The Effect of Different Modified Multiwalled Carbon Nanotubes on Tribological Behaviors of Poly(furfuryl alcohol) Composite Coatings

Xue Hu Men,^{1,2} Zhao Zhu Zhang,¹ Jin Yang,^{1,2} Kun Wang,¹ Wei Jiang¹

¹State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China ²Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received 24 March 2009; accepted 16 March 2010 DOI 10.1002/app.32491 Published online 30 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Three kinds of modified multiwalled carbon nanotubes (MWNTs) with different length were obtained by grafting carboxylic groups on long MWNTs or copolymer groups on short and long MWNTs. The modified MWNTs were examined by infrared spectroscopy, thermal gravimetric analysis, X-ray photoelectron spectroscopy, and field emission scanning electron microscopy (FESEM). Afterward, the modified MWNTs were introduced into poly (furfuryl alcohol) (PFA), and the tribological behaviors of the resultant PFA composite coatings were investigated using a ring-on-block wear tester under dry friction condition. The dispersion of MWNTs in PFA composites and the worn surfaces were investigated

INTRODUCTION

Carbon nanotubes (CNTs) are crystalline carbon nanostructures consisting of single or multiple concentric graphite cylinders. Since its discovery,¹ theoretical and experimental predictions have demonstrated that CNTs possess outstanding mechanical and tribological behaviors.²⁻⁵ The better properties of CNTs, as well as their low density and enormous aspect ratio (and hence surface area) make them an ideal candidate to act as reinforcement for polymer composites.^{6,7} Lots of researches have been carried out, and their main aims were developing new nanocomposites with greatly improved mechanical properties or reduced flammability.⁶ Some researchers also paid their attention to investigate the tribological behaviors of CNTs based nanocomposites.^{8–11} It was found that CNTs based nanocomposites exhibited lower friction coefficient and wear rate in

by FESEM. The results indicated that the MWNTs dispersion and the tribological behaviors of PFA composite coatings could be obviously improved by modification with the copolymer. More significantly, under similarly uniform dispersion of MWNTs, the tribological properties of PFA composite coatings with short nanotubes presented better results when compared with those with long nanotubes because of the influence of nanotube length on the degree of modification of the MWNTs surfaces. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2881–2889, 2010

Key words: carbon nanotube; modification; composites; coatings; tribological behaviors

comparison with their pure substrate matrices because of the special effects of CNTs.

However, the effect of the variations (e.g., length, diameter, modified groups) of CNTs on the tribological behaviors of CNTs/polymer nanocomposites is still an open question. Gu and coworkers¹² have investigated the effects of the variations of CNTs on the microtribological behavior of CNTs/bismaleimide nanocomposite. The CNTs used in the nanocomposite were raw CNTs and carboxyliated CNTs, which readily changed the dispersion of CNTs in matrix, the interfacial strength between them and further affected the main wear mechanism of the nanocomposite. In general, two main issues are widely recognized as being critical for the development of tribological behaviors of CNTs based nanocomposites: (i) adequate dispersion of CNTs within the matrix, and (ii) strong interfacial bonding between CNTs and matrix. According to our previous works,13,14 chemical modification of multiwalled carbon nanotubes (MWNTs) showed an important role in tailoring the structures and properties of MWNTs, improving the dispersibility of MWNTs in polymer matrix, and further enhancing the tribological behaviors of the resultant nanocomposites. Further, using adequate chemical modification, it is

Correspondence to: Z. Z. Zhang (zzzhang@lzb.ac.cn).

Contract grant sponsor: National nature science foundation of china; contract grant numbers: 50773089, 50835009 and 973 Project of China 2007 CB607601.

Journal of Applied Polymer Science, Vol. 118, 2881–2889 (2010) © 2010 Wiley Periodicals, Inc.

possible to increase the material homogeneity and also enhance the dispersion of MWNTs in the polymer matrix. Therefore, it will be imperative and interesting to study the effects of the variations of modified MWNTs with different sizes on the tribological behaviors of MWNTs/polymer composites.

Poly(furfuryl alcohol) (PFA) is a common thermosetting resin that is usually synthesized by the cationic condensation of its monomer furfuryl alcohol (FA).^{15,16} Importantly, PFA is compatible with many organic polymers and inorganic materials, and it gives high carbon yield when pyrolyzing. Compared with other polymers, PFA is important not only for the use as adhesives and binders but also widely used to synthesize nanoporous carbons, glassy carbons, and polymer nanocomposites for a wide range of applications, such as adsorbents, separation membranes, and catalysts^{17,18}; moreover, the use of PFA as lubricating materials is rarely reported, so it is imperative to study the tribological properties of PFA composites. Therefore, in this article, PFA is used as the polymer matrix, however, how to select the proper modified method to obtain the uniform dispersion of MWNTs in matrix is important. Sulfonic acids, such as arylsulfonic acid, are commonly used as catalyst for polymerization of furfuryl alcohol (FA) and they have good solubility in both FA and PFA.¹⁹ We think that the incorporation of sulfonic acid groups onto MWNTs would help PFA to coalesce strongly on the MWNTs through electrostatic interactions between the hydroxyls of PFA and the sulfonic groups, thereby improving the dispersion of MWNTs in polymer. Furthermore, we postulate that MWNTs dispersion and the interfacial interactions in polymer matrix would be further improved if the amount of sulfonic acid groups on MWNTs is increased. Thus, we choose a copolymer of poly(*m*-aminobenzene sulfonic acid) (PABS) as the grafting groups on MWNTs because of the more sulfonic acid groups on the copolymer. The approach of MWNTs modification has been carried out according to the protocol originally described by Haddon and coworkers for single-walled carbon nanotubes.²⁰ The advantage of this chemical approach over our method lies in its catalysis for the polymerization of FA and high degree of modification, which makes it suitable for large-scale CNTs modification.

To our knowledge, no attempt has been made so far to develop such a relatively systematic study on the tribological behavior of PFA composites reinforced with different modified MWNTs. Thus, the study of the variations of modified MWNTs with different length and their effects on tribological behaviors will provide important guidelines to design novel high-performance nanocomposites for various tribological applications.

EXPERIMENTAL

Materials

Two types of pristine MWNTs produced by catalytic chemical vapor deposition were purchased from Chengdu Organic Chemicals Co, Chinese Academy of Sciences. Both pristine MWNTs possess the same diameter of about 8 nm but different lengths, the one with short length of 0.5–2 μ m is coded as S-MWNTs and the other with long length of about 50 μ m is coded as L-MWNTs.

M-aminobenzene sulfonic acid, aniline, and ammonium persulfate were purchased from the Alfa Aesar company. Furfuryl alcohol was purchased from Shanghai Hengxin Chemical Reagent Plant. Polyfluo150 Wax (PFW) with density of 1.17 g/cm³ and particle sizes of 3–4 μ m was purchased from the Mircopowder Co, USA. The mixed acetone/ethyl acetate in 1 : 1 (V/V) was employed in this work as a mixed solvent. FA was distilled under reduced pressure before use. A steel 45 (12.7 mm × 12.7 mm × 19 mm) was used as substrate of the coating. An AISI-C-52100 ring of 49.2 mm in diameter and 12 mm in thickness (Hardness Hv850) was made of bearing steel.

Synthesis of PABS

The synthesis procedure of PABS was as follows: m-aminobenzene sulfonic acid (17.3 g) and aniline (1.656 g) were mixed in 1*M* HCl with ammonium persulfate (22.8 g) as the oxidation reagent. Aniline was used as initiator for the m-aminobenzene sulfonic acid polymerization. The mixture was stirred at 1–5°C for 6 h and then the solution was concentrated and filtered at room temperature, and the solid washed with acetone. The solid was purified by dissolving in water, and adding the solution slowly to excess of acetone with stirring, until most of the product precipitated out and a black polymer was obtained. The black polymer was collected by filtering and dried at room temperature, and the final product was PABS (6.2 g) (Scheme 1).

Modification of MWNTs

In a typical experiment, MWNTs were added to a 3 : 1 (V/V) mixture of concentrated H_2SO_4 and HNO_3 . The mixture was sonicated for 10 min and stirred for 40 min under reflux at 80°C, and then filtered through a 0.22 µm Millipore polytetrafluoro-ethylene membrane. The solid collected was washed with distilled water until pH of the filtrate was 7 and then dried under vacuum overnight, obtaining MWNT-COOH.

MWNT-COOH (0.12 g) was sonicated in 100 mL of dry DMF for 20 min to give a homogeneous



Scheme 1 Fabrication procedure of MWNT-PABS.

suspension. Oxalyl chloride (6 mL) was added dropwise to the suspension at 0°C under N₂. The mixture was stirred at 0°C for 2 h and then at room temperature for another 2 h. Finally the temperature was raised to 70°C and the mixture was stirred overnight to remove excess oxalyl chloride. 0.8 g of PABS dissolved in DMF was added to the mixture and then stirred at 100°C for 5 days. After cooling at room temperature, the mixture was filtered through the polytetrafluoroethylene membrane and washed thoroughly with DMF and ethanol. The black solid was collected and dried under vacuum, obtaining MWNT-PABS (Scheme 1). Both S-MWNTs and L-MWNTs modified with PABS were coded as S-MWNT-PABS and L-MWNT-PABS, respectively. The L-MWNTs modified with carboxylic groups was coded as L-MWNT-COOH.

Preparation of PFA/MWNTs composite coating

Modified MWNTs (0.09 g) were added to a mixture of concentrated HNO_3 (0.05 ml) and FA (6 mL), the suspension was sonicated for 20 min and then stirred for 12 h at room temperature to obtain PFA/MWNTs composites.

The steel block was polished with 300 grade water proof abrasive paper and cleaned with acetone in an ultrasonic bath for 5 min. To obtain a uniform suspension, the powder of PFW (2.6 g) and PFA/ MWNTs composite were ultrasonically dispersed in the mixed solvent for 20 min. The coatings on blocks were prepared by spraying the suspension with 0.2 MPa nitrogen gas using spray gun at room temperature. After the evaporation of the solvent, a film was formed on the substrate and then cured at 70°C for 12 h, 120°C for 1.5 h and 170°C for 1.5 h, respectively. The thickness of the cured PFA/MWNTs composite coatings was measured with a Minitest 1100 microprocessor coating thickness gage (ElektroPhysik, Köln). The thickness of the cured coating was 50–100 µm. According to the initial mass ratio of component, the estimated content of the solid lubricant of PFW and MWNTs in the composite coatings was about 30 wt % and 1 wt %, respectively. In terms of the corresponding modified MWNTs used in the composites, the resultant PFA/MWNTs composite coatings were designed as PFA/L-MWNT-COOH, PFA/L-MWNT-PABS, and PFA/S-MWNT-PABS, respectively. For comparison purposes, pure PFA composite coating without MWNTs was prepared, which was designed as preA/L.

Characterization of the modified MWNTs and PFA/MWNTs composites

Bruker IFS66/S Fourier transform infrared (FTIR) spectrometer and VG ESCALAB 210 X-ray photoelectron spectroscopy (XPS) were used to investigate the chemical composition of the surface of the modified MWNTs. TGA data were recorded on a Perkin-Elmer Instruments Pyris Diamand Thermogravimetric/Differential Thermal Analyzer. JEOL JSM-6701F field emission scanning electric microscope (FESEM) was used to characterize the morphology and the dispersion of the modified MWNTs in matrix.

Evaluation of the tribological behavior of PFA composite coatings

An MHK-500 ring-on-block wear tester (made by the Jinan Testing Machine Factory, China) with a similar configuration to a Timken tester was used to evaluate the friction and wear behaviors of PFA composite coatings under dry condition. The contact schematic of the frictional couple is shown in Scheme 2. A steel ring was rotated against the PFA composite coating at different speeds (1.28-3.08 m/s) and different applied loads (320-620 N). The sliding time of 60 min was used in all friction tests. Before each test, the counterpart ring was rubbed with No. 900 abrasive paper, and then cleaned with acetone followed by drying. At the end of every test, the sliding distance was calculated from the product of the sliding speed and the sliding time. The wear life of the coatings was calculated after dividing the sliding distance by the corresponding coatings thickness in micrometers. All the friction and wear tests were carried out at 20-25°C and a relative humidity of 40-60%. Three specimens of each sample were tested and the average values of the data were reported. After the wear test, FESEM was used to observe the worn surfaces of PFA composite coatings.



Scheme 2 Contact diagram for the frictional couple (unit : mm).

RESULTS AND DISCUSSION

FTIR of modified MWNTs

FTIR spectra of PABS, L-MWNT-COOH, and L-MWNT-PABS are shown in Figure 1(a). The spectrum of L-MWNT-COOH shows an absorbance at 1721 cm⁻¹, which is due to carbonyl stretch of the carboxylic acid group. The spectrum of L-MWNT-PABS is quite different. A strong absorbance at 1653 cm⁻¹ is assigned to the carbonyl stretch of the amide group.²¹ The aromatic C—H stretch at 3053 cm⁻¹ can also be seen, together with signals at 1580–1600 cm⁻¹ (benzenoid ring stretch), 1485–1500 cm⁻¹ (quinonoid ring stretch), 1100–1150 cm⁻¹ (S=O), 1300–1345 cm⁻¹ (O=S=O or C—N stretch), 693 and 616 cm⁻¹ (S=O and S—C stretch), which are consistent with the presence of PABS. These results indicate that PABS was covalently bonded to the MWNT via the formation of



Figure 1 FTIR (a) and XPS (b) spectra of the different modified MWNTs.



Figure 2 XPS spectra of the different modified MWNTs.

an amide bond. The FTIR spectrum of S-MWNT-PABS is the same as that of L-MWNT-PABS (not shown).

XPS and TGA analysis of modified MWNTs

Figure 2 shows XPS survey spectra of the modified MWNTs. It can be seen that both spectra of S-MWNT-PABS and L-MWNT-PABS are similar greatly. On the contrary, the spectrum of L-MWNT-COOH is obviously different. The main differences among three spectra is the S2p peak at 168.5 eV and the N1s peak at 400.3 eV, which can be clearly found in the spectra of both MWNT-PABS; moreover, both peaks of the S2p and the N1s are the proof that PABS groups were grafted onto MWNTs. Energy dispersive X-ray spectroscopic (EDS) analysis was performed to determine the elements presented in the modified MWNTs, the atomic percentages of S-MWNT-PABS are: N 9.551% and S 9.285%, whereas those of L-MWNT-PABS are: N 7.130% and S 6.775%. Thus, the results of EDS reveal that the content of PABS group in S-MWNT-PABS is more than that in L-MWNT-PABS. Owing to the length of L-MWNTs was about 40 times than that of S-MWNT, it can be postulated that the content of grafting groups on the surfaces of MWNTs could be affected by the MWNT length.

Because of the strong intrinsic Van der Waals forces, CNTs tend to congregate ropes and bundles, and the degree of the congregation increases with the increscent aspect ratio of CNTs.²² Therefore, during the grafting reaction, compared with S-MWNTs, the high aspect ratio of L-MWNTs might made the grafting efficiency be weaker and further leaded to a relatively low content of grafting groups on the L-MWNT surface.

Because the defunctionalization of carbon nanotubes can be realized by thermal decomposition,



Figure 3 TGA curves of different modified MWNTs in N_2 (10°C/min).

TGA measurement was further applied to investigate the modified MWNTs. From the TGA curves shown in Figure 3, it can be seen that the difference among the three modified MWNTs is quite obvious. Compared with L-MWNT-COOH, the TGA curves of both MWNT-PABS apparently display the inflection. For the TGA curves of MWNT-PABS, the weight-loss region ($120 \sim 450^{\circ}$ C) should correspond to the decomposition of the grafted PABS chains. It is clearly shown that the loading of MWNTs in L-MWNT-PABS is higher than that in S-MWNT-PABS, which indicates that more PABS were attached onto S-MWNTs. Presumably the short length of S-MWNTs may be responsible for the higher concentration of PABS functional groups. According to the data of TGA, the content of grafting copolymer corresponding to L-MWNT-PABS and S-MWNT-PABS is about 38.6 and 45.2 wt %, respectively.

Morphology of modified MWNTs

FESEM images of the different modified MWNTs are shown in Figure 4(a–c). The images of both MWNT-PABS show that MWNTs are entrapped in PABS matrix to give a composite-like appearance [Fig. 4(b,c)], while the image of L-MWNT-COOH shows a network of interconnected MWNTs [Fig. 4(a)]. Moreover, it is clearly observed that more PABS wrap up the MWNTs of S-MWNT-PABS [Fig. 4(c)] when compared with L-MWNT-PABS [Fig. 4(b)]. Figure 4(d) depicts that dispersion status of the modified MWNTs in FA. Both L-MWNT-PABS and S-MWNT-PABS dissolved in FA result in deepdark solutions while L-MWNT-COOH is absolutely insoluble in FA. This phenomenon suggests that the



Figure 4 FESEM images of (a) L-MWNT-COOH, (b) L-MWNT-PABS, and (c) S-MWNT-PABS; a photo for the dispersion status of (d) the modified MWNTs in FA after 12 h.



Figure 5 FESEM images of the fracture surfaces of (a) PFA/L-MWNT-COOH, (b) PFA/L-MWNT-PABS, (c) PFA/S-MWNT-PABS and (d) magnified image of marked region in (c).

grafting PABS groups increased the solubility of MWNTs and might further enhance the dispersibility of MWNTs during the polymerization of FA.

Dispersion of the modified MWNTs in PFA/MWNTs composites

Figure 5 shows the FESEM images of fracture surfaces of the PFA/MWNTs composites. From Figure 5(a), poor dispersion of MWNTs in PFA/L-MWNT-COOH can be detected, especially some bundles of MWNTs are clearly found on the fracture surface. In contrast, as seen in Figure 5(b,c), the images of both PFA/MWNT-PABS composites show that the distribution of MWNTs within the PFA matrix is very homogeneous. For illustrating in more detail, the high-magnification image of PFA/S-MWNT-PABS show some individual MWNTs [Fig. 5(d)], implying that MWNTs were availably prevented from aggregating each other after the modification. These phenomena can be explained as follow: as PABS was grafted on the surfaces of MWNTs, the sulfonic acid groups in the PABS acted as catalyst for FA polymerization, allowing the attachment of PFA on the surface of MWNT-PABS via the electrostatic attraction between the sulfonic acid groups and the hydroxyl group in PFA.¹⁹ Therefore, the good dispersion of MWNT-PABS within PFA is mainly

attributed to the attached polymer chains on MWNTs.

Friction and wear behaviors of PFA composite coatings

The effects of applied load on the tribological behaviors of PFA composite coatings are shown in Figure 6. Evidently, the friction coefficient of PFA composite coatings [Fig. 6(a)] tends to decrease with the increase of the applied load. In addition, it can be seen that the friction-reduction behaviors of PFA/MWNTs composite coatings have been obviously enhanced becaue of the reinforcement of MWNTs when compared with the pure PFA. Figure 6(b) shows the wear life of PFA composite coatings under different load. Interestingly, the wear life of PFA composite coatings slightly decreases when the applied load is below 420 N and then increases but at a slower rate with further increase of the applied load. These coatings failed in many cases, as highapplied load would tend to severe plastic deformation of polymer composite coatings.²³ However, when the applied load increased above 420 N, the MWNTs in the composite coatings could slowly release onto the metal surface during the friction process,⁸ the MWNTs on the metal surface served as spacers, preventing rough contact between



Figure 6 Effect of (a) applied load on the friction coefficient and (b) wear life of the PFA composite coatings at 1.28 m/s (60 min).

counterparts, thereby slowing the wear rate considerably. Thus, it can be indicated that the combination of above facts resulted in the variational tendency of the wear life under different loads. It is worth noting that both MWNT-PABS can obviously reduce the friction coefficient and significantly enhance the wear resistance when compared with L-MWNT-COOH. It is evident that PFA/S-MWNT-PABS holds the lowest friction coefficient and the highest wear life at 1.28 m/s under different loads.

Variations of the friction coefficient and the wear life with sliding speed for PFA composite coatings under a load of 320 N are plotted in Figure 7(a,b), respectively. It can be seen that the friction coefficient of PFA composite coatings records an obvious decrease with the increase of sliding speed. For PFA/S-MWNT-PABS, the friction coefficient gradually decreases when the speed is below 2.6 m/s and then sharply decreases with further increase of the sliding speed. At the same time, the wear life of PFA composite coatings increases almost linearly with the increasing sliding speed. It is supposed that the variations in the friction coefficient and wear life with sliding speed are closely related to the frictioninduced heat. Namely, the friction-induced heat plays a larger role in the frictional interface at a

higher sliding speed than at a lower one, this is because more energy dissipated was transformed into heat during the higher speed friction process and a high temperature gradient developed in the normal direction to the surface,²⁴ so the heat effect reduced the friction coefficient and further prolonged the wear life. In addition, we find that both PFA/MWNT-PABS coatings show lower friction coefficient and higher wear life in comparison with the pure PFA and PFA/L-MWNT-COOH throughout the sliding speed range; meanwhile, PFA/ S-MWNT-PABS still possesses the better tribological properties compared with PFA/L-MWNT-PABS.

It is known that MWNTs have good self-lubrication properties because they are composed of graphite-like sp2-bonded cylindrical layers or shells. Nevertheless, the tribological behaviors of polymer/ MWNTs composites mainly depend on the adequate dispersion of MWNTs within the polymer and the strong interfacial bonding between MWNTs and the polymer. Therefore, the reason that the tribological properties of PFA/L-MWNT-COOH are worse than those of both PFA/MWNT-PABS composites is attributed to the poor dispersion of L-MWNT-COOH in matrix, which could easily lower the interfacial bonding and further weaken



Figure 7 Effect of (a) sliding speed on the friction coefficient and (b) wear life of the PFA composite coatings under 320N (60 min).



Figure 8 FESEM micrographs of worn surfaces of the PFA composite coatings (320 N, 2.56 m s⁻¹, 60 min): (a) pure PFA, (b) PFA/L-MWNT-COOH, (c) PFA/L-MWNT-PABS, and (d) PFA/S-MWNT-PABS. (The sliding direction is shown by the black arrow.).

the tribological properties of the nanocomposite. Furthermore, MWNTs agglomerates arising from the bad dispersion sometimes can induce the abrasive wear behavior between both surfaces of the sliding components,¹³ which lead to failure of the inherent properties of MWNTs and result in poor tribological properties of PFA/MWNTs composites. More interestingly, there are some distinct differences present between both PFA/MWNT-PABS composites on the tribological behaviors, in spite of their similar good dispersion of MWNTs in PFA composites. Owing to the uniform dispersion of MWNTs in both PFA/ particular MWNT-PABS composites, attention should be paid to investigate the interfacial bonding between MWNTs and the polymer matrix. As illustrated above, there exists a strong interfacial bonding between MWNT-PABS and PFA matrix because of the electrostatic attraction between the sulfonic acid groups and PFA. Moreover, the content of PABS groups on the surface of S-MWNT-PABS is more than that of L-MWNT-PABS. Therefore, the electrostatic attraction between S-MWNT-PABS and PFA would be stronger when compared with L-MWNT-PABS. Furthermore, Yang and coworkers²⁵ reported that the high density of grafting groups on nanotubes can improve the stress transfer of nanocomposites, which is closely correlative with the tribological behaviors of composites. Inferentially, it can be

indicated that the short-length modified MWNTs with higher amount of PABS groups are more effective on the improvement of tribological properties of PFA nanocomposite as compared with the long-length modified MWNTs.

FESEM analysis of worn surfaces

To further understand the effect of the modified MWNTs with different size on the friction and wear behavior of the PFA composite coatings, the worn surface morphologies of the composite coatings as well as wear debris were studied by FESEM. Figure 8 shows FESEM images of the worn surfaces of the different PFA composite coatings at 2.56 m s⁻¹ under 320 N. There is much debris and crack on the worn surface of the pure PFA [Fig. 8(a)], but the surface of PFA/L-MWNT-COOH is relatively clean except for a little crack and some MWNT clusters on the surface [Fig. 8(b)]. In contrast, both PFA/L-MWNT-PABS [Fig. 8(c)] and PFA/S-MWNT-PABS [Fig. 8(d)] have relative smooth worn surfaces without obvious crack or debris. This is indicative for the reinforcement of the modified MWNTs on wear resistance of PFA composite coatings. As seen in Figure 8(c) and d, the images of PFA/MWNT-PABS identify the presence of some individual MWNTs embedded uniformly within PFA matrix, suggesting that MWNTs were

well separated in PFA matrix and tightly embedded into the sliding interface because of the modification with PABS. According to the above phenomena, it can be inferred that some L-MWNTs-COOH were easily pulled out from the sliding surface under repeated loading during sliding process due to the weak interfacial bonding between the nanotubes and PFA matrix; moreover, the pulled MWNTs were easily congregated to form clusters. Therefore, it can be further shown that the influence of modification with PABS on the tribological behaviors of PFA nanocomposites is much more effective than that with carboxyl groups because of the relatively strong electrostatic attraction between PABS and PFA. Wang et al.²⁶ reported that short length of CNTs can improve the nanotube dispersion in matrix and further enhance the thermal conductivity of nanocomposite. In addition, it is well known that the enhanced thermal conductivity of a polymer nanocomposite can facilitate heat transport,²⁷ thereby it is believed that most of the friction heat could be dissipated by the enhanced thermal conductivity to cool down the counterpart ring because of the incorporation of the short CNTs in the PFA composites. Consequently, the combination of the PABS modification and the short length is the main dominant factor for the better tribological properties of PFA/S-MWNT-PABS.

CONCLUSIONS

We have prepared three types of modified MWNTs by chemical grafting with carboxylic groups and a copolymer of PABS. In contrast, two MWNT-PABS with different length disperse uniformly in the monomer of FA and the PFA matrix, and the tribological properties of the resultant PFA/MWNT-PABS composite coatings are improved obviously. Specifically, under the similar good dispersion of MWNTs in polymer matrix, both PFA/MWNT-PABS composite coatings present different tribological behaviors because of the effect of MWNTs length. Comparatively, the length of MWNTs play an important role for the tribological behaviors of PFA/MWNT-PABS: better tribological properties of PFA/MWNT-PABS are achieved when the length of the modified MWNTs is shorter. It is concluded that apart from the good dispersion of MWNTs, different interfacial bonding between MWNTs and matrix also affects the tribological behaviors, which caused by the content of functional groups on the surfaces of the different length MWNTs. The results reported herein may shed some light on the experimental results of carbon nanotube composites reported by the scientific community.

References

- 1. Iijima, S. Nature 1991, 354, 56.
- 2. Lu, J. P. Phys Rev Lett 1997, 79, 1297.
- 3. Srivastava, D.; Wei, C.; Cho, K. Appl Mech Rev 2003, 56, 215.
- Buryachenko, V. A.; Roy, A.; Lafdi, K.; Anderson, K. L.; Chellapilla, S. Compos Sci Technol 2005, 65, 2435.
- Thostenson, E. T.; Ren, Z.; Chou, T. W. Compos Sci Technol 2001, 61, 1899.
- 6. Moniruzzaman, M.; Winey, K. I. Macromolecules 2006, 39, 5194.
- 7. Coleman, J. N.; Khan, U.; Gun'ko, Y. K. Adv Mater 2006, 18, 689.
- 8. Zhang, L. C.; Zarud, I. I.; Xiao, K. Q. Wear 2006, 261, 806.
- Zhou, S. M.; Zhang, X. B.; Ding, Z. P.; Min, C. Y.; Xu, G. L.; Zhu, W. M. Compos part A 2007, 38, 301.
- 10. Xia, Z. H.; Loub, J.; Curtin, W. A. Scr Mater 2008, 58, 223.
- 11. Xue, Y.; Wu, W.; Jacobs, O.; SchäDel, B. Polym test 2006, 25, 221.
- Liu, L.; Gu, A. J.; Fang, Z. P.; Tong, L. F.; Xu, Z. B. Compos PART A 2007, 38, 1957.
- 13. Song, H. J.; Zhang, Z. Z.; Men, X. H. Eur Polym J 2007, 43, 4092.
- Men, X. H.; Zhang, Z. Z.; Song, H. J.; Wang, K.; Jiang, W. Compos Sci Technol 2008, 68, 1042.
- 15. Choura, M.; Belgacem, N. M.; Gandini, A. Macromolecules 1996, 29, 3839.
- 16. Gandini, A.; Belgacem, N. M. Prog Polym Sci 1997, 22, 1203.
- 17. Wang, H. T.; Yao, J. F. Ind Eng Chem Res 2006, 45, 6393.
- Gonzalez, R.; Figueroa, J. M.; Gonzalez, H. Eur Polym J 2002, 38, 287.
- Yi, B.; Rajagopalan, R. H.; Foley, C.; Kim, U. J.; Liu, X. M.; Eklund, P. C. J Am Chem Soc 2006, 128, 11307.
- Zhao, B.; Hu, H.; Yu, A. P.; Perea, D.; Haddon, R. C. J Am Chem Soc 2005, 127, 8197.
- Hamon, M. A.; Chen, J.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. Adv Mater 1999, 11, 834.
- 22. Dyke, C. A.; Tour, J. M. J Phys Chem A 2004, 108, 11151.
- Holmberg, K.; Matthews, A.; Ronkainen, H. Tribol Int 1998, 31, 107.
- 24. Chen, Z. B.; Li, T. S.; Yang, Y. L.; Liu, X. J.; Lv, R. G. Wear 2004, 257, 696.
- Xie, L.; Xu, F.; Qiu, F.; Lu, H. B.; Yang, Y. L. Macromolecules 2007, 40, 3296.
- 26. Wang, S.; Liang, R.; Wang, B.; Zhang, C. Carbon 2009, 47, 53.
- Gao, J.; Itkis, M. E.; Yu, A.; Bekyarova, E.; Zhao, B.; Haddon, R. C. J Am Chem Soc 2005, 127, 3847.