Preparation and Tribological Properties of Poly(methyl methacrylate)/Styrene/MWNTs Copolymer Nanocomposites

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ABSTRACT: Poly(methyl methacrylate)/styrene/multi-walled carbon nanotubes (PMMA/PS/MWNTs) copolymer nanocomposites with different contents have been prepared successfully by means of *in situ* polymerization method. The structure and the microhardness of PMMA/PS/MWNTs copolymer nanocomposites were characterized. The tribological behaviors of the copolymer nanocomposites were investigated by a friction and wear tester under dry conditions. The relative humidity of the air was about 50% ± 10%. Comparing with pure PMMA/PS copolymer, the copolymer nanocomposites showed not only better wear resistance but also smaller friction coefficient. MWNTs could help the nanocomposites dramatically improve the wear resistance property. The mechanisms of the improvements on the tribological properties of the PMMA/PS/MWNTs copolymer nanocomposites were also discussed in detail. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1675–1679, 2008

Key words: multi-walled carbon nanotubes; PMMA/PS copolymer; nanocomposites; wear; block copolymers; composites; copolymerization; polystyrene

INTRODUCTION

Poly (methyl methacrylate) (PMMA) and Polystyrene (PS) are all important thermoplastic and widely used in many kinds of fields. Because PMMA and PS are produced by free radical polymerization from the monomer, PMMA/PS copolymer is easy to be fabricated to improve the properties of the pure PMMA or PS. PMMA/PS copolymer is widely used in architecture, automotive, air and railway transport fields because of its favorable properties. However, its use in some applications is limited by its relatively worse tribological properties. Carbon nanotubes (CNTs)[1,2] have excellent mechanical, electrical, thermal properties. Single-walled nanotubes (SWNTs) consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. Multi-walled nanotubes (MWNTs) comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk.[3] Measured Young's moduli and tensile strengths of MWNTs are as high as 950 GPa and 63 GPa, respectively.[4,5] The tensile strength of CNTs are up to 100 times stronger than steel, whereas its density is one-sixth to one-seventh that of steel.[6] So CNTs are expected to be a potential candidate as reinforcement for polymeric materials and build lightweight composites matrix. So far, the CNTs-based polymer composites have been studied intensively.[7–17] Because of the effects of the reinforcement, MWNTs can be used to fabricate the composites with excellent tribological properties. The tribological behaviors of the epoxy based,[18,19] polyimide based[20] and polytetrafluoroethylene based[21] CNTs composites have been investigated.

It was found that CNTs-based nanocomposites exhibited lower friction coefficient and wear rate compared with the pure substrates matrix, which resulted in the improvements on reduced friction and wear resistance. So it can be expected that the tribological properties of PMMA/PS/MWNTs copolymer nanocomposites would be also improved significantly in spite of reduced transparency. However, few reports have been available on the tribological behavior of PMMA/PS/MWNTs copolymer nanocomposites.

Considering the above factors, PMMA/PS/MWNTs copolymer nanocomposites 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/PS/MWNTs copolymer nanocomposites. The effects of MWNTs reinforcing on the tribological properties of the copolymer nanocomposites were investigated. The improved friction and wear mechanisms were also discussed.

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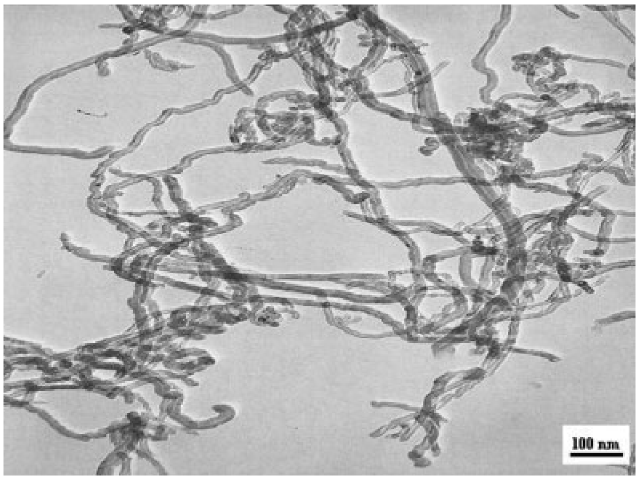

Figure 1 Typical TEM image of MWNTs.

EXPERIMENTAL

The analytical grade methyl methacrylate (MMA) monomer and styrene (ST) monomer were dried and purified by distilling under reduced pressure before use. 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.[22] The purified MWNTs were characterized by a transmission electron microscope (TEM, JEM-1200EX, Japan). Figure 1 shows TEM image of MWNTs. As is shown, the average outer diameter of MWNTs was about 10–20 nm and the length range was 1–2 μm. The structure of MWNTs are obviously central hollow tubes and the tube's surface is very clean.

PMMA/PS copolymer was produced in a process of addition polymerization. The reactivity ratios of the two monomers are similar, which also helps to fabricate the copolymer. The free radical initiator, BPO molecule formed two free radicals during the reaction. According to previous report,[8] with the effect of these free radicals, the C=C double bonds in MMA and ST would be opened, and then linked with each other to form long chain molecules. The MMA/ST (1 mol : 1 mol) and the benzoyl peroxide (BPO) were mixed and the reaction lasted for about 40 min at the temperature 358–363 K. Then the viscous mixture was poured to a tube and put into the vacuum oven for removing the bubbles in the mixture. Finally, the N_2 was put into the tube and sealed under the gaslight. After being poured into the tube, the mixture was heated at a rate of 1 K/min to 343 K for 72 h and lastly cooled to room temperature in the water oven. Thus, the homogeneously transparent mixture was obtained. The PMMA/PS/MWNTs composites were synthesized by the same means using 0.1, 0.5, 1.0, 1.5, 2.0, 3.0 wt % of CNTs material (weight percent with respect to monomer). The reaction lasted for 40 min before MWNTs were added into reacting mixtures. Then the viscous mixtures were fully mixed ultrasonically, stirred for 10 min. In this case, PMMA/PS copolymer could grow more and MWNTs would be better dispersed in copolymer matrix. Finally, the tube was broken and the cylindrical composites were obtained. The cylindrical composites were incised and the $30 \times 7 \times 6$ mm^3 block specimens were prepared for friction and wear tests.

The structure of PMMA/PS/MWNTs copolymer nanocomposites was characterized by field emission scanning electron microscopy (FE-SEM JSM-6335F-NT).

The microhardness measurements of specimens were performed using a microhardness indenter (VDMH-5 Version 2.01, China). A load of 10 gf with a loading time of 5 s was used. Each specimen was measured five times, respectively. The average result of measurements was taken as the reported hardness value in this article.

The friction and wear tests of PMMA/PS/MWNTs copolymer nanocomposites were conducted on an ring-on-block M-2000 model friction and wear tester under dry conditions. The contact schematic diagram of the frictional couple is shown in Figure 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 conditions at sliding velocity of 0.428 m/s, normal load of 50*N*, and test duration of 1 h. The ambient temperature was roughly 298 K and the relative humidity about 50% ± 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 friction force was measured using a torque shaft equipped with strain gauges. The friction coefficient was recorded under

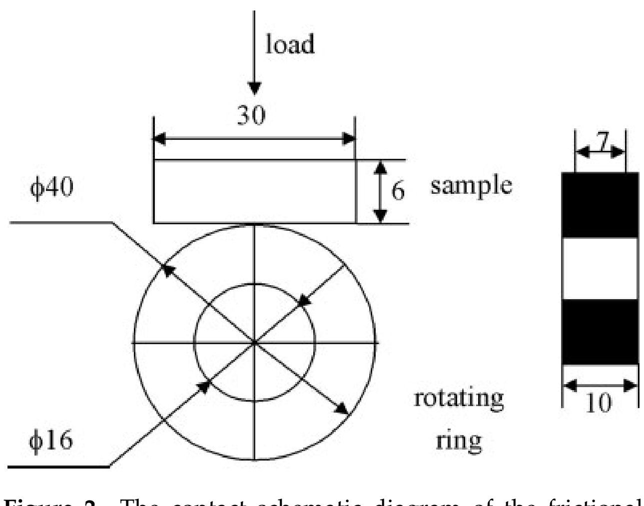

Figure 2 The contact schematic diagram of the frictional couple for M-2000 friction and wear tester.

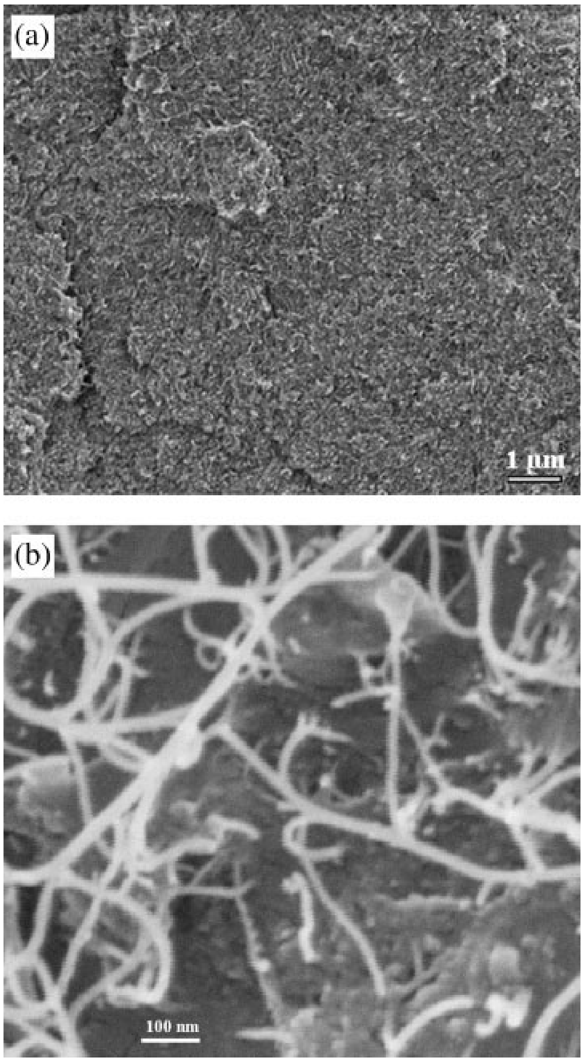

Figure 3 The FE-SEM images of fractured surface of the PMMA/PS/MWNTs copolymer nanocomposites: (a) low magnification; (b) high magnification.

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) and the wear rate (ω) of the block specimen were calculated. The average of the three replicate test results was reported in this article.

To explain the effects of MWNTs on tribological behaviors of PMMA/PS/MWNTs copolymer nanocomposites, the morphologies of the worn surfaces of the composites blocks were observed using scanning electron microscope (SEM, JOEL, JSM-5600LV).

RESULTS AND DISCUSSION

Figure 3 shows FE-SEM images of fractured surface of the PMMA/PS/MWNTs copolymer nanocomposites. The images showed that MWNTs dispersed well in the PMMA/PS copolymer matrix and contacted with the copolymer closely. PMMA/PS/MWNTs copolymer nanocomposites have been prepared successfully by means of *in situ* polymerization method. The *in situ* polymerization method can make the dispersion of MWNTs very good in the PMMA/PS copolymer.

Figure 4 gives the microhardness of PMMA/PS/MWNTs copolymer nanocomposites as a function of MWNTs concentration. According to the previous report,[8] due to the addition of MWNTs, the PMMA/PS/MWNTs composites obtained the better mechanical properties. The phenomena were proved by the increasing of the microhardness of the copolymer. The microhardness of the copolymer nanocomposites increases sharply when the MWNTs content is below 1.5 wt %. The microhardness values decrease slightly when the MWNTs content is above 1.5 wt %. It is attributed to the conglomeration of MWNTs in the PMMA/PS copolymer.

Figure 5 shows the friction coefficients of PMMA/PS/MWNTs copolymer nanocomposites as a function of MWNTs concentration. It can be seen that the friction coefficients of the copolymer composites decrease with increasing MWNTs concentration. The friction coefficients values of the copolymer composites slowly decrease when the MWNTs content is below 1.5%. As the concentration of MWNTs is higher, the friction coefficient of the copolymer composites becomes lower and reaches a relatively stable value.

Figure 6 indicates the effects of MWNTs concentration on wear rate of PMMA/PS/MWNTs copolymer nanocomposites. It can be clearly seen that the incorporation of MWNTs decreases the wear rate of

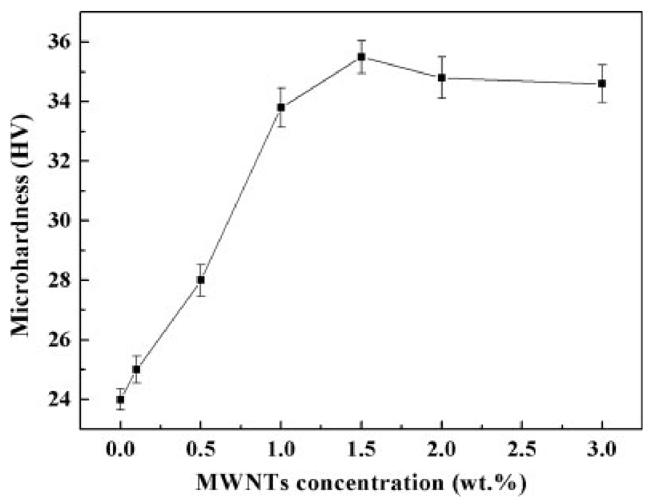

Figure 4 The microhardness of PMMA/PS/MWNTs copolymer nanocomposites as a function of MWNTs concentration.

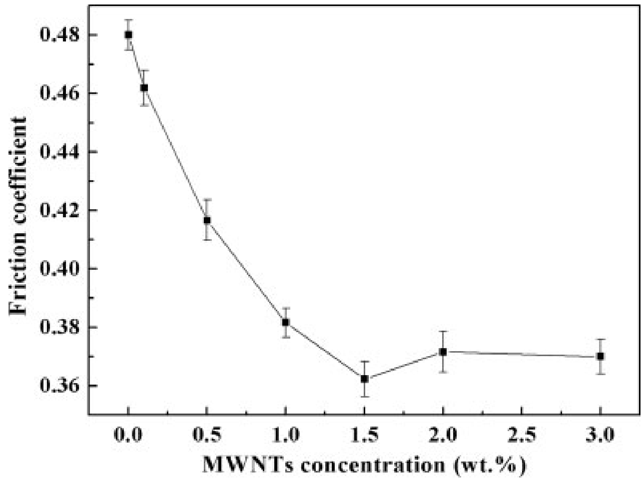

Figure 5 The friction coefficients of PMMA/PS/MWNTs copolymer nanocomposites as a function of MWNTs concentration.

PMMA/PS copolymer. The wear rate of the copolymer composites with only from 0 to 1.5 wt % of MWNTs concentration decreases from 2.3×10^{-4} to 1.3×10^{-4} $mm^3\ N^{-1}\ m^{-1}$. The wear rate of PMMA/PS/1.5 wt % MWNTs copolymer nanocomposites is the smallest. However, the wear rate of the copolymer composites increases slightly when the MWNTs concentration exceeds 1.5 wt %. It may be attributed that MWNTs begins to conglomerate in the PMMA/PS copolymer when the concentration of MWNTs is above 1.5 wt %.

The SEM images of the worn surfaces of PMMA/PS copolymer and PMMA/PS/MWNTs copolymer nanocomposites under same testing conditions are shown in Figure 7(a,b), respectively. As shown in the Figure 7, PMMA/PS/1.5 wt % MWNTs copolymer nanocomposites has smoother worn surface

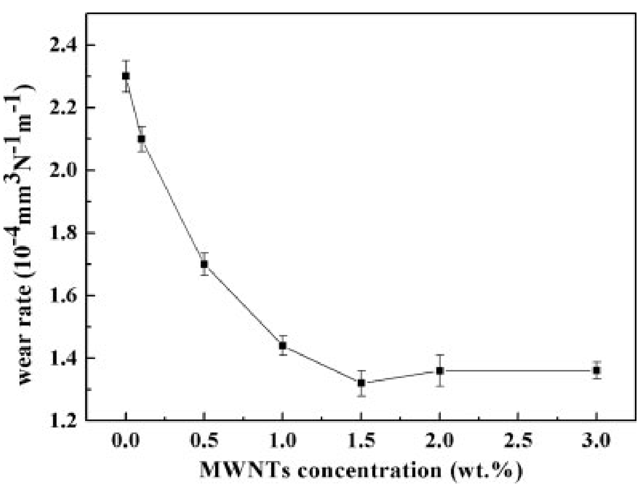

Figure 6 Effects of MWNTs concentration on wear rate of PMMA/PS/MWNTs copolymer nanocomposites.

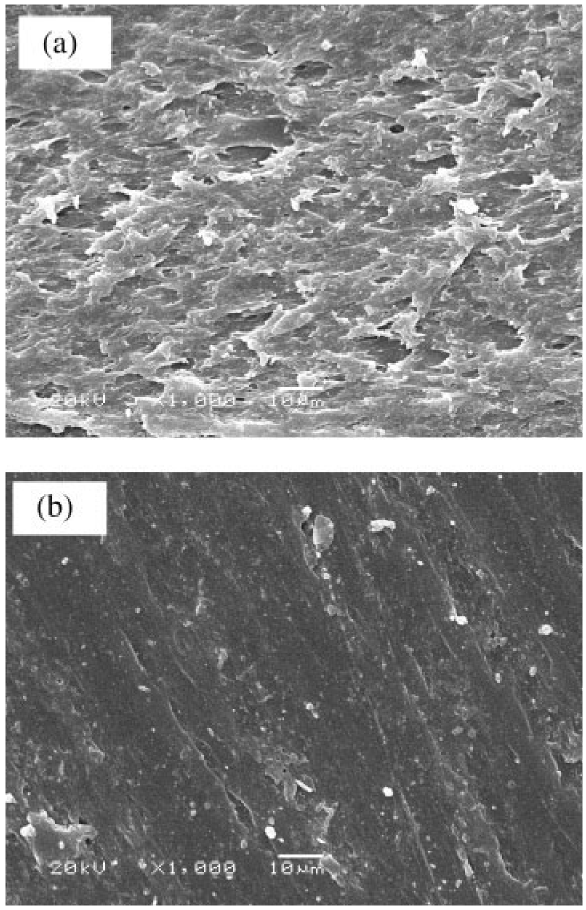

Figure 7 SEM images of the typical worn surfaces of PMMA/PS (a) and PMMA/PS/MWNTs (b).

than the PMMA/PS copolymer, which indicates difference in the wear mechanism. The worn surface of PMMA/PS copolymer shows obvious signs of adhesion and abrasive wear [Fig. 7(a)]. The worn surface in Figure 7(a) is very rough, displaying a lot of plucked and lowed marks which are indicative of typically adhesive wear and lowing. This proved that PMMA/PS copolymer had poor wear resistance properties. By contrast, the scuffing and adhesion on the worn surface of the PMMA/PS/1.5 wt % MWNTs copolymer nanocomposites can be almost neglected [Fig. 7(b)]. 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.[23] The relatively smooth, uniform, and compact worn surface is formed in the copolymer nanocomposites. This results in agreeing well with the considerably increased wear-resistance of PMMA/PS/MWNTs copolymer nanocomposites. Therefore, it can be deduced that the incorporation of MWNTs contributes to restrain the scuffing and adhesion of PMMA/PS copolymer in sliding against the steel counter face. Subsequently, the PMMA/PS/MWNTs copolymer nanocomposites show much better wear-resistance than PMMA/PS copolymer.

Nearly all of the PMMA/PS/MWNTs copolymer nanocomposites had lower friction coefficients than PMMA/PS copolymer. The mechanism for this reduction in friction coefficient is believed to originate from the following factors. Firstly, the dispersion of the MWNTs in the PMMA/PS copolymer is homogeneous and uniform because of the use of *in situ* polymerization process. So the mechanical properties of the composites may be enhanced remarkably. Secondly, the thin running films of MWNTs that are drawn out over PMMA/PS copolymer appeared during the course of wear and friction. The running films then slide against a transfer film that develops on the surface of the stainless steel counterface. The films can reduce the friction and wear volume. Moreover, the self-lubricating properties of MWNTs also result in reduction of the wear rate and the friction coefficient.

CONCLUSIONS

In this study, PMMA/PS/MWNTs copolymer nanocomposites with different concentrations of MWNTs were synthesized by *in situ* polymerization process. The tribological properties were investigated using a ring-on-block under dry conditions. It was found that MWNTs decreased their friction coefficient and increased the wear resistance of the PMMA/PS copolymer. We also found that PMMA/PS/MWNTs copolymer nanocomposites with 1.5 wt % MWNTs content exhibited both the highest wear resistance and the lowest friction coefficient. The significant improvements on the tribological properties of PMMA/PS/MWNTs copolymer nanocomposites are attributed to the excellent mechanical properties and unmatched topological tubular structure of MWNTs. 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. In conclusion, the *in situ* polymerization process and the incorporation of MWNTs help the significant improvements of tribological mechanisms of the PMMA/PS/MWNTs copolymer nanocomposites.

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