Preparation and tribological properties of poly(methyl methacrylate)/multi-walled carbon nanotubes composites

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Since the discovery of carbon nanotubes (CNTs) by Iijima [1], the novel mechanical properties and potential applications have been proposed and investigated. There are two main types of CNTs: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). CNTs are the most typical one-dimensional nanomaterial [2] with excellent mechanical properties. The Young's modulus of a SWNTs might be as high as 1 TPa [3]. Measured Young's moduli and tensile strengths of MWNTs are as high as 950 and 63 GPa, respectively [4, 5]. CNTs are able to withstand repeated bending, buckling, and twisting, which result in building lightweight composites matrix. So far, the CNTs-based polymer composites have been studied intensively [6–10].

Poly methyl methacrylate (PMMA) is an important thermoplastic and widely used in architecture, automotive, air and railway transport systems because of its favorable properties. However, its use in some applications is limited by its relatively worse tribological performance (e.g. erosion or abrasion damage of windows). Due to the effects of the reinforcement of MWNTs, they can be used to fabricate the composites with excellent tribological properties. The tribological behaviors of the copper based [11], carbon based [12], Ni-P based [13, 14], polyimide based [15] and polytetrafluoroethylene based [16] CNTs composites have been investigated. MWNTs-based composites exhibited lower friction coefficient and wear rate compared with the pure matrix. So it can be expected that the tribological properties of PMMA/MWNTs composites would be also improved significantly in spite of reduced transparency. However, few reports have been available on the tribological behavior of PMMA/MWNTs composites.

In this paper, PMMA/MWNTs composites with excellent tribological properties were prepared by means of *in situ* polymerization process. To the best of our knowledge, our work firstly dealt with the tribological behaviors of PMMA/MWNTs composites. The effects of MWNTs reinforcing on the tribological properties of the composites were investigated. The improved friction and wear mechanisms were also discussed.

The MWNTs used in this work were synthesized by the catalytic chemical vapor deposition (CVD) method. The details of the growth and purification of MWNTs have been described in previous works [13]. As-synthesized MWNTs with a purity exceeding 98% are obtained after subsequent purification treatment. The purified MWNTs were characterized by a transmission electron microscope (TEM, JEM-1200EX, Japan). Fig. 1 shows TEM image of MWNTs. As is shown, MWNTs are typically central hollow tubes. The outer diameters of most MWNTs range from 10 to 20 nm, and their lengths are several micrometers.

The analytical grade methyl methacrylate (MMA) monomer was dried and purified by distilling under reduced pressure. PMMA was produced in a process of addition polymerization. The free radical initiator, benzoyl peroxide (BPO), was added into MMA at the reaction temperature (85–90 °C). With the initiation of the free radicals, the C=C double bonds in MMA molecules were opened, and then linked each other to form long chain of PMMA molecules [8]. The reaction lasted for 1 hr before MWNTs were added into reacting mixtures. Then the viscous mixtures were fully mixed ultrasonically, stirred for 0.5 hr. In this case, PMMA molecules could grow more and MWNTs would be better dispersed in polymer matrix. After being poured into the mold, the mixture was heated at a rate of 1 °C/min to 40 °C, held there for 20 hr, then stepped up to 105 °C for 3 hr, and lastly cooled to room temperature in the mold. Thus the homogeneous mixtures were molded into the block specimens. Finally the resultant 30 × 7 × 6 mm block specimens were prepared for friction and wear tests. PMMA/MWNTs samples were also synthesized by the same means using 0.05, 0.1, 0.25, 0.75, 1, 1.5, 2.5 wt.% of MWNTs material (weight percent with respect to MMA monomer).

The friction and wear tests of PMMA/MWNTs composites were conducted on a ring-on-block M-2000 model friction and wear tester under dry conditions. The contact schematic diagram of the frictional couple is shown in Fig. 2. The plain carbon steel ring (hardness of HRC 48–50) in a diameter of 40 mm was used as the counterpart. Sliding was performed under ambient

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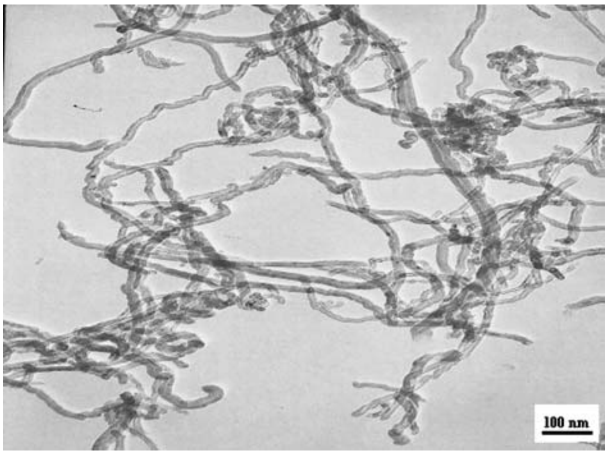

Figure 1 Typical TEM image of MWNTs.

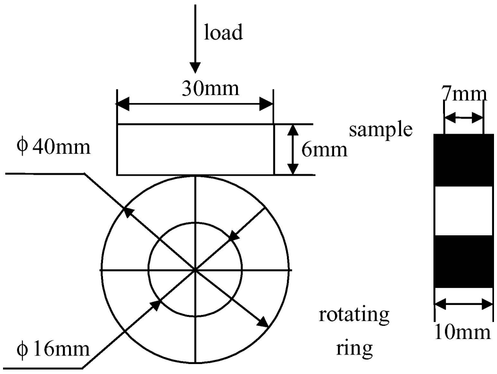

Figure 2 The contact schematic diagram of the frictional couple for M-2000 friction and wear tester.

conditions at sliding velocity of 0.431 m/s, normal load of 50 N, and test duration of 1 hr. The ambient temperature was roughly 25 °C and the relative humidity about 40 ± 10%. Before each test, the surfaces of the block specimens and the counterpart ring were abraded with No. 900 water-abrasive paper and cleaned with cotton dipped in acetone. The resultant surface roughness of both the specimen and the stainless steel ring ranged from 0.2 to 0.52 μm. The friction force was measured using a torque shaft equipped with strain gauges. The friction coefficient was recorded under steady-state conditions by a personal computer, which controlled the wear and friction tester. After each test, the width of the wear scar on the block specimens was measured with a digital optical microscope with an accuracy of 0.01 mm, then the wear volume loss V of the block specimen calculated from the relationship

$$V = B\left[\frac{\pi R^2}{180}\arcsin\left(\frac{b}{2R}\right) - \frac{b}{2}\sqrt{R^2 - \frac{b^2}{4}}\right](\text{mm}^3)$$

where V refers to the volume loss (mm^3), B to the width of the block specimen (mm), R to the radius of the steel ring (mm), and b to the width of the wear scar (mm). According to the volume loss (V), the wear rate (ω) was calculated from the relationship

$$\omega = \frac{V}{N \times L}(\text{mm}^3\text{N}^{-1}\text{m}^{-1})$$

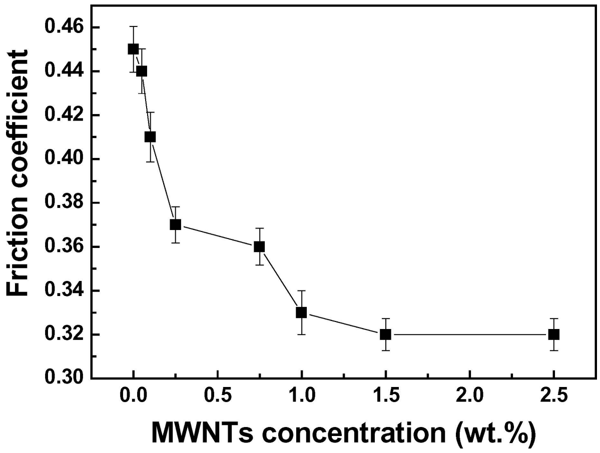

Figure 3 The friction coefficients of PMMA/MWNTs composites as a function of MWNTs concentration.

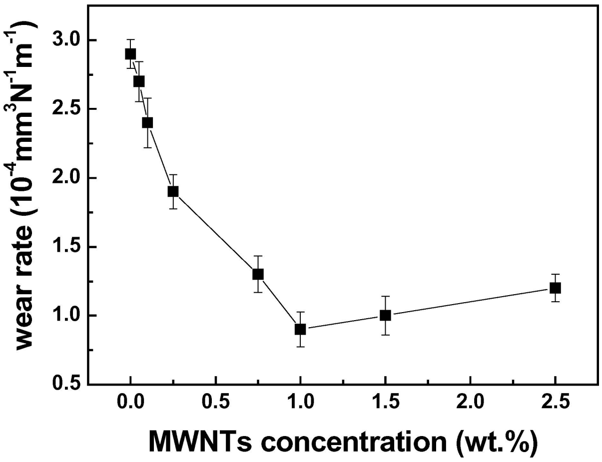

Figure 4 Effects of MWNTs concentration on wear rate of PMMA/MWNTs composites.

where N is the applied load (N) and L is the sliding distance (m). Three replicate friction and wear tests were carried out so as to minimize data scattering, and the average of the three replicate test results was reported in this paper. The deviation of the data of the replicate friction and wear test was 10%.

Fig. 3 shows the friction coefficients of PMMA/MWNTs composites as a function of MWNTs concentration. It is apparent that the friction coefficients of the composites decrease with increasing MWNTs concentration. The friction coefficients values of the composites sharply decrease when the MWNTs content is below 1.0 wt.%. As the concentration of MWNTs is higher, the friction coefficient of the composites becomes lower. This effect of MWNTs on the friction coefficients is in good agreement with that the results for Ni-P-CNTs composites coatings in our previous work [13]. Moreover, the variation of the friction coefficients reaches a relatively stable value when the MWNTs concentration surpasses 1.0 wt.%.

Fig. 4 indicates the effects of MWNTs concentration on wear rate of PMMA/MWNTs composites. It can be clearly seen that the incorporation of MWNTs significantly decreases the wear rate of PMMA. The wear rate of the composites with only from 0 to 1.0 wt.% of MWNTs concentration decreases sharply

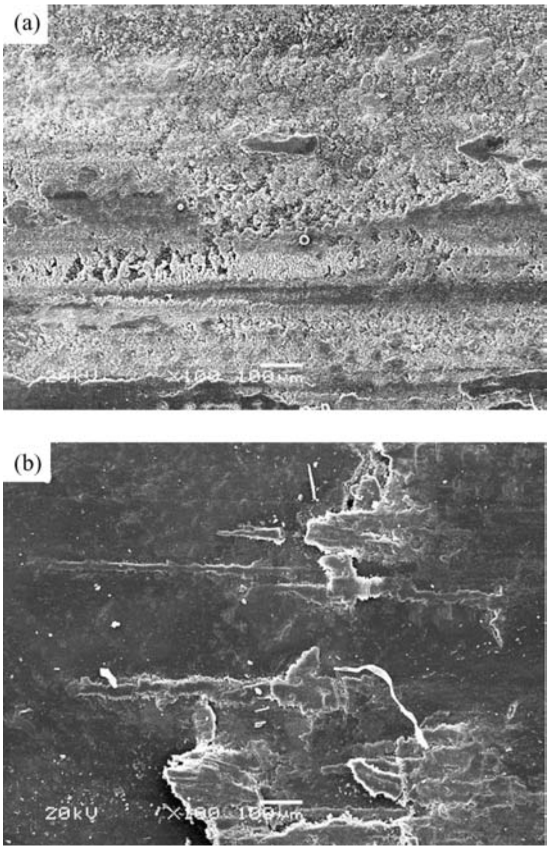

Figure 5 SEM images of the typical worn surfaces of PMMA (a) and PMMA/MWNTs (b).

from 2.9×10^{-4} to 0.9×10^{-5} mm^3 N^{-1} m^{-1}. The wear rate of PMMA/1.0 wt.% MWNTs composites is the smallest. However, the wear rate of the composites increases slightly when the MWNTs concentration exceeds 1.0 wt.%, which can be attributed to the conglomeration of MWNTs in the PMMA matrix.

In order to investigate the tribological behaviors of PMMA/MWNTs composites, the morphologies of the worn surfaces of the composites blocks were observed using scanning electron microscope (SEM, JOEL, JSM-5600LV). The SEM images of the worn surfaces of PMMA and PMMA/MWNTs composites under same testing conditions are shown in Fig. 5a and b, respectively. As shown in Fig. 5, PMMA/1.0 wt.% MWNTs composites have smoother worn surface than the pure PMMA. The phenomena indicate a change in the wear mechanism of PMMA. The worn surface of pure PMMA shows signs of adhesion and abrasive wear (Fig. 5a). The corresponding worn surface is very rough, displaying plucked and ploughed marks which are indicative of adhesive wear and ploughing. It also can be seen that more obvious ploughed furrows appear on the worn surface, which means the relatively poorer wear resistance. By contrast, the scuffing and adhesion on the worn surface of the PMMA/1.0 wt.% MWNTs composites is considerably reduced (Fig. 5b). The result suggests that both applied stress during indentation and frictional stresses transfer to the MWNTs, which might contribute to increasing the local compressive and shear strength [17]. The relatively smooth, uniform, and compact worn surface is formed in this case, which results in agreeing well with the considerably increased wear resistance of PMMA/MWNTs composites. Therefore, it can be deduced that the incorporation of MWNTs contributes to restrain the scuffing and adhesion of the PMMA matrix in sliding against the steel counter face. Subsequently the PMMA/MWNTs composites show much better wear resistance than the pure PMMA.

All in all, the mechanisms of the prominent tribological properties of PMMA/MWNTs composites may be attributed to the following factors. First, the incorporation of MWNTs helps to increase the mechanical properties of the composites. Hence the composites show much better wear-resistance than pure PMMA. Jia *et al.* [8] and Jin *et al.* [10] have stated that the mechanical behaviors of PMMA/MWNTs were significantly increased by the incorporation of nanotubes. Second, MWNTs dispersed uniformly in the composites can serve as medium and prevent the close touch of the two contact surfaces between the steel counter face resulting in slowing the wear rate and reducing the friction coefficient. Moreover, MWNTs are released from the composites during sliding and transferred to the interface between the composites and the steel counter face. So the self-lubricate properties of MWNTs also result in reduction of the wear rate and the friction coefficient. Similar observations were made with Ni-P-CNTs composite coatings [13].

For CNTs composite films [7] systems, a rather higher concentration (∼15 wt.% of CNTs) is needed for best performance. Two factors may be responsible for the different concentration of CNTs in the composites. First, the structures of the composites decide the different concentration of CNTs. The composite films probably contain more CNTs agglomeration. The bonding energy in the composite films is also weak. In our work PMMA/MWNTs composites are the bulk composites, which contain the less MWNTs agglomeration and the stronger bonding energy between the polymer matrix and MWNTs. Similar to our work, Jin *et al.* [18] have stated MWNTs concentration also ranged from 1 to 3 wt.%. Second, different preparation methods result in the difference concentration of CNTs. PMMA/MWNTs composites in our work were fabricated by means of *in situ* polymerization process, while the composite films [7] were obtained by solution mixing method. We speculate that there are more physical adsorption and weak bond force in the composite films. However, because the stiff bulk composites contain more chemical bond junctions, bulk composites are unavailable when adding MWNTs more than 4 wt.%.

Herein PMMA/MWNTs composites with different concentrations of MWNTs were prepared by *in situ* polymerization process. The tribological properties were investigated using a ring-on-block under dry conditions. It was found that MWNTs significantly decreased their friction coefficient and increased the wear resistance of composites. We also found that PMMA/MWNTs composites with 1.0 wt.% MWNTs content exhibited both the smallest wear rate and the lower friction coefficient. The significant improvements on the tribological properties of PMMA/MWNTs composites are attributed to excellent mechanical properties and unmatched topological tubular structure of MWNTs. Therefore, the wear resistance of composites is also improved. During the course of wear and friction, MWNTs dispersed uniformly in the composites can serve as medium, preventing the close touch of the two surfaces between the applied loading and the composites. Moreover, the self-lubricate properties of MWNTs result in reduction of the wear rate and the friction coefficient.

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