Tribological Behaviors of Hybrid PTFE/Nomex Fabric/Phenolic Composite Reinforced with Multiwalled Carbon Nanotubes

Hui-Juan Zhang,[1,2] Zhao-Zhu Zhang,[1] Fang Guo[1,2]

[1]*State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China*
[2]*Graduate School of Chinese Academy of Sciences, Beijing 100039, China*

Received 30 June 2010; accepted 21 October 2010
DOI 10.1002/app.33594

ABSTRACT: Modification of composites was a general method to improve their tribological behaviors. On the way to explore composites with enhanced tribological behaviors, we have successfully prepared hybrid PTFE/Nomex fabric/phenolic composite filled with multiwalled carbon nanotubes (MWCNTs) or MWCNTs modified by polystyrene (PS) with a grafting to method. The results of pin-on-disc type wear tests indicated tribological behaviors were improved both for hybrid PTFE/Nomex fabric/phenolic composite filled with MWCNTs and MWCNTs-PS, especially for that of filled with MWCNTs-PS. And the probable reason was also discussed based on the characterization results. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 235–241, 2012

Key words: PTFE/Nomex fabric; carbon nanotubes; wear

INTRODUCTION

Fabric reinforced or fabric/resin composites have emerged as viable choice in aircraft construction automobiles and pressure vessels. The merits of higher specific strength and ease of processing make them more practical materials in tribological applications in comparison with short fiber or unidirectionally reinforced composites, metals and alloys.[1,2] The practical utility of such composites is governed by the performance and reliability. However, little work has been reported in respect of their tribo-potential in comparison with and the necessity to further explore such composites with more excellent performance.[3–8]

Carbon nanotubes (CNTs), which possess unique seamless cylinders of graphite sheets either in the form of single- or multiwalled assemblies, have become the focus of considerable scientific research since their discovery by Iijima.[9] Recently, it has witnessed a growing number of studies relating to CNTs' influence on the tribological properties of polymer matrix.[10–17] The detailed research in these reports disclosed MWCNTs have good self-lubrication properties. The unique structure of graphite-like sp2 hybridization cylindrical layers or shells, where the intershell interactions is predominately controlled by the force of Van Der Waals, endows MWCNTs easily slide or rotate with each other and lead to good self-lubrication. The superior oxidation resistance and thermal stability further improve its stability during the process of wear test.

However, the demerit of the insolubility in many solvents or matrices greatly restrains its application as filler. The modification of MWCNTs has provided an effective tool to improve their compatibility with matrices and also alleviate their agglomeration.

Considering interfacial bonding plays an important role in load transfer across CNTs-matrix interface, it is necessary to pretreat composites for improving its mechanical properties. Functionalization of nanotubes with polymers represents a promising strategy to attach a limited number of functional groups onto the MWCNT surfaces to improve the solubility of MWCNTs and inhibits intertube aggregations.

The extensive investigations on this type of hybrid fabric and its composites have not yet been reported. In this work, hybrid PTFE/Nomex fabric is designed and prepared from PTFE and Nomex to combine their merits, the low friction of PTFE and high strength of Nomex. Hybrid PTFE/Nomex fabric/phenolic composites were prepared with the thermosetting phenolic resin as the binder. MWCNTs were

---

Correspondence to: Z.-Z. Zhang (zzzhang@lzb.ac.cn).
Contract grant sponsor: National Project 973; contract grant number: 2007 CB607601.
Contract grant sponsor: Fund for Creative Research Groups; contract grant number: 50721062.
Contract grant sponsor: National Natural Science Foundation; contract grant number: 50773089.

chemically modified with polystyrene by a grafting to method. Unmodified MWCNTs and MWCNTs-PS were also incorporated into the fabric/phenolic composite to investigate their effects on the friction and wear behaviors. This work may be helpful for understanding the wear mechanism of MWCNTs-filled fabric composite and providing guidance to their tribological application.

EXPERIMENTAL

Materials

The hybrid PTFE/Nomex fabric (weave: satin) was woven out of PTFE fibers and Nomex fibers (Du pont, USA). The phenolic adhesive resin (204 phenolic adhesive) was purchased from Shanghai Xin-guang Chemical Plant of China. All the chemicals used are of analytical grade. Styrene was distilled under reduced pressure before use. Benzoyl peroxide (BPO) was purified by recrystallization. 4-Hydroxy-2,2,6,6-tetramethyl piperidinooxy (TEMPO) (Beijing Yang Cun Chemical Reagent Co. Ltd.) was used as received. Multiwalled carbon nanotubes (MWCNTs) were purchased from Chengdu Organic Chemicals, Co. Ltd., Chinese Academy of Sciences (diameter: 8 nm, length: 50 μm, purity: >95%).

Preparation of TEMPO-capped polystyrene

Polystyrene (PS) capped with TEMPO radicals were prepared by nitroxide-mediated free radical polymerization according to reference.[18] In a typical procedure, styrene was polymerized under Ar atmosphere at 95°C for 3.5 h in the presence of BPO and TEMPO (weight ratio = 1/1.2), followed by further reaction at 125°C for another 6 h. Upon cooling, the resulting mixture was dissolved in chloroform, precipitated in methanol and dried under vacuum to obtain TEMPO capped PS (TEMPO-PS).

Preparation of composites of MWCNTs grafted with PS

The TEMPO-capped PS was grafted onto MWCNTs via the radical coupling reaction of TEMPO according to reference.[18] In a typical procedure, appropriate amounts of MWCNTs, TEMPO-PS and dimethylformamide (DMF) were added into a flask, and the grafting reaction proceeded under Ar atmosphere at 125°C for 12 h. Upon cooling, the resultant was precipitated in methanol and washed with DMF to remove the ungrafted PS. After that, the resultant was dried under vacuum.

Specimen preparation

The hybrid PTFE/Nomex fabric was cleaned by Soxhlet extractor in petroleum ether and ethanol in sequence and dried at 80°C. The fillers were mixed uniformly with the phenolic resin (diluted with mixed solvent $V_{\text{acetone}} : V_{\text{ethanol}} : V_{\text{ethyl acetate}} = 1 : 1 : 1$) at proper mass fractions under magnetic stirring and ultrasonic stirring. Afterwards, the hybrid PTFE/Nomex fabric was immersed in the mixed adhesive containing the fillers and dried in the temperature range of 45–50°C. A series of repetitive immersions and coatings of the hybrid fabric were performed and the mass fraction of the hybrid PTFE/Nomex fabric in the composite coating was about 70–75%. Finally, the filled PTFE/Nomex fabric composite was affixed onto the AISI-1045 steel (size of Φ 45 mm × 8 mm^2) with the phenolic resin and then cured at 180°C for 2 h under a certain pressure. By comparison, an unfilled hybrid PTFE/Nomex fabric composite was also prepared by the same procedure. A series of unfilled, MWCNTs-filled, and MWCNTs-PS-filled hybrid PTFE/Nomex fabric composite specimens were prepared and tested.

Friction and wear tests

Sliding experiments were performed in a Xuanwu-III pin-on-disk tribometer, as described elsewhere.[19] In the pin-on-disk tester, a stationary steel pin slides against a rotating steel disk which was affixed with the hybrid PTFE/Nomex fabric composite specimens. The flat-ended AISI-1045 pin (diameter 2 mm) was secured to the load arm with a chuck. The distance between the center of the pin and the axis was 12.5 mm. The pin stays over the disk with 2 degree of freedom: a vertical one, for normal load application by direct contact with the disk, and a horizontal one, for friction measurement.

Prior to the tests, the pin was polished with 350, 700, and 900 grade water-proof abrasive paper to a surface roughness $R_a = 0.15$ μm, and then cleaned with acetone. The sliding was performed at varied temperatures, loads between 156.80 and 376.32 N, speeds between 0.26 and 0.42 m/s and over a period of 2 h under dry condition. At the end of each test, the corresponding wear volume loss (V) of the composite was obtained by measuring the depth of the wear scar on a micrometer (±0.001 mm). The wear performance was expressed by wear rate (w, m^3(N m)$^{-1}$) as follows: $w = V/P.L$, where V is the wear volume loss in m^3; P the load in Newton; L the sliding distance in meter. The friction coefficient was measured from the frictional torque gained by a load cell sensor, which could be obtained directly from the computer running the friction-measure software. Each experiment was carried out three times and the average value was used.

The morphology of the worn surfaces of the composites and the transfer film formed on the counterpart pin was analyzed by scanning electron microscopy (SEM, JEOL JSM-5600LV). The morphology of

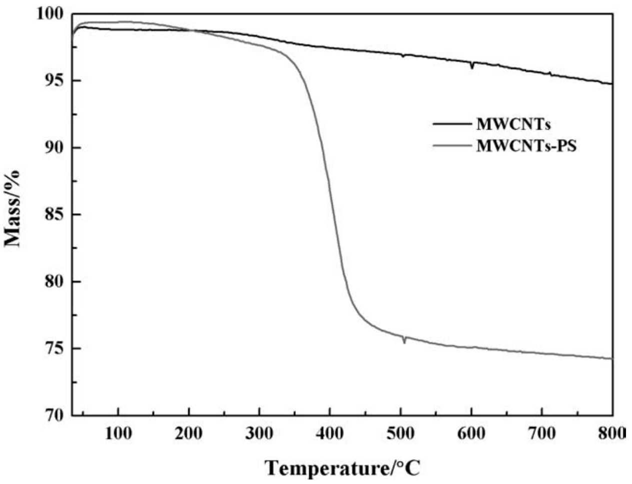

Figure 1 Typical TGA curves for MWCNTs and MWCNTs-PS.

MWCNTs and MWCNTs-PSt was observed by field emission scanning microscopy (FESEM, JEOL JSM-6701F). Bruker IFS/66v Fourier transform infrared spectroscopy (FT-IR) was used to characterize the changes in surface structures of MWCNTs. Thermal Gravimetric Analysis (TGA) was conducted on a Netzsch STA 449 C apparatus with a heating rate of 10°C/min under an air atmosphere.

RESULTS AND DISCUSSION

Characterization of MWCNTs-PS

Figure 1 presents the TGA traces of MWCNTs and MWCNTs-PS. Compared with pure MWCNTs, two main weight-loss regions can be found in MWCNTs-PS. The weight-loss region (~ 342–522°C) for MWCNTs-PS can be assigned to the decomposition of polystyrene, as also evidenced in literature.[18] From the result of TGA, the amount of the polystyrene bonded to MWCNTs can be calculated according to the mass weight loss and the value was approximately 8 wt %. As shown in Figure 2, the FT-IR spectrum of MWCNTs-PS exhibited signals in the region of 1400–1600 cm^{-1}, which can be ascribed to the stretching of aromatic C=C. The peaks between 670 and 800 cm^{-1} was attributed to the aromatic or vinyl C-H with the mode of out-of-plane bending. These results strongly corroborated that MWCNTs had been successfully functionalized by polystyrene.

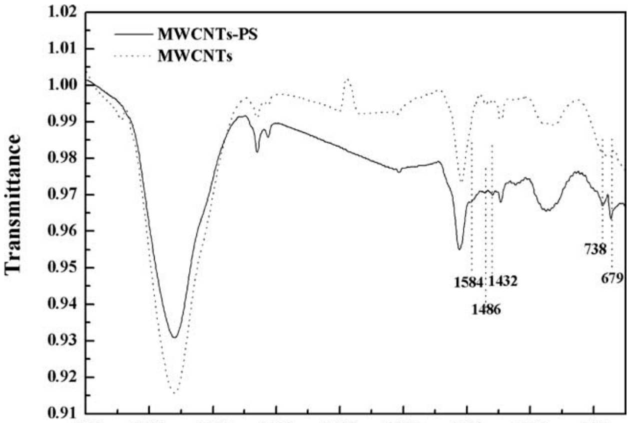

Figure 2 FT-IR of MWCNTs and MWCNTs-PS.

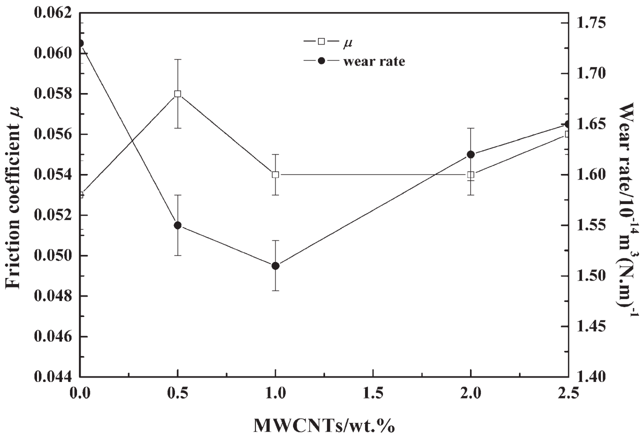

Figure 3 Variation of the friction coefficient and wear rate of hybrid PTFE/Nomex fabric composite with the amount of MWCNTs. (0.26 m/s; 282.24 N).

Friction and wear behaviors

The friction coefficient and wear rate variation of hybrid PTFE/Nomex fabric composite containing different amounts of MWCNTs is shown in Figure 3. It can be seen that the amount of MWCNTs content has an obvious influence on the wear behaviors of fabric composites. For the pure MWCNTs examined, the friction coefficient of PTFE/Nomex fabric composite filled with varied amounts of MWCNTs differed slightly from each other. Among all nanotube contents used, a lower wear rate was obtained over the hybrid PTFE/Nomex fabric composite filled with MWCNTs than that of the unfilled counterpart. An obvious reduction of wear rate can be observed when 0.5% MWCNTs were incorporated into hybrid PTFE/Nomex fabric composite. When the amount was increased to 1%, a lowest wear rate can be obtained. When the amount was further increased to 1.5% ~ 2.5%, unfortunately, the wear rate increased, indicating there exists an optimal amount. The deterioration of tribological behavior may result from the agglomeration of MWCNTs in composite matrix with the increase of MWCNTs content.

We then modified the MWCNTs with PS and investigated its influence on the frictional performance of hybrid PTFE/Nomex fabric composite.

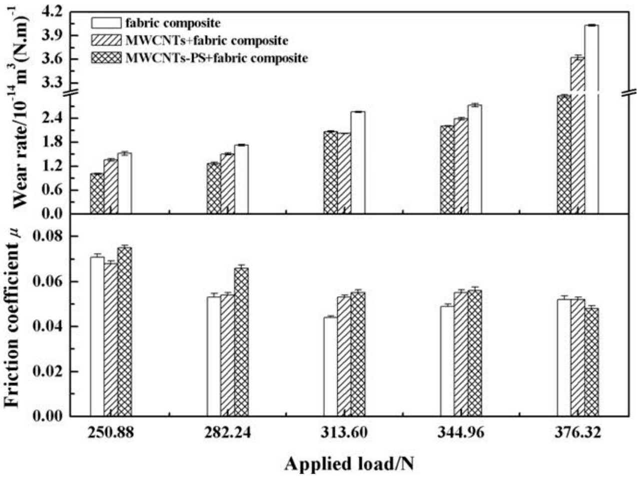

Figure 4 Friction coefficient and wear rate versus applied load for unfilled, MWCNTs-filled, and MWCNTs-PS-filled fabric composite (0.26 m/s).

Totally, 1% identical amount of MWCNTs-PS in comparison with that of MWCNTs was chosen as an optimal amount and added into the hybrid PTFE/Nomex fabric composite. The effect of the increasing loads on the friction and wear behaviors of unfilled, MWCNTs-filled, and MWCNT-PS-filled fabric composite is investigated and the results are shown in Figure 4. The friction coefficient of unfilled and MWCNTs-filled composite decreased initially and then exhibited an increase with the higher load. The friction coefficient of MWCNTs-PS-filled composite was not very sensitive to the applied loads and showed slight differences when the loads were varied in the range of 250.88 ~ 376.32 N. The wear rate of three composites had the similar trends with the increasing loads. That is, the wear rate gradually increased with the increasing loads. Under every applied load, the wear rate of three composites followed the order of MWCNT-PS/composite<MWCNT/composite<unfilled composite.

The effect of the sliding speeds was further investigated on the three composites at a fixed load of 282.24 N. Friction coefficient and wear rate of three composites plot as a function of the sliding speed were presented in Figure 5. The friction coefficient of the unfilled composite exhibited some irregular variations as the speed increased. Among them, a lower friction coefficient was obtained at 0.36 m/s. The friction coefficient of MWCNTs-filled composite did not show many differences among varied sliding speeds, although an increase was seen at 0.36 m/s. In the case of MWCNTs-PS-filled composite, the friction coefficient exhibited somewhat different characteristics. No distinct variations can be seen for the friction coefficient of MWCNTs-PS-filled composite. It is notable that the wear rate of three composites almost followed the similar trend when the sliding speeds increased. Specifically, the wear rate decreased as the sliding speed was elevated and a lowest value was obtained when the sliding speed was 0.31 m/s. The wear rate of three composites increased with the further increasing sliding speed. Under the same speed, the wear rate of three composites followed the order of MWCNT-PS/composite<MWCNT/- composite<unfilled composite. It is believed that with the increase of sliding speed, transfer film can be more easily formed on the frictional surfaces. Thus, the lubrication condition at the rubbing surfaces can be greatly improved, leading to the decrease of the friction and wear of three composites. However, with further increasing sliding speed, the friction heat was accumulated and could not be efficiently dissipated since the polymer is a poor heat-conductor. Therefore, the temperature increased at the rubbing surfaces. The reduction of mechanical strength and the load-supporting capacity of three composites may occur, which in turn led to the wear of three composites.

It is widely accepted that the tribological property of a composite is dependent on the internal strength and lubricating property of matrix, reinforcement as well as the interfacial adhesion between the matrix, and the reinforcement. Carbon nanotubes (CNTs) possess unique seamless cylinders of graphite sheets either in the form of single-walled or multiwalled assemblies. Their seamless structure helps to inhibit the sticking and burnishing of the nanoparticles by the rubbing metal surfaces. These tubular particles slide and roll during sliding contact, resulting in a low friction and wear. The primary structures may also crack open during contact between the tribo-couples leading to small graphitic layers with low surface energy, which behave similar to graphite. The spherical nanoparticles can also serve as

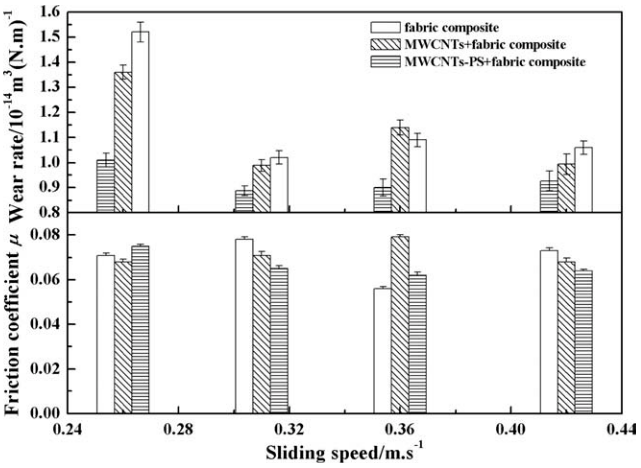

Figure 5 Friction coefficient and wear rate versus sliding speed for unfilled, MWCNTs-filled, and MWCNTs-PS-filled fabric composite (250.88 N).

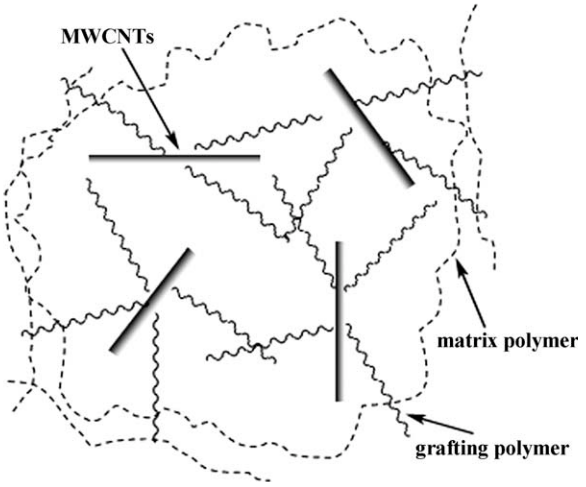

Figure 6 Schematic drawing of the interaction between grafted MWCNTs and the matrix.

effective spacers, prohibiting contact and wear of the polymer surfaces under heavy loads whereas fluid lubricants are normally squeezed out. For the MWCNTs-filled composites, MWCNTs near the surface were probably released from the fabric composite during sliding and transferred to the interface between the fabric composite and the steel counterface. MWCNTs in the interface served as spacer to prevent the direct contact between the two mating surfaces and lower the wear rate. This will produce a smoother worn surface and improved wear resistance comparing with the sample without MWCNTs as fillers. This effect is specially strengthened with the appropriate MWCNTs concentration in the composite. From the results obtained above, it is clear that there exists an appropriate MWCNTs concentration in the composite to obtain a better wear performance.

However, the effect of MWCNTs on the tribological property of the composites cannot only be attributed to the self lubrication of MWCNTs. In fact, the dispersion of MWCNTs in the matrix, the interfacial adhesion and the internal strength of the composites do play an important role in the tribological property of the composites. It is believed that the difference in improving the wear resisting ability between the composites with untreated and treated MWCNTs should result mainly from the filler/matrix adhesion strength and the interfacial

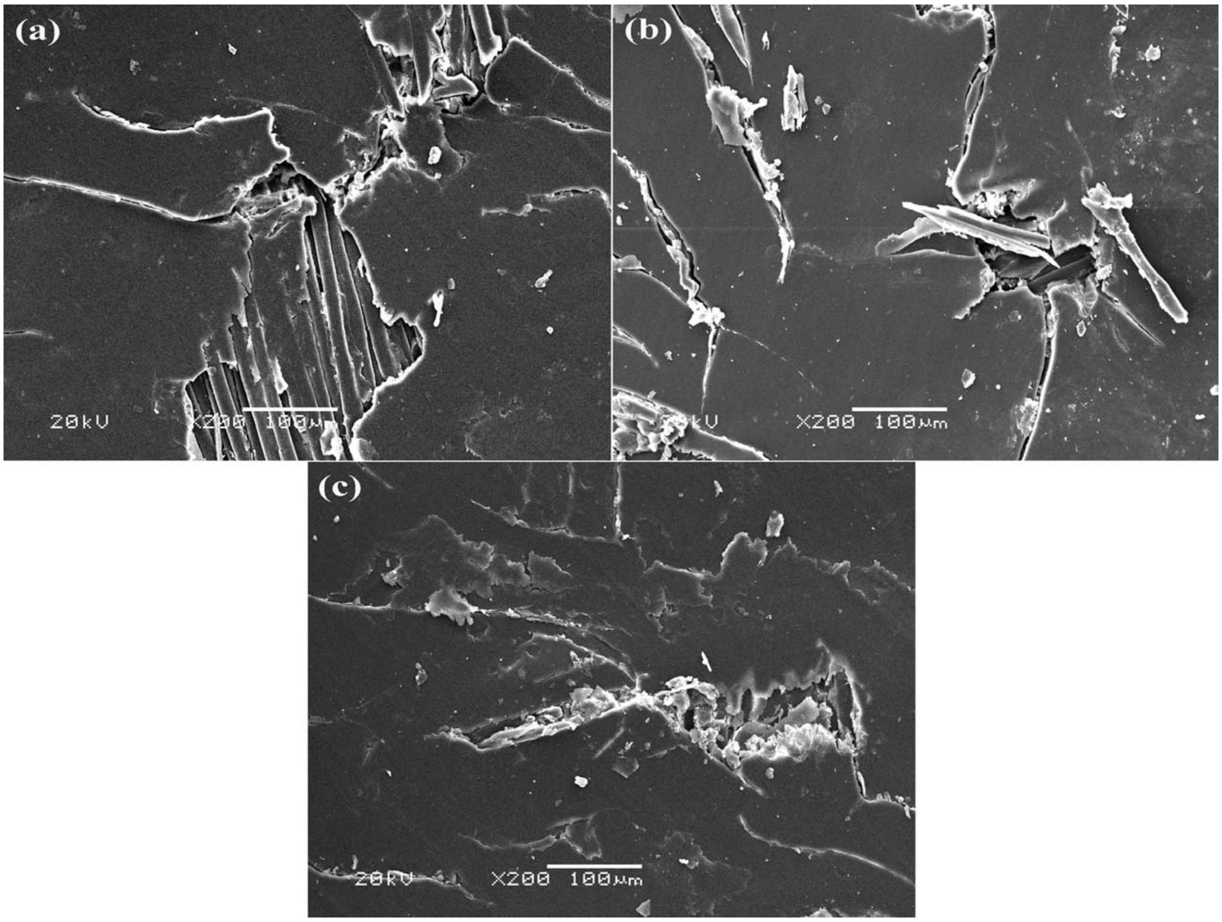

Figure 7 SEM micrographs of the worn surfaces of (a) unfilled fabric composite, (b) MWCNTs-filled fabric composite and (c) MWCNTs-PS-filled fabric composite (282.24 N).

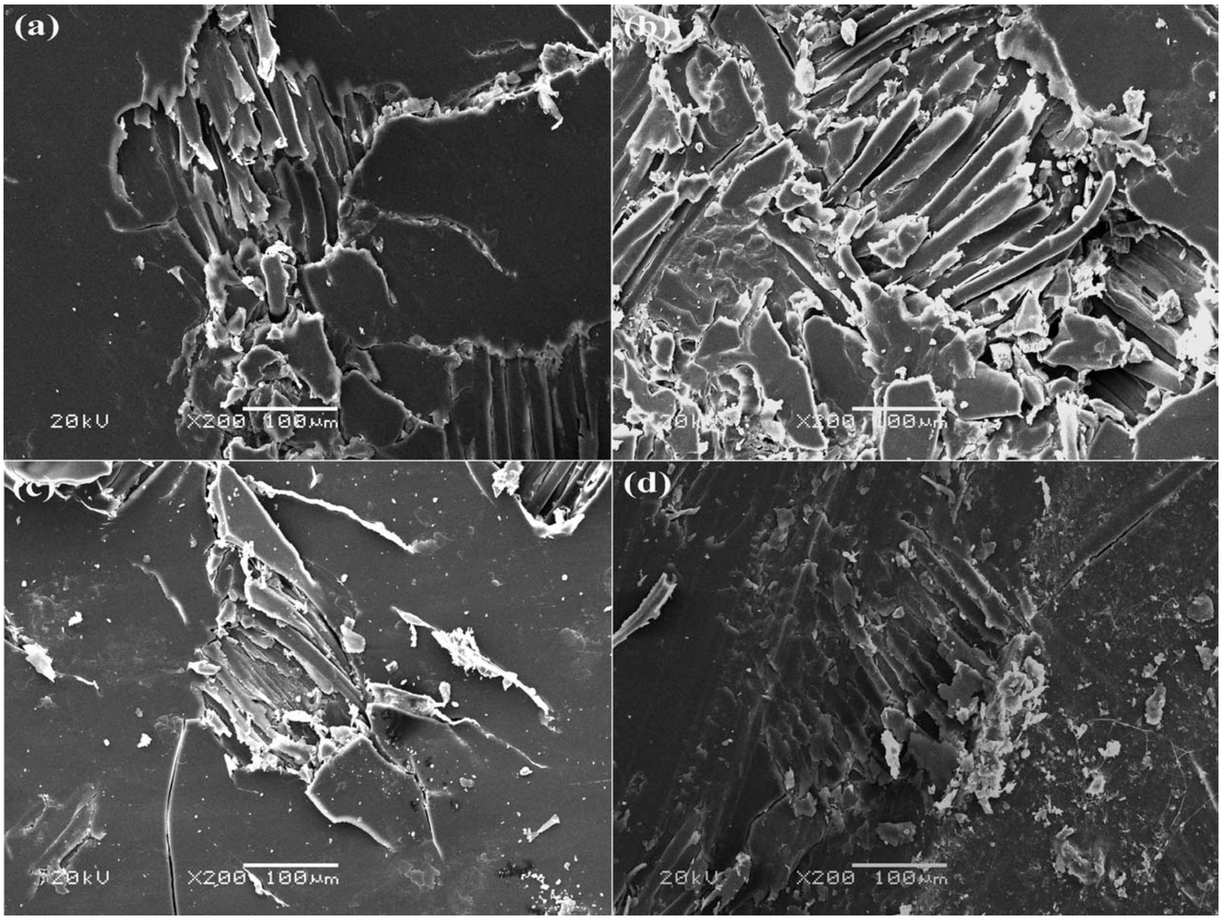

Figure 8 SEM micrographs of the worn surfaces of the unfilled and MWCNTs-PS-filled fabric composite sliding under different loads (a) unfilled composite at 313.60 N, (b) unfilled composite at 376.32 N, (c) MWCNTs-PS-filled composite at 313.60 N, (d) MWCNTs-PS-filled composite at 376.32 N.

miscibility. To understand the beneficial effect caused by the grafting polymer, a possible structure representing interactions between grafting polystyrene and the matrix is constructed and shown in Figure 6. According to the preparation scheme, the MWCNTs were surface modified with polystyrene with grafting-to method and the grafted MWCNTs were mechanically mixed with polymeric composite. The polymeric composite with an integrated structure was thus obtained. The following effects can be predicted based on this structure: (a) The grafting polymer chain interacts with the matrix polymer by the entanglement and facilitates the filler/matrix miscibility; (b) The grafting polymer binds the small MWCNTs aggregates together and eliminated the possible defects. In the case of MWCNTs-PS-filled fabric composite, both the mechanical properties and MWCNTs/matrix adhesion strength were expected to be improved. When the fabric composite was subjected to wearing, damage induced by localized shear stress concentration at the MWCNTs agglomerate was postulated to be avoided efficiently. As a result, the stress can be transferred evenly across the composite, protecting the composite from being destroyed even at higher applied load.

SEM observations

SEM morphology of the worn surfaces of the unfilled, MWCNTs-filled, and MWCNTs-PS-filled fabric composites was studied to understand the effect of MWCNTs on the friction and wear behaviors of the filled fabric composite (Fig. 7). It can be seen that a severe surface damaging was caused in the form of resin crack and fiber pull-outs for unfilled composite [Fig. 7 (a)], which was an indication of severe wear. The wear of MWCNTs-filled composite was less severe. The amount of the fiber pull-outs is less and the worn surface was smoother [Fig. 7(b)]. The different wear characteristics of unfilled and MWCNTs-filled composite can probably be ascribed to the excellent performance of carbon nanotubes. It is well known that the CNTs are extraordinarily flexible under large strains and resist failure under repeated bending,[20] and therefore the addition of CNTs in the composite matrix allowed the fracture energy absorption or dissipation under stress and significantly improved the toughness of fabric composite. As shown in Figure 7(c), the severe fiber pull-outs were effectively prohibited in the case of the MWCNTs-PS-filled composite in comparison with the unfilled and MWCNTs-filled composites, and the fiber exposure and resin crack were the main wear characteristics of the MWCNTs-PS-filled composite. It indicated that MWCNTs-PS-filled fabric composite became more difficult to be deformed and destructed during sliding tests, which was probably due to the strengthening effect of MWCNTs-PS. It is believed by Wetzel et al. that localized stress concentrations can be induced by angularities in regions of particle edges and corners and would therefore deteriorate the wear performance under abrasion conditions.[21] MWCNTs-PS can effectively avoid stress concentrations aforementioned due to the better filler/matrix by the grafting polymer interaction with the matrix. Therefore, the wear rate was decreased due to a more integrated structure.

SEM images of unfilled and MWCNTs-PS-filled fabric composites sliding under different loads were examined and shown in Figure 8. At a load of 313.60 N, the wear of unfilled composite was characteristic of fiber exposure and fiber pull-outs [Fig. 8(a)]. As the load increased to 376.32 N, a large surface damage became clear by the evidence of a large amount of fiber pull-outs [Fig. 8(b)]. Contrary to the above, MWCNTs-PS-filled composite showed mild wear characteristics. Only a few fibers were exposed at the load of 313.60 N [Fig. 8(c)] and a small quantity of fibers were pulled out at the load of 376.32*N* [Fig. 8(d)]. It is very likely that the carbon nanotubes served as spacers, prohibited the direct contact between the fabric composite and the metal counterface and reduced the wear of the polymer composites under heavy loads. It is known that the shear stress increased with the increasing applied load. The crack observed on the worn surfaces of unfilled composite experienced the process of initiation, growth, and fracture. Under the higher load, the debonding between fabric and resin occurred and PTFE or Nomex fibers were pulled out of the steel substrate. Thus, fiber pull-outs became a dominant damaged form. Consequently, the wear was severe and the unfilled composite was destructed severely.

CONCLUSIONS

1. MWCNTs had an obvious effect of enhancing the antiwear ability of the hybrid PTFE/Nomex fabric/phenolic composite at low filler content (∼ 1 wt %). Grafting of polystyrene onto MWCNTs increased the interfacial interaction between filler and matrix. It provided an efficient way to further increase the wear resistance of the hybrid PTFE/Nomex fabric/phenolic composite.
2. The wear rate increased with the increasing applied load for three composites. The wear rate decreased as the sliding speed was elevated and a lowest value was obtained when the sliding speed was 0.31 m/s for three composites.
3. The self-lubrication of MWCNTs and interaction between the grafting polymer chain and matrix polymer are believed to contribute to the better wear properties of MWCNTs-PS-filled hybrid PTFE/Nomex fabric composite.

References

1. Hanchi, J.; Eiss, N. S., Jr. Wear 1997, 203–204, 380.
2. Chang, L.; Zhang, Z.; Zhang, H.; Friedrich, K. Tribol Int 2005, 38, 966.
3. Mody, P. B.; Chou, T. W.; Friedrich, K. J. Mater Sci 1988, 23, 4319.
4. Zhang, H. J.; Zhang, Z. Z.; Guo, F.; Jiang, W.; Liu, W. M. Tribol Int 2009, 42, 1061.
5. Xiang, D.; Shu, W.; Li, K. Mater Sci Eng A 2008, 483–484, 365.
6. Xiang, D.; Shan, K. Wear 2006, 260, 1112.
7. Vishwanath, B.; Verma, A. P.; Rao, C. V. S. Wear 1993, 167, 93.
8. Bahadur, S.; Polineni, V. K. Wear 1996, 200, 95.
9. Iijima, S. Nature 1991, 354, 56.
10. Yang, Z.; Dong, B.; Huang, Y.; Liu, L.; Yan, F. Y.; Li, H. L. Mater Chem Phys 2005, 94, 109.
11. Cai, H.; Yan, F. Y.; Xue, Q. J Mater Sci Eng A 2004, 364, 94.
12. Chen, W. X.; Li, F.; Han, G.; Xia, J. B.; Wang, L. Y.; Tu, J. P.; Xu, Z. D. Tribol Lett 2003, 15, 275.
13. Lim, D. S.; An, J. W.; Lee, H. J Wear 2002, 252, 512.
14. Giraldo, L. F.; López, B. L.; Brostow, W. Polym Eng Sci 2009, 49, 896.
15. Liu, L.; Gu, A.; Fang, Z.; Tong, L.; Xu, Z. Compos A 2007, 38, 1957.
16. Xue, Y.; Wu, W.; Jacobs, O.; Schädel, B. Polym Test 2006, 25, 221.
17. Meng, H.; Sui, G. X.; Xie, G.Y.; Yang, R. Compos Sci Technol 2009, 69, 606.
18. Wang, H. C.; Li, Y.; Yang, M. J Sensor Actuat B 2007, 124, 360.
19. Guo, F.; Zhang, Z. Z.; Liu, W. M.; Su, F. H.; Zhang, H. J Tribol Int 2009, 42, 243.
20. Wetzel, B.; Haupert, F.; Friedrich, K.; Zhang, M.Q.; Rong, M. Z. Polym Eng Sci 2002, 42, 1919.
21. Falvo, M. R.; Clary, G. J.; Taylor, R. M.; Chi, V.; Brooks, F. P., Jr.; Washburn, S. Nature 1997, 389, 582.