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ScienceDirect
Wear 261 (2006) 806–811
WEAR
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Novel behaviour of friction and wear of epoxy composites reinforced by carbon nanotubes

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Received 12 August 2005; received in revised form 16 December 2005; accepted 24 January 2006
Available online 2 March 2006

Abstract

This paper investigates the wear properties of a carbon nanotube reinforced epoxy composite. The study shows that the surface coverage area of CNTs, $R_{c/m}$, plays a significant role in the wearability of the composites. With $R_{c/m} > 25\%$, the wear rate can be reduced by a factor of 5.5. With the aid of the transmission electron microscopy, the study concluded that the improvement of the wear resistance of a high $R_{c/m}$ composite was due to the CNTs exposed to the sliding interface which protected the epoxy matrix effectively. It was also shown that the contact sliding in a wear test can deform a CNT significantly and cause its fragmentation.

Keywords: Carbon nanotubes; Composite; Wear; Deformation; Microstructure

1. Introduction

Owing to their unique mechanical, electrical and thermal properties, carbon nanotubes (CNTs), both single- and multi-walled, have attracted extensive research attention world wide [1–3]. It has been found that composites reinforced by CNTs can have very improved properties [4–6]. For example, it was reported that adding 1 wt.% of CNTs to a polymer matrix brought about an increase of tensile modulus and strength of up to 42 and 25%, respectively [7].

However, studies on the tribological properties of CNT–polymer composites [8–12] have been relatively fewer. Zoo et al. [8] reported that an addition of 0.5 wt.% CNTs to an ultra-high molecular weight polyethylene could significantly reduce the wear loss of the composite but increase its friction coefficient. It was considered that this was mainly caused by the increased shear strength of the composite. An et al. [9] acknowledged an improved wear and mechanical properties of alumina-based composites containing CNTs up to 4 wt.%, though without a mechanism explanation. Chen et al. [10] believed that the favorable tribological properties of a CNT–polytetrafluoroethylene composite was due to the high strength and high aspect ratio of the CNTs. They commented that the CNTs might have been released from the composite during sliding, which then prevented direct contact of worn surfaces and hence reduced both the wear rate and friction coefficient. However, no direct evidence was given. Cai et al. [11] reported that the contribution of CNTs in a polyimide composite was to restrain the scuffing and adhesion of the polyimide matrix in sliding, providing a much better resistance than the neat polyimide. Lim et al. [13] concluded that Raman spectra could not characterise the difference between a worn and an unworn surface of CNTs and carbon/carbon composites because the spectra were nearly the same.

The above review shows that although a number of investigations have been conducted on the tribological behaviour of various CNT-reinforced composites, the mechanisms of wear resistance and variation of friction coefficient has not been well understood. The aim of the present work is to take CNT-reinforced epoxy as an example to explore the role of CNTs in the wear of the composite.

2. Experiment

The multi-walled CNTs used in the present experiment were prepared by chemical vapour deposition (provided by Nanolab) with their diameters ranging from 10 to 25 nm and their lengths

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0043-1648/$ – see front matter
doi:10.1016/j.wear.2006.01.033

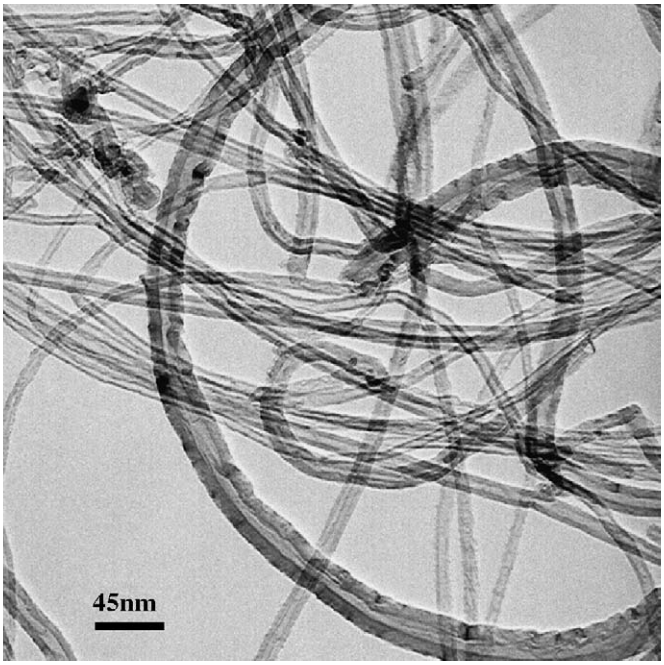


Fig. 1. CNTs in their initial state.

from 10 to 20 μm (Fig. 1). To properly mix them with the epoxy matrix, the CNTs 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. A thermal gravimetric analysis showed that over 99.6% of the solvent was removed by this process.

Pins for wear tests were cut off from the bulk composite material prepared above. Because the dispersion of the CNTs in epoxy was not absolutely uniform, particular attention was paid to monitor the coverage area ratio of CNTs to matrix on a pin surface, $R_{c/m}$. In addition to those randomly cut, a special group of pins with $R_{c/m} > 0.25$ were prepared to explore the effect.

Dry wear tests of the CNT–epoxy composites were carried out on a Plint–Cameron pin-on-disc machine. As illustrated in Fig. 2, two composite pins were held against a rotating high-speed steel disc of hardness $H_{MV} = 720$. A fixed track diameter of 80 mm was used in all the tests. However, each test was run on a fresh track, with a sliding distance from 500 to 3500 m, a normal stress of 1 MPa and a sliding velocity of 0.98 m/s. A transducer attached to the specimen holder recorded the tangential force. The volumetric wear was measured by the weight loss of a specimen using an analytical balance of resolution 0.1 mg.

To obtain optical micrographs, samples were thinned down mechanically to a thickness of about 3 μm. Micrographs were acquired in the transmission mode by means of an optical microscope.

The topography of a sample surface after a wear test was studied on a high resolution scanning electron microscope (HRSEM), JSM-6000F. The conventional transmission electron microscopy (TEM) studies were performed on a Philips CM12, operating at 120 kV. The high resolution transmission electron microscopy (HRTEM) investigations were performed on a JEOL JEM-3000F, operating at 300 kV.

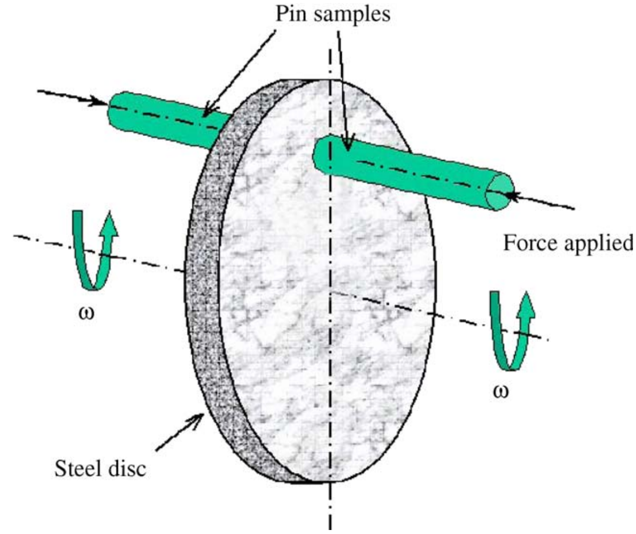


Fig. 2. A schematic diagram of the pin-on-disc wear test used in this study.

The plan-view TEM specimens were prepared in a standard manner using a tripod [14]. The thinning procedure was performed from the side opposite to wear surface. To insure that no changes of epoxy microstructure would take place during its exposure to acetone, the surface of a sample was covered with thin amorphous chromium film which would be completely removed at the last stage of preparation. Ion-beam thinning was used to achieve a sufficiently thin area for TEM analysis. Also, wear debris were examined with TEM.

3. Results and discussion

3.1. Composite before wear testing

Fig. 3 is a typical image showing the structure of the composite before wear testing. It is clear that the CNTs in the composite have the same structure as that supplied (Fig. 1). This implies that the morphology and structure of the CNTs were not altered by the composite preparation process described in the above section.

Fig. 3. The CNTs in an epoxy composite before a wear test.

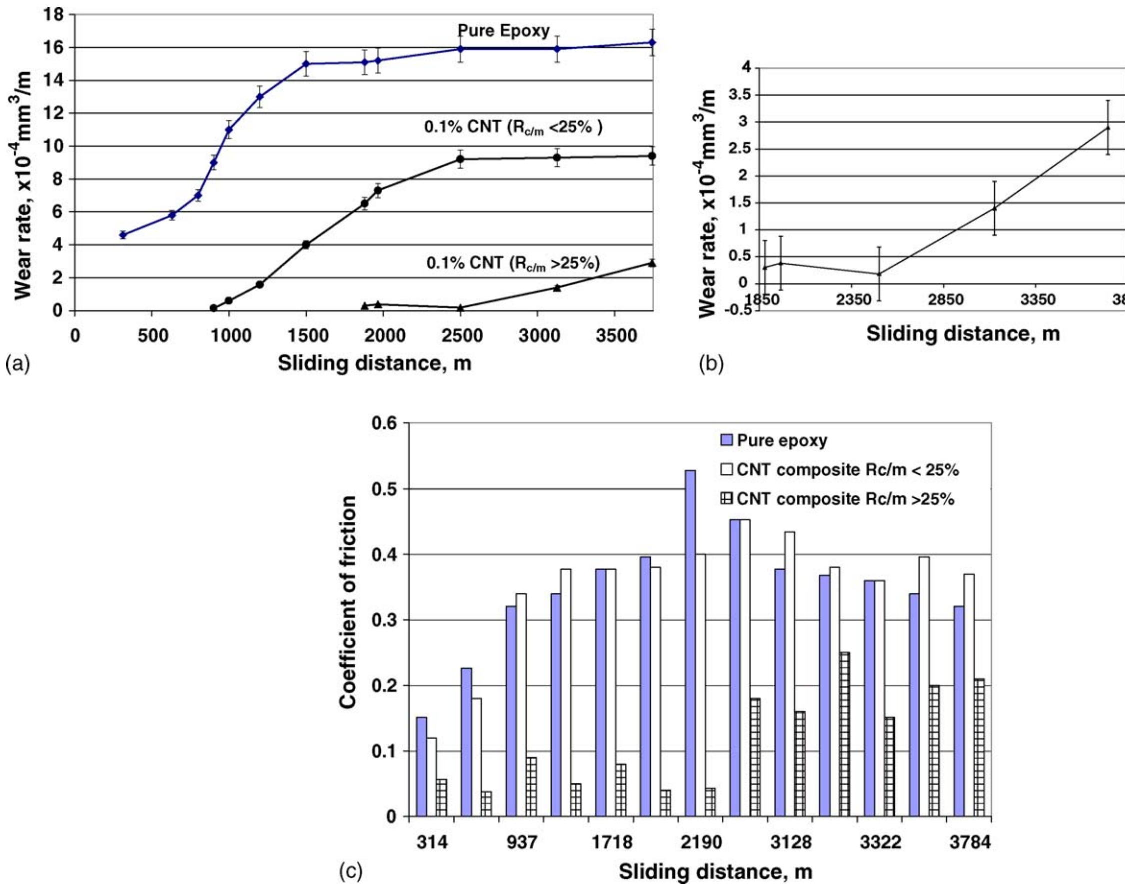


Fig. 4. Effect of CNTs (a) wear resistance; (b) curve with $R_{c/m} > 25\%$ from (a) in more details; (c) coefficient of friction.

3.2. Wear resistance

Results of the wear tests are presented in Fig. 4(a). The phenomenon of running-in wear is obvious for both the pure epoxy and the nanotube-reinforced epoxy composite. A stable wear then takes place after a sliding distance of about 2000 m. The wear rate at this stage was 16×10^{-4} mm^3/m for the pure epoxy. It is clear that an addition of only 0.1 wt.% nanotubes to the epoxy matrix dramatically reduces the wear rate. The samples with $R_{c/m} < 25\%$ had a wear rate of 8×10^{-4} mm^3/m, which is over 1.7 times lower than that of the pure epoxy. These samples had rough surfaces as presented in Fig. 5(a). Brittle fragments and multiple microcracks were evident, indicating that the material removal was via brittle fracture. More significantly, the samples with $R_{c/m} > 25\%$ had a remarkably lower wear rate (see the bottom curve with triangular dots in Fig. 4(a) and (b)), with an extremely small weight loss up to a sliding distance of 1700 m. The wear rate upon further sliding remained low, varying in the range of 0.05×10^{-4} to 2×10^{-4} mm^3/m Fig. 4(a) and (b), about 3.2 times smaller than that of the sample with $R_{c/m} < 25\%$ and 5.5 times lower then that of pure epoxy. The surface of these samples appeared very smooth. A more close look at the surface topography (Fig. 5(b)) did not detect a single brittle fragmentation, which seems to suggest that the mechanism of the materials removal in the wear process was ductile. The electron micrograph of the worn surface, Fig. 5(c), clearly indicates that the CNTs covered the surface greatly slowed down the wear process of the epoxy matrix.

The coefficient of friction for the composites with $R_{c/m} > 25\%$ was much lower (Fig. 4(c)) for all sliding distances checked. Again, the surface microstructure, as shown in Fig. 5(c) and to be discussed later, suggests that the CNTs exposed to the sliding interface were acting as a solid lubricant at the sliding interface which reduced the coefficient of friction. After a wear test, a specimen surface subjected to sliding became very shiny and smooth. For the composite with $R_{c/m} < 25\%$, on the other hand, the coefficient of friction varied. A further study is necessary to clarify the mechanism.

3.3. Debris topography

The debris topography is presented in Fig. 6. It is clear that bulky fragments of 1.5 μm in width and up to 6–7 μm in length were formed for samples with a low $R_{c/m}$ (Fig. 6(a)). The debris of irregular shapes with sharp and fractured parts demonstrated a brittle mode of material removal. In contrast the debris fragments of samples with a high $R_{c/m}$ were 0.5 μm in width and 3–4 μm in length and had a feature of a rod like structure (Fig. 6(b)).

CNTs could easily be detected in debris of samples with a lower $R_{c/m}$ (Fig. 7(a)) and they appeared bent with their initial lengths of 1–2 μm, suggesting that no fragmentation of the

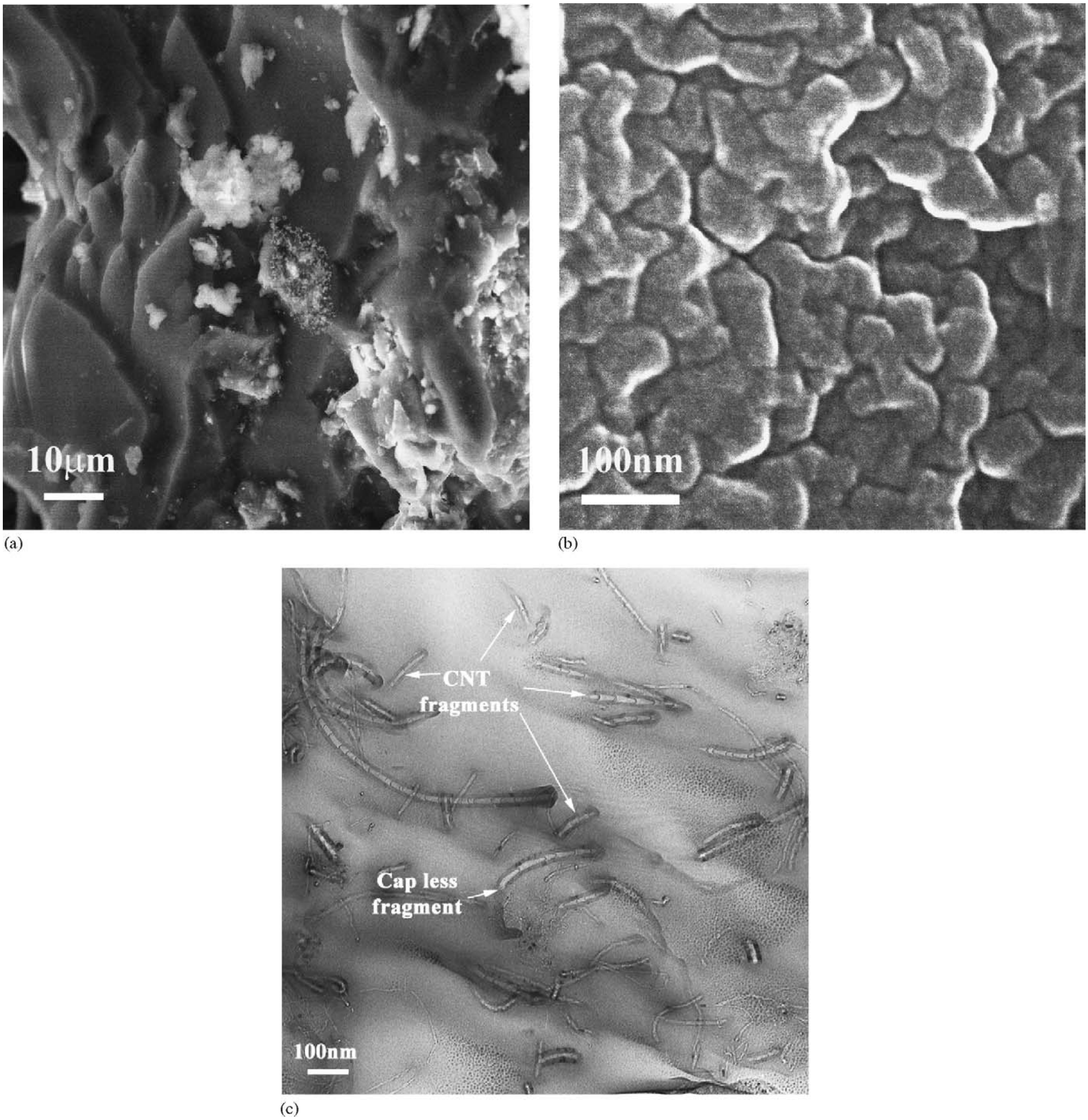


Fig. 5. Sample surfaces after wear test (sliding distance 2500 m): (a) $R_{c/m} < 25\%$; (b) and (c) $R_{c/m} > 25\%$; (a) and (b) surface topography; (c) electron micrograph.

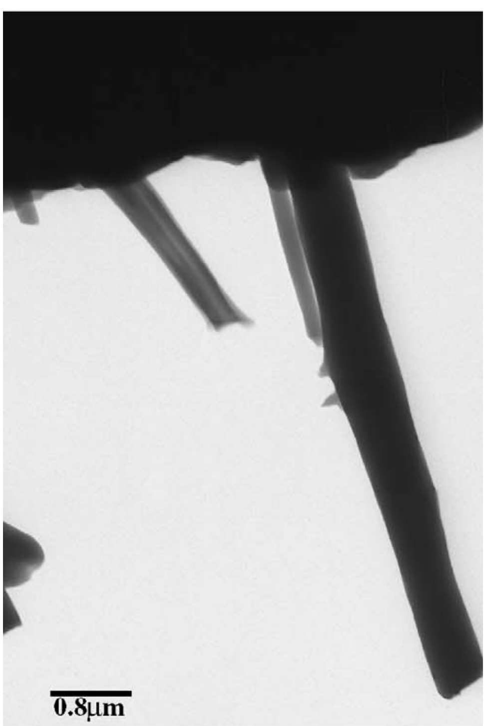
CNTs took place. An examination in the HRTEM mode confirmed a good adhesion between the epoxy matrix and the CNTs (Fig. 7(b)). No debonding and cracking were detected [15]. The diameters of the CNTs measured in the HRTEM mode were from 10 to 25 nm, demonstrating that the diameters were similar to their initial values in average. On the other hand, however, the CNT walls were deformed, as can be seen in Fig. 7(b).

In summary, CNTs in bulky debris were bent and had deformed walls, but the changes of their diameters and lengths were minor.

3.4. Structure of worn surfaces

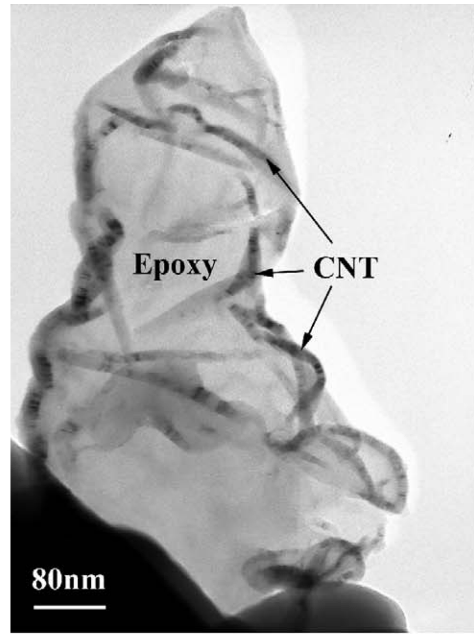
The distribution of the nanotubes on a sample's surface appeared not homogeneous. Fig. 5(c) gives the distribution of CNTs on a sample's surface with a high $R_{c/m}$. The high concentration of CNTs, most with bamboo structures, is obvious. The exposed length of CNTs varies from 100 to 400 nm, and it is evident that the fragmentation of CNTs during a wear test did take place, maybe caused by the high contact stress and abrasion at the sliding interface, because many CNTs no longer have their

(a)

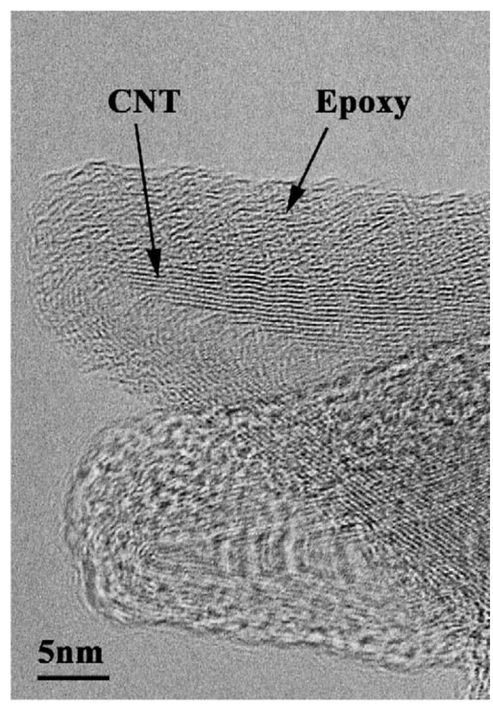


(b)

Fig. 6. Wear debris: (a) $R_{c/m} < 25\%$ and (b) $R_{c/m} > 25\%$.



(a)



(b)

Fig. 7. CNTs in wear debris: (a) conventional TEM mode; (b) HRTEM; note the boundary between CNT and epoxy and the details of the CNT walls deformation.

caps (see CNTs 1–9 in Fig. 5(c)). The orientation of the CNTs with a short length exposed to the sliding surface scatters, but those with longer exposed lengths have obviously been aligned along the sliding direction of the wear test (from right to left in Fig. 5(c)). The fragmentation of the CNTs was also coupled with sever deformation of the walls. The removal of the CNT caps seems to occur always at the end exposed to the sliding surface. The above observation suggests the following wear mechanism. At the first stage of sliding wear, the epoxy matrix on a sample's surface was removed in a brittle mode. The CNTs were then exposed to the sliding interface. Because the CNTs have a high strength, they reduce the wear rate significantly. Nevertheless, the CNTs underwent severe deformation leading to the removal of their caps and distortion of their walls. Meanwhile, the rotation of the steel disk aligned the CNTs along the sliding direction. As a result, the structure seen in Fig. 5(c) was formed with aligned capless CNTs.

4. Conclusions

The above investigation into the wear of CNT-reinforced epoxy composites brings about the following conclusions:

1. The surface coverage area of CNTs, $R_{c/m}$, plays a significant role in the wearability of the composites. With $R_{c/m} > 25\%$, the wear rate can be reduced by a factor of 5.5. The improvement of the wear resistance of a high $R_{c/m}$ composite was due to the CNTs exposed to the sliding interface which protected the epoxy matrix effectively.
2. In samples with a low $R_{c/m}$, material removal was via brittle fracture; however in those with a high $R_{c/m}$ it is rather ductile.
3. The contact sliding in a wear test can deform a CNT significantly and cause its fragmentation.
4. When $R_{c/m}$ is high, the CNTs exposed to the sliding interface reduce the coefficient of friction significantly. However, when $R_{c/m}$ is low, the coefficient varies. The mechanism of the phenomenon needs to be further explored.

Acknowledgement

This work was continuously supported by the Australian Research Council (ARC). The authors appreciate the access to the Electron Microscope Unit of Sydney University for use of its facilities.

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