Structural evolution of carbon nanotubes in composites under contact sliding stresses

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We discovered a new structural evolution of carbon nanotubes (CNTs) in epoxy composites subjected to contact sliding stresses. Our analysis under high resolution transmission electron microscopy showed that the evolution has three stages which are (a) the bonding breakage of the CNTs, (b) the formation of sinusoidal shells, and (c) the consolidation of nanoparticles. We then explored the evolution mechanisms theoretically. © 2006 American Institute of Physics. [DOI: 10.1063/1.2212063]

Deformation of carbon nanotubes (CNTs), including those in composites, has attained extensive research attention.1–5 For example, Marques et al.1 considered the performance of CNTs under tension and showed that the brittle or plastic response under high stretching conditions is controlled by the rate of straining and number of defects in a nanotube. Wagner et al.2 studied the fragmentation of CNTs in polymer composites under tension and compression. They concluded that the fragmentation was due to either (1) compressive thermal residual stresses resulting from polymer shrinkage during polymerization or (2) tensile stresses generated by polymer deformation and transmitted to CNTs during testing.

It was demonstrated that during the deformation of CNTs by ball milling3 a high percentage of CNTs had partially or completely collapsed openings. Also an incident of carbon nanoparticles was reported after 10–15 min of high speed milling.5

This letter studies the deformation and structural transformation of CNTs in an epoxy composite when subjected to contact sliding stresses (wear tests). The deformation mechanism revealed by our study was never discovered before, but it is critical to the tribological behavior of composites reinforced by CNTs.

The multiwalled CNTs 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.

Dry wear tests were carried out on a Plint-Cameron pin-on-disk machine,7 on which two pin samples were held against a rotating high speed steel disk of hardness $H_{MV} = 720$. A fixed track diameter of 80 mm was used in all the tests with a sliding distance of 2500 m, normal nominal stress of 1 MPa, and sliding velocity of 0.98 m/s.

Conventional transmission electron microscopy (TEM) studies were performed in a Philips CM12 transmission electron microscope, operating at 120 kV. The high-resolution transmission electron microscopy (HRTEM) investigations were performed on a JEOL JEM-3000F transmission electron microscope, operating at 300 kV.

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Fig. 1. CNTs in composite. (a) before wear test and (b) after wear test.
dislocations, Figs. 2(a) and 2(b). These types of permanent deformation of the walls due to the repeated interaction of composite with the steel disk surface in contact sliding of the wear test led to the outer shell breakages of the CNTs.

We discovered several very interesting deformation mechanisms of CNTs. Figure 2(a) shows zones A–C of a bamboo CNT structure. Zone A [Fig. 2(b)] features a sinusoidal distortion of six carbon outer shells. Zone B presents an altered CNT wall with another type of deformation [Fig. 2(b)]. The carbon shells deform to the whole depth of CNT walls and have nearly semicircular shapes. It seems that the pattern can be the result of indentation of a sharp asperity into the outer shell perpendicular to the CNTs’ axis. The same type of deformation occurs in zone C. The above deformation mechanisms have never been reported. In contact sliding the composite is interacting with asperities of steel disk. These asperities can act as sharp indenters that deform CNT walls. Asperities can also cause tensile deformation as CNTs are fixed in epoxy matrix and can be stretched. For example, about six outer shells were stretched in zone A, forming a sinusoidal shape on stress release. Surprisingly, even after heavy deformation, no gaps were detected between CNTs and epoxy matrix. It seems that the adhesion and stress transfer ability between CNTs and epoxy are strong. Also, elevated temperatures arising in a wear test could possibly softened the epoxy, but the high strain rate in the test could make it harder at the elevated level.8

CNTs with open and closed ends were detected after the wear tests. Those with closed ends were not altered by contact sliding. However, CNTs with open ends (Fig. 3) were generated during wear. (The CNTs were tilted inside TEM, which confirmed the observation.) An open end of the CNT is asymmetric with one side 5 nm longer than the other (Fig. 3), indicating that breakage did not take place perpendicular to the CNT’s axis but at an inclined angle. The other feature of the end is its partial imperfection of the right wall, demonstrating that the breakage of the CNT could be the result of the multiple asperity-CNT interactions. Directions of breakage can be seen in Fig. 3, indicated by the arrows.

More interestingly, nanoparticles were found in the composite after the wear tests. These nanoparticles were similar to those obtained by electron irradiation10 or ball milling and were of two main kinds. Some of them has faceted or partly faceted walls [Fig. 4(a)]. These nanoparticles had an inner diameter of 5–8 nm and a moderate number of shells (about 15–18). Another kind of nanoparticles has spherical shapes, resembling an onionlike structure [Fig. 4(b)], which is clearly different from those reported by Ugarte et al.10
because in the present case, the inner core of a nanoparticle is amorphous with a diameter of 4–5 nm and the particle shells have a large number of defects. In addition, the outer and inner shells are not continuous. As concluded by Iijima,11 the onionlike nanoparticles are the most stable. An irradiation treatment transforms metastable faceted nanoparticles to more stable circular onionlike particles,10 because the system under irradiation is stabilized by the energy gain from the van der Waals interaction between shells.12 In our present case, an irradiation source does not exist and hence the system under irradiation is stabilized by the energy gain that the evolution has three stages which are critical and the sliding stress must be high enough to enable the evolution to occur.

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