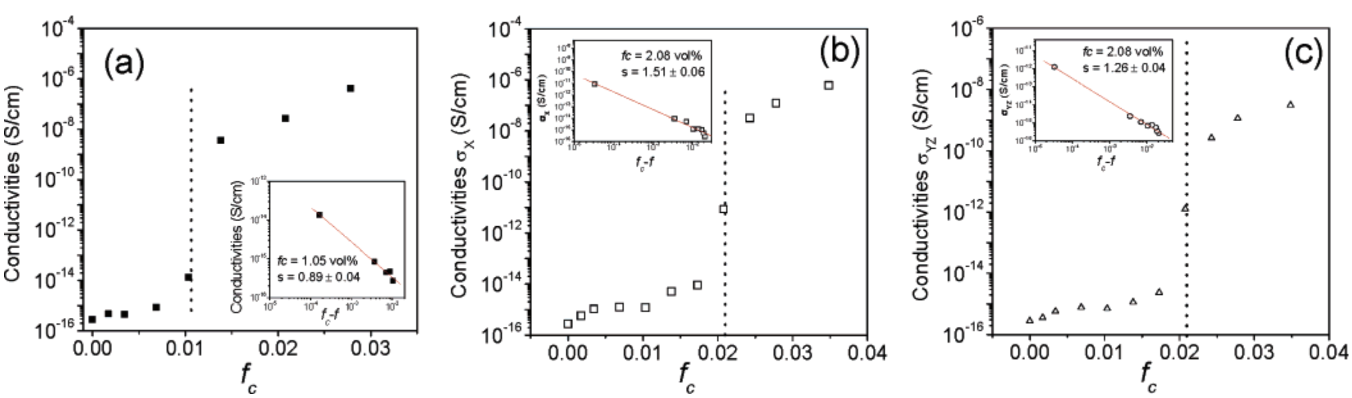

Figure 5. Electrical conductivities vs CNT volume fraction of (a) unsheared CNT/epoxy composites and shear flow processed CNT/epoxy composites with thickness directions (b) along the *X* axis and (c) along the *Y* /*Z* axes. Insets in each graph show the best fits of the electrical conductivities to the percolation theory when $f < f_c$, which give (a) $f_c = 1.05\%$, $s = 0.89 \pm 0.04$, (b) $f_c = 2.08\%$, $s = 1.51 \pm 0.06$, and (c) $f_c = 2.08\%$, $s = 1.26 \pm 0.04$.

TABLE 1: Anisotropic Electrical Properties of Sheared CNT Composites

filler loading (vol %)	σ_X (S/cm)	σ_{YZ} (S/cm)	σ_X/σ_{YZ}
0.17	5.75×10^{-16}	3.53×10^{-16}	1.6
1.38	5.17×10^{-15}	1.13×10^{-15}	4.5
2.43	3.23×10^{-8}	2.59×10^{-10}	124
3.48	6.1×10^{-7}	3.05×10^{-9}	200

composites is 0.89 ± 0.04, which is slightly larger than the theoretic value of $s \approx 0.7$ for the three-dimensional percolation network formed by complex resistors.[27]

To study the effect of shear flow processing on the percolation transition, we used a fixed shear time of 18 min for preparing shear-aligned CNT/epoxy composites at all filler loadings. For the same sheared composites, the electrical conductivities along the shear direction (σ_X) are higher than those along the other two directions (σ_{YZ}) (Figure 5b,c). By fitting the experimental conductivity data into eq 1, we obtained an isotropic percolation threshold $f_c = 2.08$ vol % for shear flow aligned CNT composites along all three (X, Y, and Z) directions (Figure 5b,c insets). Due to the alignment of CNTs along the shear flow direction, the percolation transitions of sheared composites take place at a much higher filler loading than unsheared composites, and the percolation threshold increases as much as 98%, from 1.05 vol % to 2.08 vol %. The dramatic increase of percolation threshold makes the originally conductive composites insulating, which explains the dramatic change of electrical conductivities of sheared composites in Figure 3.

We obtained the scaling components $s = 1.51 \pm 0.06$ and 1.26 ± 0.04 along the X axis and the Y/Z axes, respectively (Figure 5b,c insets). The scaling components of shear processed CNT composites are higher than the unsheared composites and close to the theoretic value of $s \approx 1.43$ for the two-dimensional percolation network formed by resistors.[27,28] The scaling component along the Y/Z axes is lower than that along the X axis. Therefore, in the sheared CNT/epoxy composites, the anisotropic electrical conductivities along different directions come from the anisotropy of the scaling component rather than the anisotropy of the percolation threshold, because the percolation threshold is isotropic.

It is worthwhile to mention that the anisotropic electrical properties of sheared CNT composites depend on the filler loading. Table 1 shows that in sheared composites σ_X are always higher than σ_{YZ}, because of the alignment of CNTs along the shear flow direction. The ratio of σ_X/σ_{YZ} is related to the percolation threshold. When the filler loading is below the percolation threshold, σ_X/σ_{YZ} is small; however, the ratio can be more than 2 orders of magnitude at high filler loadings above the percolation threshold, as shown in Table 1.

Conclusions

Shear flow processing has been shown to have a significant effect on the dispersion state of CNTs in epoxy composites. SEM observations show that the CNTs were aligned along the shear flow direction. Evolution of electrical conductivities with shear time suggests that the alignment of CNTs in epoxy composites was time dependent. The shear flow processed CNTs/epoxy composites showed a higher percolation threshold, and the scaling components were nonuniversal along different directions, which results in the anisotropic conductivities in shear processed CNT/epoxy composites. The understanding of the effect of shear flow processing on the CNT dispersion state and the correlation of CNT orientation with anisotropic percolation behavior may help the development of CNT composites for applications where electrical conductivities are desired.

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