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Effect of Surface-Treated Carbon Nanotubes on the Mechanical and Tribological Performances of Phenolic Resin

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Reinforced phenolic resin (PF) was prepared by in situ polymerization of different fractions of carbon nanotubes (CNTs) that had undergone oxidation. The compressive strength and hardness of the material, according to mechanical property testing, was improved by the modified CNTs. The tribological properties of PF composites were investigated by a block-on-ring friction and wear tester. The results indicated that CNTs reinforced PF showed lower friction coefficient and higher wear resistance, compared with pure PF. The morphologies of the worn surfaces, debris, and transfer films were observed by scanning electron microscopy (SEM) and optical microscopy (OM). A continuous and thinner transfer film formed during the friction test of the composites led to the significant improvement of the tribological properties.

Keywords CNTs, friction, mechanical property, oxidation, phenolic resin, wear

1. Introduction

Phenolic resin (PF), as the first synthetic resin, due to its good thermal stability, mechanical properties, and good solvent resistance, is still attracting a great deal of research interests, especially for such applications as thermal insulation, coatings, aeronautic high temperature resistant ablative materials, electro-optical devices, sensors, and friction materials. PF-based friction materials usually contain a large number of reinforcing and filler constituents, such as reinforcing fibers, abrasives, binders, fillers, and friction modifiers (solid lubricants).[1–6] This accounts for the great dependence of their properties on the interactions and synergistic effects among the multiphase ingredients. In this sense, it is very important to correctly select and properly combine the different components so as to satisfy a number of requirements for the properties of the friction materials, such as good wear resistance, stable friction coefficient, and reliable strength.

Since Iijima[7] discovered carbon nanotubes (CNTs), greatly increasing scientific and technological interest in their novel properties and potential applications has occurred.[8–10]
In particular, significant improvements of mechanical and tribological properties of the CNTs-based nanocomposites have been found.[11–16]

It is well known that the CNTs are not compatible with most solvents because of their chemical inertness. As a result, there is a difficulty in obtaining a homogenous solution. This results in the use of CNTs as reinforcing elements suffering from poor dispersion capability and weak interfacial interactions.[17] Therefore, to enhance the dispersibility of CNTs in polymers, it is necessary to physically or chemically attach polar functional groups to the sidewalls without significantly changing the desirable properties of CNTs by, e.g., plasma treatment,[18] oxidation,[19] or coating with coupling agents[20] to improve the wettability and create active bonding sites.

Considering the above factors, the objective of the research described in this paper was to study the effect of CNTs on the tribological properties of reinforced PF composites. The CNTs were modified through oxidation for better dispersion in the composites. The CNTs reinforced PF composites were synthesized by means of in situ polymerization. According to this method, monomers can penetrate into the agglomerated nanoparticles easily due to their low molecular weight nature and react with the activated sites inside and outside the agglomerates.[21,22] The polymer molecules could grow more and the CNTs would be better dispersed in the polymer matrix.

2. Experimental Details

2.1. Materials

Phenol (analytical reagent grade) was purchased from Shanghai LingFeng Chemical Reagent Co., Ltd., (China). Formaldehyde (analytical reagent grade) was supplied by Sinopharm Group Chemical Reagent Co., Ltd., (China). Ammonia water (analytical reagent grade) was provided by Shanghai Jufeng Chemical Technology Co., Ltd., (China). CNTs were supplied by Chengdu Institute of Organic Chemistry Co., Ltd., (China). Oil of vitriol and nitric acid (analytical reagent grade) were purchased from Taicang Zhitang Chemical Co., Ltd., (China). Ethanol (analytical reagent grade) was purchased from Shanghai First Chemical Factory (China). Acetone (analytical reagent grade) was obtained from Shanghai Dahe Chemical Co., Ltd., (China). All the reagents were used without further purification.

2.2. Oxidation of CNTs

Pristine CNTs were added to a mixed solution in which the concentration of oil of vitriol was 3M and the concentration of nitric acid was 1M. The mixture was treated in an ultrasonic bath for 30 min and stirred for 1 h under reflux. Then, the mixture was vacuum-filtered through a 0.22 µm Millipore polytetrafluoroethylene membrane and washed with distilled water until the pH value approached seven. The filter cake was dried under vacuum at 40°C for 24 h, obtaining CNTs-COOH. Figure 1 shows the fabrication procedure for the CNTs-COOH.

2.3. Synthesis of PF and CNTs-COOH/PF Nanocomposites

Appropriate amounts of phenol and ammonia water were put into a three-neck flask heated in an oil bath, stirred and refluxed, then the formaldehyde was added in batches to the mixed solution. The temperature was maintained at around 70°C until the solution became
obviously stratified and hard to stir; the water was then removed as well as phenol in a low vacuum condition of 0.6 MPa. The products were kept in a vacuum oven for 24 h at the temperature of 50°C before being ground into powder. The CNTs-COOH, when desired, were added after the reaction had been carried out for about 90 min.

2.4. Preparation of the Friction Specimen

The composites for the tests were prepared by hot compression molding. The dried PF or CNTs-COOH/PF nanocomposite powder was put into a metal mould and pressed under the pressure of 10 MPa, then degassed. A typical multistage schedule was employed including 15 min resident time at 120°C, followed by a relatively rapid temperature rise to 170°C, being maintained for 30 min under 20 MPa, and an unloading as soon as the temperature dropped to 110°C. For frictional measurements, the specimens were cut and ground to the size of 6 mm × 7 mm × 30 mm.

2.5. Friction and Wear Test

The tribological tests were conducted on an M-2000 friction and wear tester (Zhangjiakou Xuanhua Kehua Testing Machine Manufacturing Co., Ltd. China). The contact schematic diagram of the frictional couple is shown in Fig. 2.

Figure 1. Fabrication procedure of CNTs-COOH.

Figure 2. Schematic diagram of the contact configuration of the ring-on-block (M-2000 type) wear tester (unit: mm).
During the tests, the friction coefficient was calculated from the friction force torque according to the following equation:

$$\mu = \frac{M}{W \times r},$$

(1)

where $\mu$ is the friction coefficient, $M$ the friction force torque (N $\cdot$ mm), $W$ the load (N), and $r$ the radius of the steel ring (mm). Sliding was performed under ambient conditions over a period of 120 min at a sliding speed of 0.42 m/s. The ambient temperature was 20 $\pm$ 2°C and the relative humidity was 35 $\pm$ 5%. Before each test, the surface was polished with abrasive paper to Ra 0.17 $\sim$ 0.23 $\mu$m for the specimen and Ra 0.09 $\sim$ 0.11 $\mu$m for the counterpart. Then the counterpart ring and the composite blocks were cleaned with acetone followed by drying. At the end of each test, the length of the wear scar was measured with a measuring microscope, and the wear volume $V$ of the specimen was calculated from the following equation:

$$V = B \left[ \frac{\pi r^2}{180} \arcsin \left( \frac{b}{2r} \right) - \frac{b}{2} \sqrt{r^2 - \frac{b^2}{4}} \right],$$

(2)

where $V$ is the wear volume (mm$^3$), $B$ the length of the specimen (mm), $r$ the radius of the counterpart ring (mm), and $b$ the length of the wear scar (mm). The wear rate $K$ of the specimen was calculated from the following equation:

$$K = \frac{V}{PL},$$

(3)

where $K$ is the wear rate (10$^{-6}$ mm$^3$/N $\times$ m), $V$ the wear volume (mm$^3$), $P$ the applied load (N), and $L$ is the sliding distance (m). In this study, three replicates of friction and wear tests were carried out to minimize data scattering, and the average was reported. The deviation of the data of the replicate fiction and wear tests was <10%.

2.6. Analysis Methods

The pristine and modified CNTs were characterized by Fourier transform infrared spectroscopy (FTIR, NEXUS-470, Thermo Nicolet, USA).

The decomposition behavior of the CNTs was investigated using thermo gravimetric analysis (TGA, Model 951, Du Pont Co., USA). The measurement was conducted in flowing nitrogen at a heating rate of 20°C/min.

The compressive strength and Rockwell hardness of the specimens were tested by an universal electronic testing machine (CMT-4104, Shenzhen Sans Material Testing Co. Ltd. China) and Rockwell hardness tester (XHK-150, Shanghai Material Testing Machine Co. Ltd. China.), respectively.

To investigate the wear mechanism, the worn surfaces and debris of the specimen were coated with a thin layer of gold and then observed by scanning electron microscopy (SEM, 5136MM, TESCAN s.r.o. Co., Czech). The transfer films formed on the surface of the counterpart ring were characterized by optical microscopy (OM).
3. Results and Discussion

3.1. Characterization of CNTs

Figure 3 shows FTIR spectra of pristine and modified CNTs. The band at 1710 cm\(^{-1}\) in Fig. 3b is assigned to the stretching mode of carboxyl groups, indicating the presence of –COOH on the surfaces of CNTs. In addition, a broad shoulder band in the 3200–3600 cm\(^{-1}\) region is attributed not only to the presence of hydroxyl groups but also to the traces of water in the KBr pellet used for the analysis which was inaccessible to be fully removed.

The thermal behavior of CNTs was evaluated by means of TGA. Figure 4 shows the TGA traces of the pristine-CNTs and CNTs-COOH with a heating rate 20°C/min in
nitrogen. An obvious difference between the TGA curves of CNTs and CNTs-COOH was observed. CNTs-COOH showed weight loss at about 200°C and the residue at 800°C was 85% while the pristine-CNTs exhibited no weight loss. The results suggested that –COOH groups were introduced on the surface of the CNTs.

3.2. Mechanical Properties of the PF Composites

Figure 5 shows the dependence of compressive strength of CNTs-COOH reinforced PF composites on the CNTs-COOH content. The compressive strength showed an upward trend. Compared with pure PF, the compressive strength of PF reinforced with 5 wt% CNTs-COOH was enhanced by 12%.

Surface hardness is one of the most important factors that governs materials’ wear resistance. A harder surface often has a higher wear resistance. Figure 5 also shows the Rockwell hardness of the specimens. The incorporation of modified CNTs enhanced the hardness of the PF composites, with the highest hardness being obtained for the CNTs-

Figure 5. Dependence of the mechanical properties on the CNTs-COOH of PF composites.

Figure 6. Dependence of the friction coefficient on the CNTs-COOH of PF composites.
COOH content of 2 wt%. However, the composites with higher content (above 2 wt%) of CNTs-COOH exhibited decreasing hardness, which may results from the fact that with the increase of CNTs content, poorer dispersion of CNTs in PF matrix and defects such as CNTs agglomeration are more inclined to appear.

Figure 7. Dependence of the wear rate on the CNTs-COOH of PF composites.

Figure 8. The SEM morphologies of the worn surfaces of PF and PF nanocomposites: (a) PF; (b) PF + 1 wt% CNTs-COOH; (c) PF + 2 wt% CNTs-COOH; (d) PF + 3 wt% CNTs-COOH; (e) PF + 5 wt% CNTs-COOH.
3.3. Friction and Wear Properties

The friction coefficient and wear rate of surface treated CNTs reinforced PF composites were investigated under a load of 100N, a sliding velocity of 0.42 m/s, and dry conditions. Figure 6 shows the dependence of the friction coefficient of CNTs-COOH reinforced PF composites on CNTs content. Compared with the pure PF, the friction coefficients of the modified CNTs reinforced PF composites decreased with the increase of CNTs-COOH content. When the content reached 5 wt%, the friction coefficient of the composites decreased about 10%, from 0.40 to 0.36.

Figure 7 shows the dependence of wear rate of modified CNTs reinforced PF composites on CNTs-COOH content. It can be seen that the incorporation of CNTs-COOH could reduce the wear rate of PF. It was also found that PF composite reinforced with 5 wt% CNTs-COOH exhibited the best antiwear property even though it had the lowest surface hardness, the wear rate of the composites decreased about 43%, from $4.74 \times 10^{-6}$ mm$^3$/N × m to $2.69 \times 10^{-6}$ mm$^3$/N × m.

3.4. Discussion

To make clear the tribological mechanisms of surface treated CNTs reinforced PF, the morphologies of the worn surfaces and debris of the nanocomposites blocks were observed.
by scanning electron microscopy and the transfer films formed on the surface of the counterpart ring were investigated by optical microscopy. The SEM images of the worn surfaces of PF and PF nanocomposites are shown in Fig. 8. The worn surface of pure PF (Fig. 8a) is rough, displaying holes and plough marks, indicating fatigue wear and ploughing. Since PF is somewhat brittle, it should crack and break away easily from the surface of the specimen and form brittle cleavage fracture surfaces. The fragments could generate third body friction, which would lead to higher friction and wear rate. By contrast, the scuffing on the worn surfaces of the PF nanocomposites decreased with increasing CNTs-COOH content, and relatively smooth surfaces can be observed (Figs. 8b–8e). However, the worn surfaces of composites with higher content of CNTs-COOH showed small pieces of films (Figs. 8d–8e).

Figure 9 shows optical micrographs of the transfer films formed on the surface of the counterpart ring. The transfer film on the worn surface of the counterpart ring sliding against the pure PF was rough and sparse (Fig. 9a), which corresponds to the poor wear-resistance of the pure PF composite. Similarly, the transfer films formed from 1 wt%, 2 wt%, and 3 wt% CNTs-COOH filled PF composite were rough and many plucked film scars appeared on the counterpart ring surface (Figs. 9b–9d). Contrary to the above, the transfer film formed from 5 wt% CNTs-COOH filled PF composite is comparatively thin, uniform, and continuous with only a few plucked scars on the counterpart surface (Fig. 9e), which conforms to the best wear resistance of the 5 wt% CNTs-COOH filled PF composite despite its low hardness.
Wear debris is a product of frictional experiments, and it is helpful to evaluate it to comprehend the friction and wear mechanisms. Figure 10 shows the morphologies of the wear debris of the nanocomposites. The debris size of the PF composites showed a downward trend with the increasing weight percentage of CNTs-COOH, which agreed with the decreasing of the wear rate of the modified CNTs filled PF composites.

4. Conclusions

PF composites reinforced with CNTs that had undergone oxidation were prepared by in situ polymerization method. The tribological properties of PF composites were investigated by a block-on-ring friction and wear tester. The friction and wear mechanism was discussed by analyzing the worn surface, wear debris, and transfer films. The main conclusions are as follows:

1) FTIR and TGA results indicated that –COOH groups were successfully introduced on the surface of CNTs through oxidation.
2) The addition of modified CNTs increased the mechanical properties of PF nanocomposites. The highest Rockwell hardness was obtained at the CNTs-COOH content of 2 wt%, while the highest compressive strength was at 5 wt%.
3) The incorporation of CNTs-COOH into PF led to a significant improvement of the tribological properties. The composite with 5 wt% CNTs-COOH showed the lowest friction coefficient and wear rate.

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