Synthesis of Polyacrylamide-Wrapped Carbon Nanotubes and Their Lubrication Properties as Water-Based Fluids

Yifeng Liu, Wenchao Guan, Xuefeng Li, Mingxing Huang

Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT: Carbon nanotubes (CNTs) wrapped by polyacrylamide (PAM) were synthesized through the *in situ* free-radical polymerization of acrylamide in the presence of the CNTs. Transmission electron microscopy was used to characterize the synthetic CNTs/PAM. This product dissolved easily in water. The effects of the synthetic product as an additive on the load-carrying capacity and antiwear behavior of a water-based fluid were investigated with a four-ball tribotester. The worn surface images of the steel balls were observed by scanning electron microscopy. The results showed that CNTs/PAM at a certain concentration in the base stock effectively raised the load-carrying capacity and antiwear ability. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1–4, 2007

Key words: additives; core-shell polymers; water-soluble polymers

INTRODUCTION

Since Iijima[1] discovered carbon nanotubes (CNTs) in 1991, their usefulness in the fields of mechanics, photics, electrics, magnetics,[2–6] and so on has been revealed. The unique tubelike structures of CNTs make them have high load-carrying capacities (P_B's). However, there is no good solvent that can dissolve them;[7,8] this dramatically limits the research and exploitation of CNTs as lubricant additives. As shown in the literature, compounds containing nitrogen have high-load bearing capacities, antiwear properties, high heat stabilities, and antierosion properties. In this study, CNTs/polyacrylamide (PAM) were prepared through *in situ* free-radical polymerization. The CNTs' hard tubelike structure with soft and elasticity modifying polymer links effectively improved the antiwear properties and P_B values. Their lubrication properties as aqueous additives were evaluated with a four-ball tribotester.

EXPERIMENTAL

Synthesis of CNTs/PAM

Multiwall CNTs were produced via the chemical vapor deposition method and purified with methods similar to those reported in the literature.[9] CNT samples (300 mg) were suspended in an aqueous solution of hydrofluoric acid (20 wt %, 60 mL), exposed to prolonged sonication for 5 h, and filtered. The remaining solids were washed repeatedly with distilled water. The CNT samples were thus refluxed with an aqueous solution of nitric acid (22 wt %, 60 mL) for 10 h. The mixture was centrifuged, and the remaining solids were washed repeatedly with distilled water until the pH value of the CNT solution approached 7 and were then dried in a vacuum oven to eliminate impurities.

CNTs/PAM were synthesized by typical free-radical polymerization under the same conditions as listed in ref. 10. Mixtures of 2 g of acrylamide, 0.5 g of poly(ethylene glycol), 1 mL of triethanolamine, 100 mg of $(NH_4)_2S_2O_8$, and 30 mL of distilled water containing 50 mg of CNTs were added to a 100-mL reaction flask. After it was heated at 70°C for 10 h, the solution was precipitated with 100 mL of acetone, filtered, and dried.

The morphology of the CNTs/PAM in water was measured by a Tecnai model G2 20 (FEI, Holland) transmission electron microscope with a voltage of 200 kV.

Measurement of the tribological properties

The lubrication properties of CNTs/PAM were measured with a MQ-800 four-ball tribotester at a rotational speed of 1450 rpm at room temperature. We obtained the extreme pressure value by referring to the GB3142-82 standard; the wear-scar diameter (WSD) was measured under a load of 400 N for a test duration of 30 min; the friction coefficient was measured under a load of 400 N for a test duration of 10 s.

Correspondence to: W. Guan (wcguan@hust.edu.cn).
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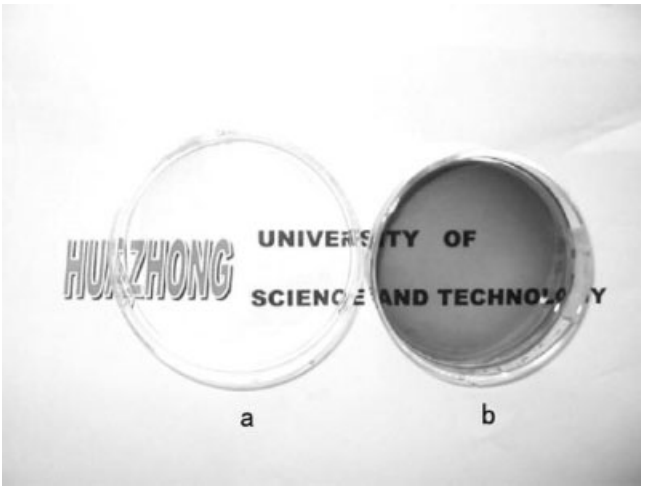


Figure 1 (a) PAM and (b) CNT/PAM water solution.

The stainless steel balls used in the tests were made of GCr15 bearing steel with 64–66 surface Hardness Rockwell C scale (HRC) hardness and 0.012 μm of surface roughness. The base stock was an aqueous solution of 2 wt % triethanolamine and 0.5 wt % OPZ (which we prepared). The CNTs/PAM were used as a lubricant additive of the base stock.

Analyses of the worn surfaces

The wear-scar images were visualized with a Quanta 200 (FEI, Holland) scanning electron microscope at a voltage of 30 kV.

RESULTS AND DISCUSSION

Configuration analyses

CNTs/PAM were soluble in water, appearing as a black transparent solution, but the solution of PAM was colorless (Fig. 1). Transmission electron microscopy analysis indicated that the CNTs of CNTs/PAM appeared as a core wrapped by polymer. Outside of the CNT wall, there was a layer of polymer-like shadow, but purified CNTs did not appear (Fig. 2). So, they could considered to have a core–shell type structure.

Lubrication properties of CNTs/PAM

The relationship between the concentration of the CNTs/PAM as additives to the base stock and the P_B values is given in Figure 3. CNTs/PAM significantly improved the extreme pressure of the stock. The P_B value of the base stock was 520 N, and the P_B value increased gradually with increasing concentration of CNTs/PAM. When the concentration reached 0.3 wt %, the P_B value reached a maximum of 730 N. When the concentration of CNTs/PAM was increased

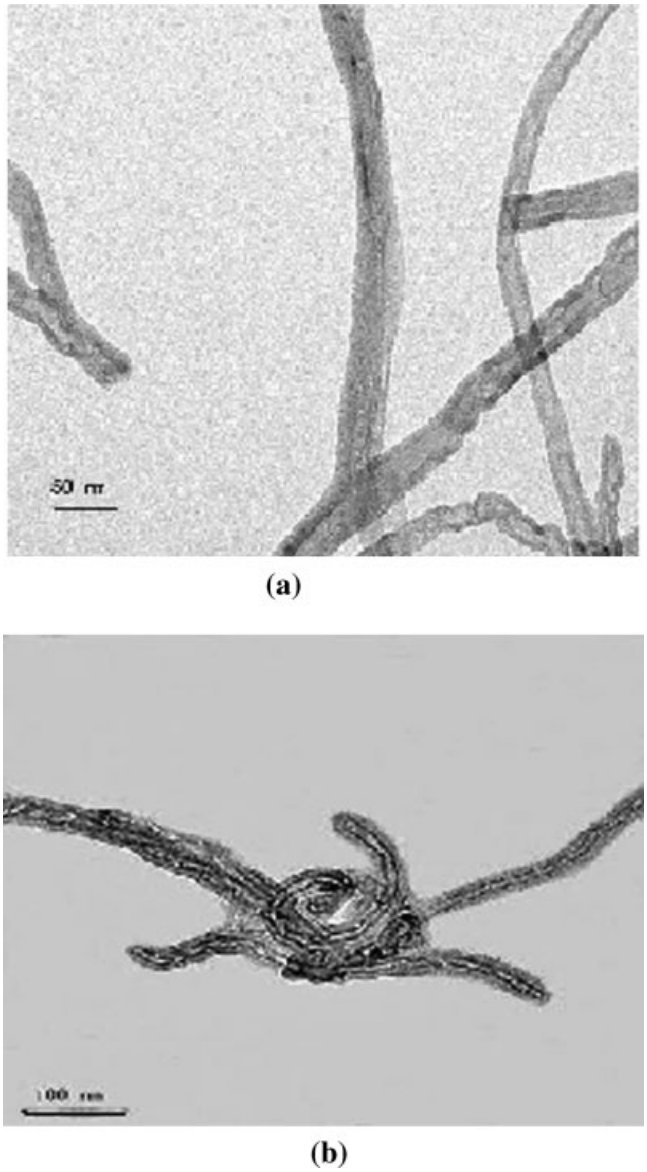


Figure 2 Typical transmission electron microscopy images of (a) CNTs and (b) CNTs/PAM.

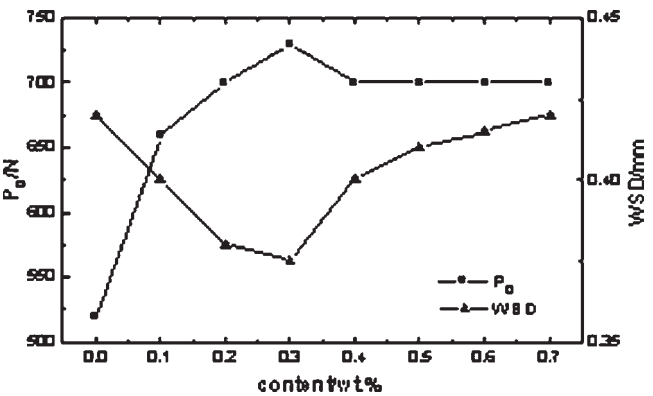


Figure 3 Effect of the CNT/PAM content on P_B and WSD.

TABLE I
Friction Coefficient Versus Concentration of the CNTs/PAM

Concentration (wt %)	0	0.1	0.2	0.3	0.5
Friction coefficient	0.052	0.045	0.043	0.046	0.048

above 0.3 wt %, the P_B value decreased slowly and stabilized at 710 N. The results indicate that CNTs/PAM strengthened P_B of the stock.

The relationship between concentrations of CNTs/PAM as additives to the base stock and WSD are also shown in Figure 3. The addition of CNTs/PAM decreased WSD of the base stock at low weight percentages of additive. When the CNT/PAM concentration reached 0.3%, WSD was minimized at 0.375 mm. When the concentration was above 0.3 wt %, WSD increased slowly. From the perspective of antiwear, the appropriate concentration effectively increased the antiwear properties.

The relationship between the concentration of CNTs/PAM as additives to the base stock and the friction coefficient is shown in Table I. With increasing concentration of CNTs/PAM, the friction coefficient changed. When the CNT/PAM concentration reached 0.2%, the friction coefficient was at a minimum of 0.043.

The dependence of friction time on WSD is shown in Figure 4. After 5 min, WSD of the base stock with 0.3 wt % CNTs/PAM was almost the same as WSD of 30 min of rubbing. However, WSD of base stock without CNTs/PAM was the same as WSD of 30 min of rubbing after 16 min of rubbing. The difference in friction time versus WSD further indicated that the presence of CNTs/PAM strengthened the antiwear performance of the base stock. As shown in Figure 4, WSD increased with increasing load.

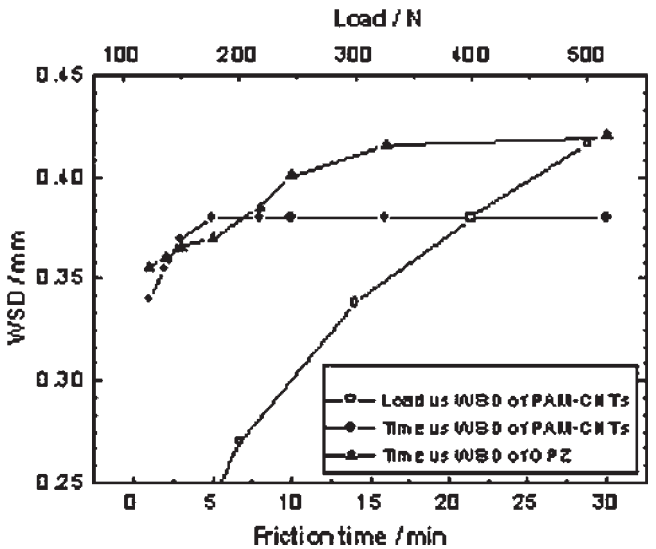
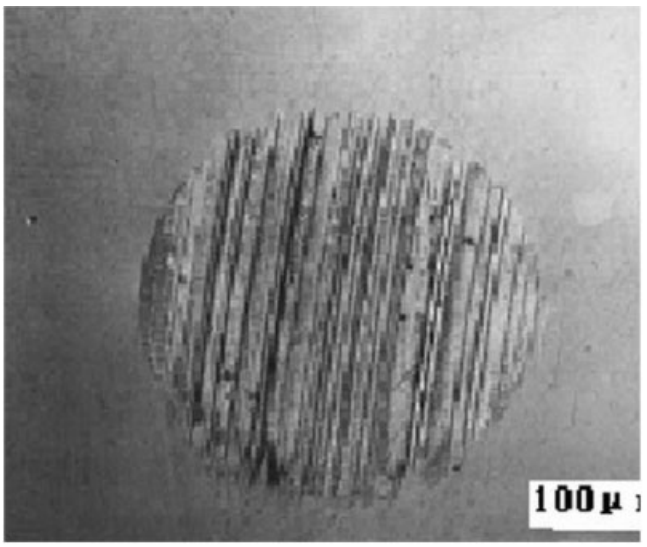


Figure 4 Effect of load and friction time on WSD.

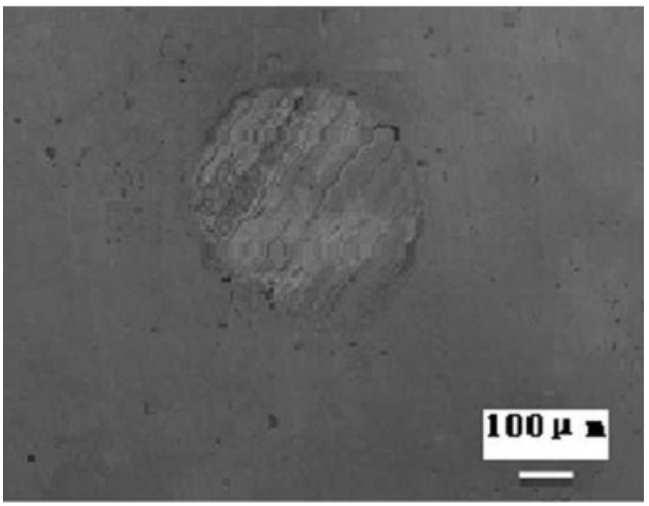
Analyses of the worn surfaces

The worn scars in the sole base stock and the base stock with an additional 0.3 wt % of compound are shown in Figures 5 and 6(a,b). The worn scar obtained with compound additive was obviously smaller and smoother than that obtained without compound additive. In other words, the compound additive improved the microcosmic wear conditions.

The physical structure of the CNT/PAM compound can be described as follows. The core was very hard CNTs, and the shell was polymer of neat acrylamide, which was relatively soft but very elastic. On the basis of these experimental results, the lubrication mechanism of the compound was deduced: the compound played the role of a molecular ball



(a)



(b)

Figure 5 Morphology of the worn surface lubricated with (a) the base stock and (b) the base stock with 0.3 wt % CNTs/PAM.

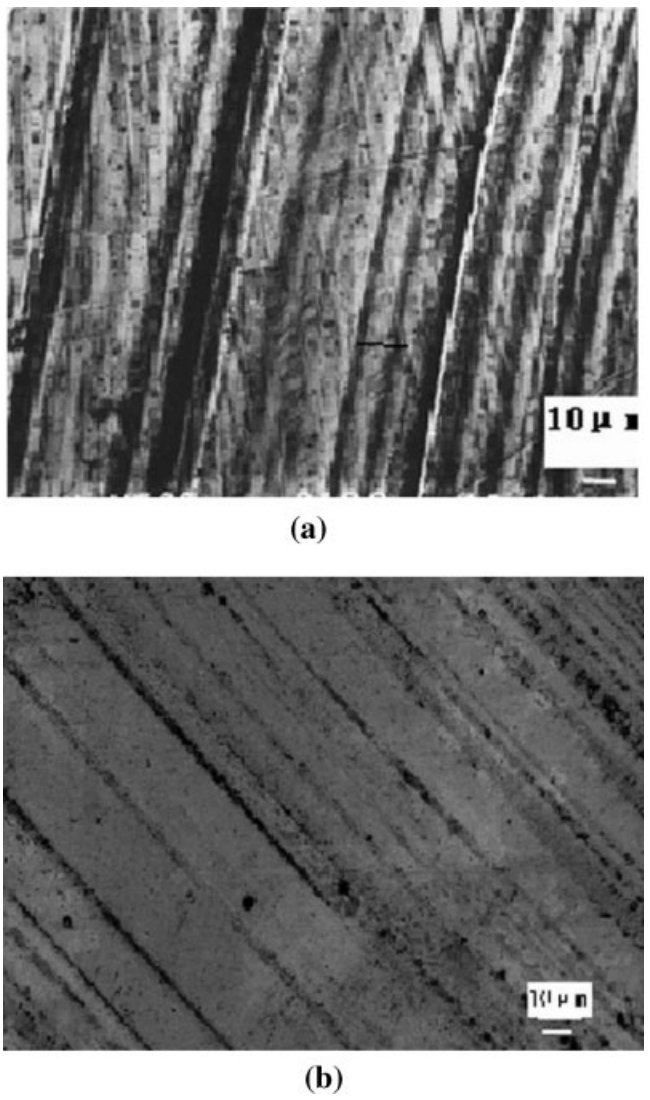


Figure 6 Partial morphology of the worn surface (a) lubricated and (b) lubricated with the base stock with 0.3 wt % CNTs/PAM.

bearing, supporting and isolating two relative motions. So, the compound obviously improved P_B of base stock.

CONCLUSIONS

A novel CNT/PAM compound was synthesized, which was soluble in water and appeared as a black transparentsolution.

The experimental results from the four-ball tribotester showed that the compound as an additive in the base stock (2 wt % of triethanolamine and 0.5 wt % of OPZ aqueous solution) raised P_B and improved the antiwear abilities. Excessive additive was disadvantageous to the antiwear properties and P_B.

Scanning electron microscopy analyses indicated that the worn scar obtained with only the base stock exhibited a sharp grooving and serious pullout phenomenon, whereas mild scratches were observed in the presence of the CNT/PAM compound.

The lubrication mechanism of the compound was likely due to its core–shell structure as a molecular ball bearing. This caused microcosmic elastic rolling between the two rubbing surfaces.

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