

Tribological properties of surface modified nano-alumina/epoxy composites

QIU LONG JI

Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou 510275, People's Republic of China; Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China

MING QIU ZHANG*, MIN ZHI RONG

Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China
E-mail: ceszmq@zsu.edu.cn

B. WETZEL, K. FRIEDRICH

Institute for Composite Materials (IVW), University of Kaiserslautern, D-67663, Kaiserslautern, Germany

Nano-sized Al₂O₃ particles grafted with polystyrene or polyacrylamide were employed as fillers for fabricating epoxy based composites. Curing habit, mechanical properties and tribological performance revealed by sliding wear tests of the composites were investigated. The experimental results indicated that the nanoparticles accelerate curing of epoxy, increase composites' impact strength and decrease wear rate and frictional coefficient of the composites. The surface modification by means of grafting polymerization can further enhance the properties improvement of epoxy due to the increased filler/matrix interfacial interaction. Compared to frictional coefficient, wear rate of epoxy can be decreased more remarkably by the addition of nano-alumina when rubbing against steel. The wear mode changes from severe peeling off of unfilled epoxy to mild micro-ploughing in the case of nano-alumina filled composites. © 2004 Kluwer Academic Publishers

1. Introduction

Owing to its excellent characteristics in chemical erosion resistance, good affinity to heterogeneous materials, thermal stability and on-the-spot processing capability, epoxy has been widely used in many fields. With respect to the operation in tribological environment, the polymer mostly could not be used alone due to its higher coefficient of linear expansion, low thermal conductivity and unsatisfactory mechanical properties. Reinforcement with fibrous materials proves to be an effective way to enhance its wear resistance [1]. However, the method is not suitable when coating application is concerned, because the critical aspect ratio required for giving play to the fibers would substantially decrease the flowability of the resultant composite system. As a result, incorporation of inorganic particles becomes an alternative, which can also improve mechanical and tribological properties of epoxy [2].

It is noteworthy that in the case of conventional micrometer-sized inorganic particulate composites, the fillers detached from the composites during wearing used to act as additional abrasives and give birth to a three-body wear mechanism [3]. The disadvantage is factually detrimental to the service life of the materi-

als in use. In contrast to micron particles, nanoparticles have a much greater surface area-to-volume ratio. This ratio is important for bonding the particle to the polymer matrix in the composite material. Moreover, the angularity of the particles is remarkably reduced with decreasing particle size, so that the hard nanoparticles which could not be used as fillers in the microscale particulate form might be suitable for sliding applications because they would not be expected to abrade the counterface [4].

In this context, utilization of nanoscale particles as fillers to construct epoxy based composites would be a way out of the aforesaid dilemma. Some pilot works have been done in this direction in hopes of improving mechanical properties [5–7] and tribological performance of epoxy [8, 9]. In the course of compounding, however, sedimentation of agglomerated nanoparticles greatly compromises the ultimate properties of the composites. Sometimes the composites perform even worse than conventional microparticles filled versions. Therefore, the authors of this study plan to modify nanoparticles via graft polymerization technique in advance. Owing to the low molecular weight nature, the monomers can penetrate into the agglomerated nanoparticles

* Author to whom all correspondence should be addressed.

easily and react with the activated sites of the nanoparticles. The interstitial volume inside the nanoparticle agglomerates will be partly filled with the grafting macromolecular chains, and the agglomerated nanoparticles will be separated further. Besides, the surface of the nanoparticles will also become “hydrocarbon” due to an increased hydrophobicity resulting from the grafting polymer. This is beneficial for the filler/matrix miscibility and hence for the ultimate properties. When the pre-grafted nanoparticles are mechanically mixed with epoxy, the former will keep their more stationary suspension state due to the interaction between the grafting polymer and the matrix. After curing of the mixture, filler/matrix adhesion would be substantially enhanced by chain entanglement and/or chemical bonding between the grafting polymer and the matrix polymer. In this case, a uniform dispersion of nanoparticles in the matrix on a nanometer level, as desired usually, might no longer be critical.

In this paper epoxy is filled with nanosized alumina particles, which are pre-grafted with either polystyrene (PS) or polyacrylamide (PAAM). PS is selected owing to its solubility parameter similar to that of epoxy, which will probably lead to good compatibility between the treated nanoparticles and the matrix. Grafting of PAAM onto the nanoparticles is because the active hydrogen atom on the amide group of PAAM can react with epoxy groups and be combined in the three-dimensional networks of the matrix throughout the composites, so that the nanoparticles can be connected with the matrix covalently [9]. Mechanical and sliding wear properties of the composites are measured as a function of nano-alumina particles' content and pre-treatments. Through these examinations, it is expected that the effects of modified and unmodified nano-alumina particles can be revealed, which will facilitate further improvement of the composites' tribological performance.

2. Experimental

Bisphenol-A epoxy resin (type E-51) was provided by Guangzhou Dongfeng Chemical Co., China. The curing agent 4,4-diaminodiphenylsulfone (DDS) was supplied by Shanghai Medical Agents Co., China. The nano-alumina particles with average size of 10.4 nm, specific surface area of 146.3 m²/g and surface hydroxyl groups of 1.16 mmol/g were produced by Zhejiang Zhoushan Mingri Nanomaterials Ltd., China. Prior to use, the particles were dried in an oven at 110°C under vacuum for 24 h in order to get rid of the physically absorbed and weakly chemically absorbed species.

Nano-alumina particles were grafted with PS and PAAM, respectively, according to the steps described elsewhere [10]. The percentage of grafting is 20% for PAAM and 25% for polystyrene, respectively. To remove the homopolymer absorbed on the particles, the grafted nanoparticles were extracted with good solvents (butyl ketone for PS and water for PAAM) for more than 72 h. For the convenience of discussion, the grafted nano-alumina particles together with homopolymer are denoted by Al₂O₃-c-PAAM and Al₂O₃-c-PS, respectively. Those without homopolymer are denoted by Al₂O₃-g-PAAM and Al₂O₃-g-PS, respectively.

Composite materials were fabricated by mixing the nanoparticles and epoxy together with a fast stirring for 2 h and then ultrasonic dispersion for 1 h. The stirring process is carried out in vacuum to get a good dispersion and to avoid the air bubbles generated during compounding. After that, the mixture was heated to 130°C and the curing agent was added under continuous stirring. Then the composite system was poured into a preheated mould and the curing procedure began after the extraction of possible air bubbles for 1.5 h. The curing proceeded step by step as follows: 3 h at 100°C, 2 h at 140°C, 2 h at 180°C, and 2 h at 200°C.

Curing behaviour of epoxy and its composites were examined by a Perkin-Elmer DSC-7 differential scanning calorimetry at a heating rate of 5°C/min. Three-point bending tests of the composites specimens were carried out by a Hounsfield universal tester in accordance with GB/T1039-92 standard at a deformation rate of 5 mm/min, while unnotched Charpy impact tests were conducted on a XJJ-5 tester according to GB1843-80(89) standard. Composites' Vickers microhardness was measured by a Shimadzu DUH-202 dynamic microhardness tester at the load of 200 N and depth of 10 μm. For each sample 10 points were measured.

Unlubricated sliding wear tests were carried out on a block-on-ring apparatus under a pressure of 3 MPa and a constant velocity of 0.4 m/s (load: 181 N, sample size: 6 × 10 × 18 mm³). The carbon steel ring (0.42–0.45 wt% C, 0.17–0.37 wt% Si and 0.5–0.8 wt% Mn, HRC 50) has a diameter of 40 mm and an initial surface roughness of 0.1 μm. Prior to wear testing, all the samples were pre-worn to average surface conditions and to reduce the running-in period. The actual steady-state test period was set to 3 h. After and before that, a weight measurement of specimens was conducted separately to calculate the weight loss during the test.

The distribution status of the nanoparticles in epoxy composites was observed by a JME-100CX II transmission electron microscope (TEM). The impact fractured surfaces and worn surfaces of the materials were characterized by a Jeol-5400 scanning electron microscope (SEM).

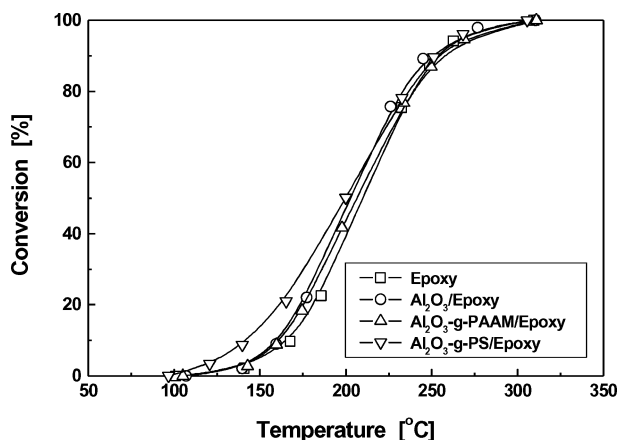


Figure 1 Curing behavior of epoxy and its composites filled with untreated and treated nano-alumina particles at a heating rate of 5°C/min (nano-alumina content: 0.98 vol%).

3. Results and discussion

When nano-alumina particles are incorporated into epoxy, the curing kinetics of the resin will be affected. Since it is closely related to the processability and the properties of the composites as well, it should be analyzed at the beginning. As shown in Fig. 1 that the conversion increases with the addition of both unmodified and modified nanoparticles at identical temperature. In addition, it also increases with a rise in the nano-alumina content (Fig. 2). Some studies have showed that filler particulates have important influences on the curing behavior of epoxy [11, 12], including (i) catalytic effect of the hydroxyl groups on the particles, (ii) accelerating effect caused by the decrease of free-volumes with the hypothesis that the volumes are occupied by

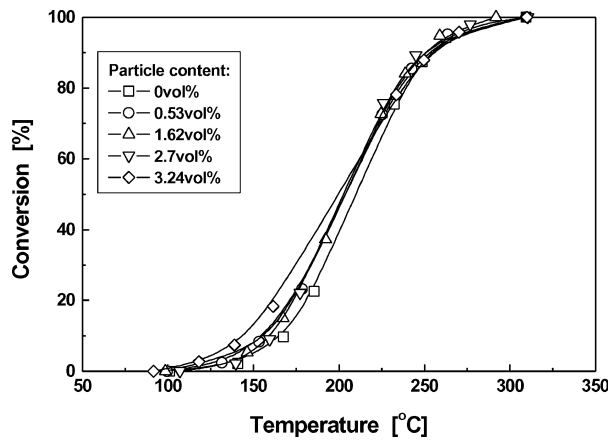


Figure 2 Curing behavior of epoxy and its composites filled with untreated nano-alumina particles at a heating rate of 5°C/min.

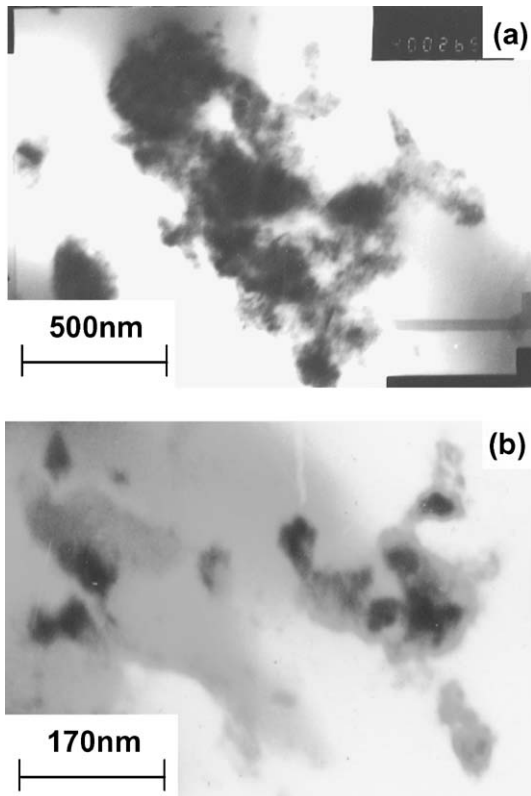


Figure 3 TEM photographs of (a) untreated nano-alumina and (b) $\text{Al}_2\text{O}_3\text{-g-PAAM}$ particles dispersed in epoxy based composites.

the fillers, which increases the local concentration of the activated components thus increasing the reaction rate, and (iii) steric effect of the particles. Returning to the results given in Figs 1 and 2, the authors consider that the second effect plays the leading role. This receives supporting evidence from Fig. 2, where an increase in filler content corresponds to increased reaction rate. On the other hand, Fig. 1 exhibits that the particles grafted with PS result in higher conversion than untreated and PAAM grafted nano-alumina when the

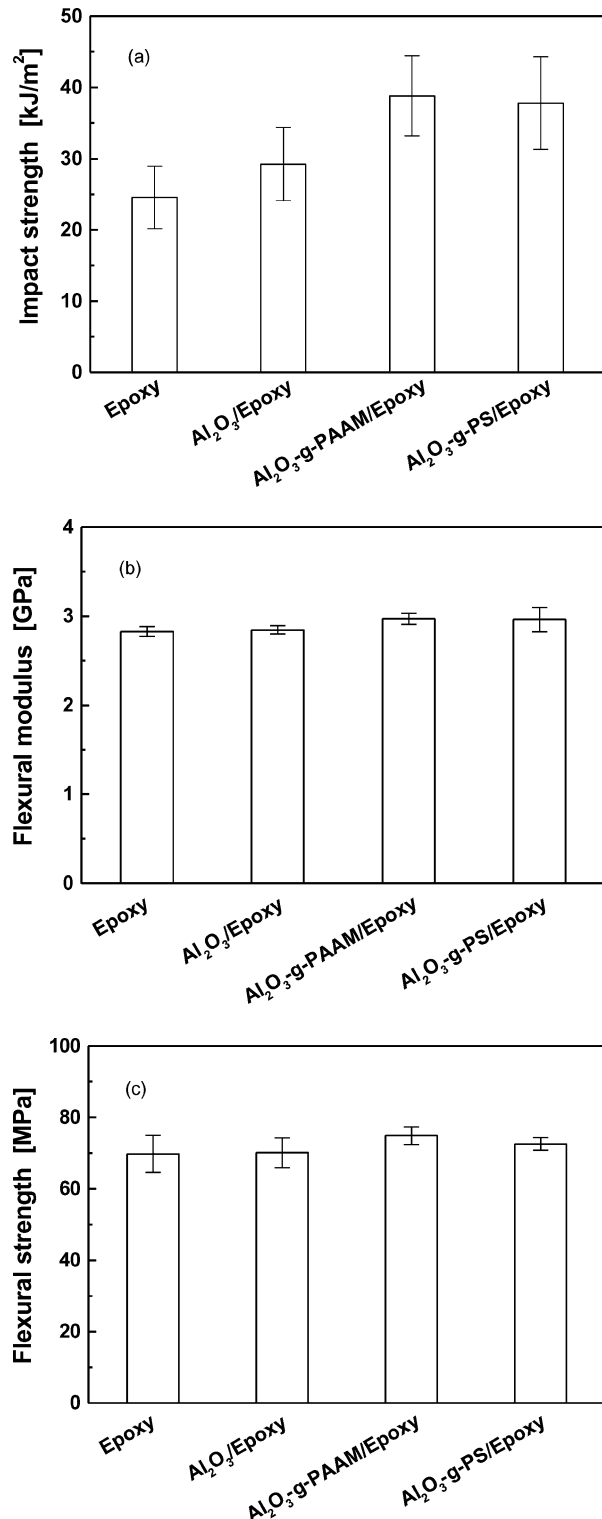


Figure 4 (a) Impact strength, (b) flexural modulus and (c) flexural strength of epoxy and its composites (nano-alumina content: 0.98 vol%).

same temperature is concerned. It can be explained by the improved compatibility of Al_2O_3 -g-PS with epoxy as compared to the other two kinds of nanoparticles. For this reason, the grafted polymer chains might be able to extend into the matrix and build up strong interfacial interaction.

To have an image of the composites microstructure, Fig. 3 shows the TEM microphotos of the composites slices containing untreated and treated nano-alumina. As portrayed by Fig. 3a, severe agglomeration of the untreated particles appears in the matrix even though mechanical stirring and ultrasonication were applied during compounding. When the nanoparticles are grafted with polymers, however, much finer dispersion of the fillers can be observed (Fig. 3b). In addition, the bound-

ary between the particles and the matrix is indistinct, which indicates the existence of the grafting polymer layer and the obvious adhesion between the particles and the matrix as well. The different morphologies shown by the TEM photos demonstrate that the proposed graft modification has changed the internal structure of the nanoparticle agglomerates and the resultant epoxy composites as expected in the introductory section.

Fig. 4 shows the result of unnotched impact and three-point bending properties of epoxy and its composites at a given nano-alumina content of 0.98 vol%. The addition of untreated nano-alumina increases the impact strength of epoxy from 24.5 to 29.2 kJ/m^2 (Fig. 4a). Moreover, in the presence of the grafted nanoparticles,

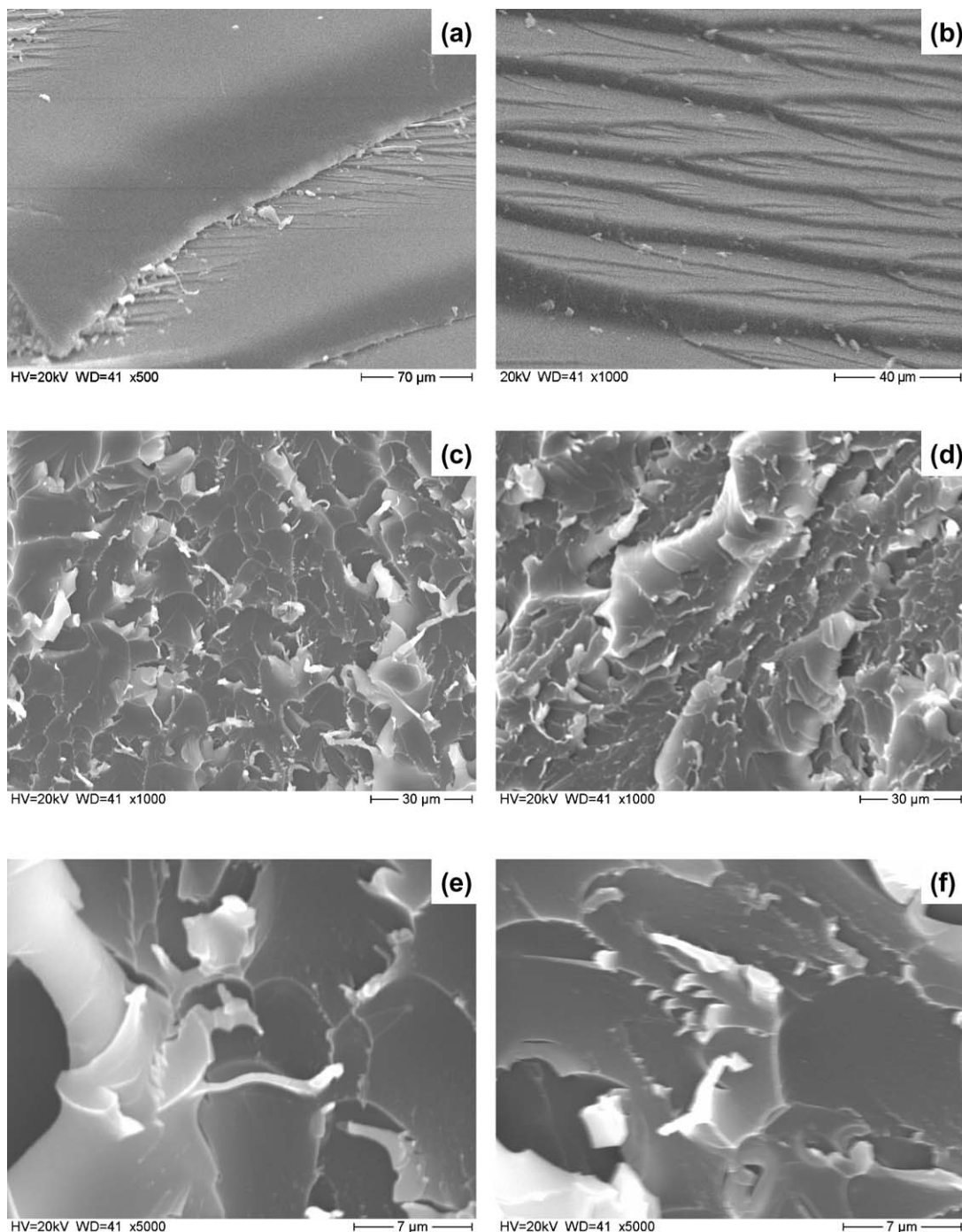


Figure 5 SEM photos of impact fracture surfaces of (a), (b) unfilled epoxy, (c) Al_2O_3 -g-PAAM/Epoxy, (d) Al_2O_3 -g-PS/Epoxy, (e) Al_2O_3 -g-PAAM/Epoxy, (f) Al_2O_3 -g-PS/Epoxy (nano-alumina content: 0.98 vol%).

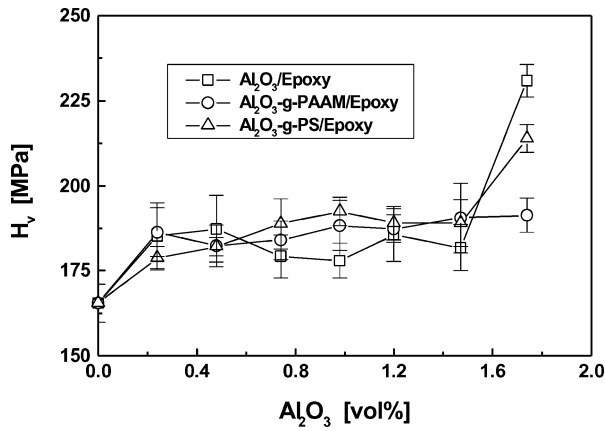


Figure 6 Filler content dependence of microhardness of epoxy and its composites filled with untreated and treated nano-alumina particles.

the impact strength can be 38.0 kJ/m². However, either flexure strength or modulus of the composites is almost unaffected by the particles (Fig. 4b and c). That means the low content nano-alumina is only able to toughen but not to strengthen epoxy no matter what surface treatment is applied to the particles.

Similar results were found by Spanoudakis and Young during their study on glass spheres/epoxy composites [13]. They reported that the flexural strength of the composites with coupling agent treated fillers is approximately the same as that of the unfilled matrix, while the untreated fillers tend to decrease the flexural strength of the composites in an exponential way with filler content [14]. Improved interfacial adhesion helps to increase critical stress intensity factor, K_{Ic} , of the composites due to the improved efficiency of crack pinning. According to their findings, it is known from the data in Fig. 4b and c that the amount of the added nanoparticles is so low in the present composites that the particles cannot bear sufficient load under static loading condition, but the filler/matrix bonding is high enough otherwise the composites strength would be reduced. On the prerequisite of good interfacial adhesion, the increase in impact strength of the composites should be attributed to crack pinning or crack front trapping mechanism. Singh and co-workers showed that aluminum particles are capable of enhancing the fracture toughness of highly crosslinked unsaturated polyester at about 0.95 vol% filler concentration owing to the effect of crack front trapping [15].

The fractographs (Fig. 5) reveal that the fractured surfaces of unfilled matrix exhibit brittle fracture feature characterized by smooth appearances (Fig. 5a and b). In the composites where cracks had propagated through the nanoparticles, some river-like patterns resulting from the joining of different fractured planes (Fig. 5c and d), as well as some tail-like patterns caused by the interaction of cracks with the particles appear in the matrix (Fig. 5e and f). This is a typical multiple cracking phenomenon. Compared to the untreated nano-alumina, the strong interfacial interaction between the grafted nanoparticles and the matrix firmly stick the particles to the matrix. Having met with obstruction (pinning) in front of the particles, the crack has to deviate from its plane so as to make a detour and propagate between the particles causing additional

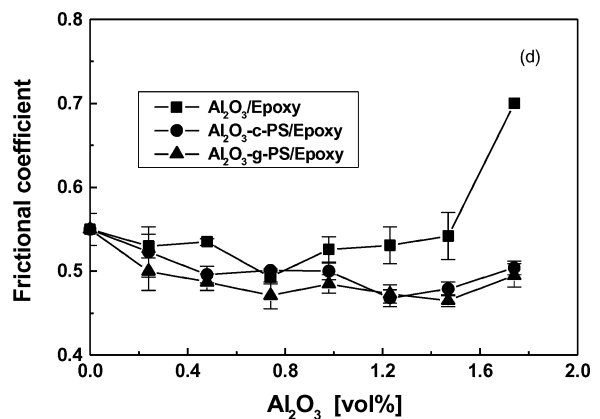
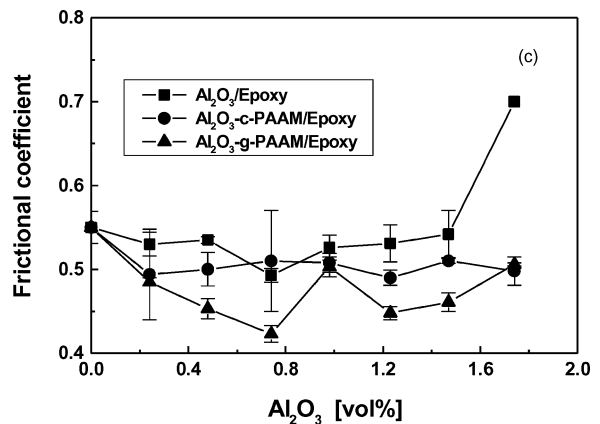
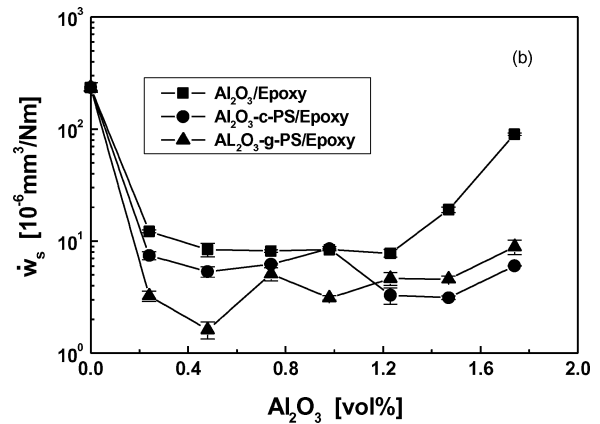
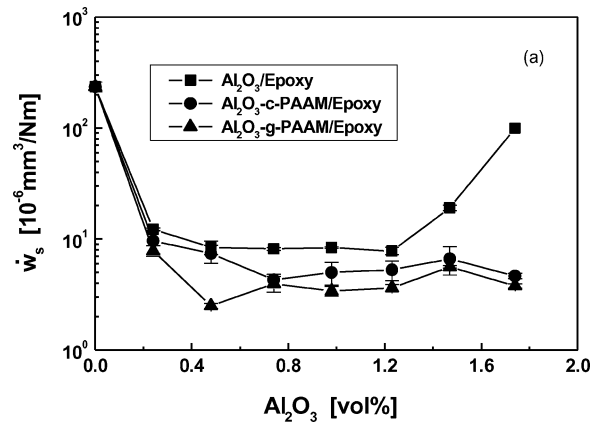


Figure 7 Filler content dependence of (a), (b) specific wear rate, w_s , and (c), (d) frictional coefficient of epoxy and its composites filled with untreated and treated nano-alumina particles.

energy dissipation. Therefore, the composites possess much higher impact toughness than the ones with untreated nanoparticles.

Besides mechanical properties, surface characteristics of a material would also influence its tribological performance. Fig. 6 examines the microhardness of the composites as a function of filler content. Due to the support effect of hard particles, all the composites have higher hardness than unfilled epoxy. With a rise in particle content (<1.5 vol%), the values of composites' hardness keep almost unchanged and there is not much difference between the composites with and without grafted nanoparticles. It implies that within the current filler content range the particles are not dense enough to resist the indentation of the microhardness tester. When the particles content is so high that severe agglomeration of the particles takes place as a result of the significantly decreased viscosity, composites' microhardness would be further raised, as evidenced by the responses at 1.74 vol% of nano-alumina in Fig. 6. In fact, the highest microhardness of untreated nano-alumina/epoxy composites at 1.74 vol% of the fillers demonstrates from another angle that the grafting pretreatment facilitates homogenisation of the particles in the matrix preventing severe agglomeration.

Friction and wear properties of the composites are plotted as a function of nano-alumina content in Fig. 7. Incorporation of the nanoparticles can drastically decrease wear rate and frictional coefficient of epoxy, while the grafted particles are able to bring about more

prominent improvement. For example, the wear rate of epoxy is decreased from $\sim 200 \times 10^{-6}$ mm³/Nm to $\sim 10 \times 10^{-6}$ mm³/Nm by the addition of 0.48 vol% of untreated nano-alumina and to 2.5×10^{-6} mm³/Nm with Al₂O₃-g-PAAM at the same nano-alumina content (Fig. 7a). It means that the nanoparticles are very effective to improve the tribological performance of epoxy, and surface grafting treatment further strengthens this positive effect. In other words, an increase in structural integrity of the composites decreases the possibility of wear loss. Relatively speaking, the reduction in frictional coefficient of epoxy due to the incorporation of nano-alumina is not as significant as that in wear rate. This might be related to the nature of the nanoparticles. It is known that the detached nanoparticles might act as tiny rolling balls at the counterface, providing the effect of solid lubricating [16]. Since nano-alumina particles still have certain angularity, the corresponding lubricating effect would be weaker than other nanoparticles.

Fig. 7 also shows the effect of homopolymer generated during grafting polymerisation onto the nanoparticles. The composites containing grafted nanoparticles without the homopolymers perform better than those with the homopolymers. It seems that thinner interphase in the composites would lead to higher wear resistance of the composites. With respect to the species of the grafting polymers, Al₂O₃-g-PS/Epoxy has the lowest wear rate of 1.62×10^{-6} mm³/Nm at 0.48 vol% of the nanoparticles, which is even lower than that of

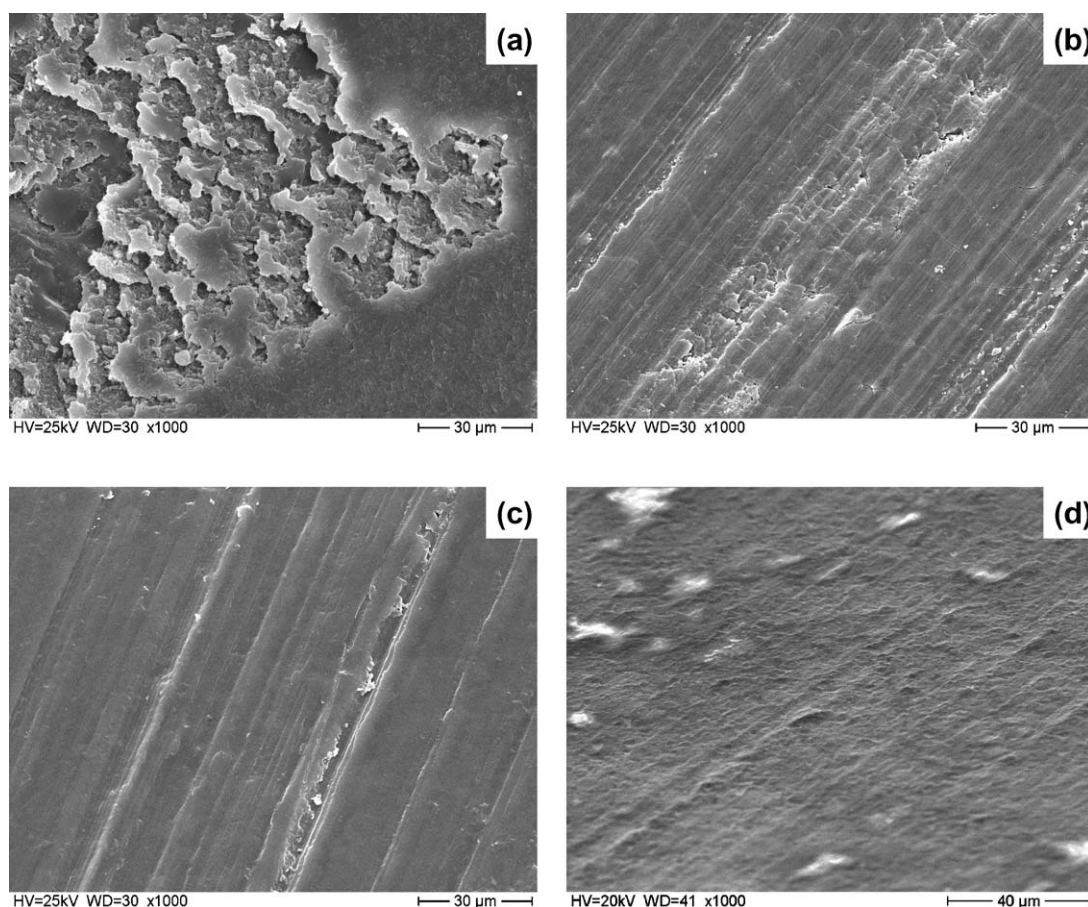


Figure 8 SEM photos of worn surfaces of (a) unfilled epoxy, (b) untreated nano-Al₂O₃/Epoxy composites (nano-alumina content: 0.48 vol%), (c) Al₂O₃-g-PAAM/Epoxy composites (nano-alumina content: 0.48 vol%), (d) Al₂O₃-g-PS/Epoxy composites (nano-alumina content: 0.48 vol%).

Al₂O₃-g-PAAM/Epoxy. It means that good interfacial compatibility is more important than direct chemical bonding between the fillers and the matrix when wear resistance of the composites is concerned.

A more careful survey of Fig. 7 indicates that in contrast to the composites filled with grafted nano-alumina, there are large increments of wear rates and frictional coefficients for untreated nano-alumina/epoxy composites at 1.74 vol% of nano-alumina. This coincides with the above analysis of the unusual increase of microhardness of the composites illustrated in Fig. 6. Evidently, the severe agglomeration of the nanoparticles makes the composites to be easily damaged under repeated frictional stress. Besides the increased amount of material loss as reflected by the increased wear rate, the large wear debris detached from the worn surface would result in abrasion that increases the frictional coefficient of the system.

By comparing Figs 4 and 7, it is seen that flexural modulus and strength are not important factors in terms of wear reduction, but there is certain correlation between impact toughness and tribological properties. It might be due to the similarity of the dynamic loading circumstances.

In order to acquire more knowledge about the variation in wear modes due to the addition of nano-alumina, SEM photos of the worn surfaces are shown in Fig. 8. Fig. 8a is taken from a typical portion of the worn surface of unfilled epoxy. It is characterized by the traces of scale-like removal of materials on the pin top due to fatigue-delamination mechanism. The damage is initiated at the subsurface and then propagates to the contact surface. Fig. 8b portrays the worn surface of untreated nano-alumina filled epoxy. The morphology is completely different from that of the unfilled epoxy, and becomes relatively smooth. The wear mode has changed to mild micro-ploughing accordingly. As compared to the untreated nano-Al₂O₃/Epoxy composites (Fig. 8b), the wear tracks on the composites with grafted nano-alumina are not sharp enough (Fig. 8c and d). It again demonstrates the effect of increased interfacial adhesion between the filler particles and the matrix, which helps to transfer the applied stress effectively and enhance the surface resistance to wear.

4. Conclusions

Nano-alumina particles prove to be promising fillers for reducing wear rate and frictional coefficient of epoxy sliding against steel. Graft polymerization onto the nanoparticles results in better dispersion, enhanced interfacial interaction in the composites and hence much remarkable improvement of the tribological performance of epoxy based composites. At the nano-alumina content of 0.48 vol%, the wear rate of Al₂O₃-g-PS/Epoxy is $1.62 \times 10^{-6} \text{ mm}^3/\text{Nm}$, which is much

smaller than that of unfilled epoxy lying at about $200 \times 10^{-6} \text{ mm}^3/\text{Nm}$.

The presence of nano-alumina accelerates curing reaction of epoxy because of the catalytic effect of hydrogen groups and the reduced free volume. Impact toughness of epoxy is raised owing to the crack pinning mechanism of the nanoparticles, especially when the grafted nanoparticles are used. The present work manifests that through proper surface treatment an overall property enhancement of epoxy can be achieved.

Acknowledgment

The financial support by the Volkswagen-Stiftung, Federal Republic of Germany (Grant No. I/76645), for the cooperation between the German and Chinese institutes on this subject is gratefully acknowledged. Further thanks are due to the National Natural Science Foundation of China (Grant: 50273047), and the Team Project of the Natural Science Foundation of Guangdong, China (Grant No. 20003038).

References

1. B. VISHWANATH, A. P. VERMA and C. V. S. KAMESWARA RAL, *Wear* **167** (1993) 93.
2. S. BAHADUR and D. GONG, *ibid.* **158** (1992) 41.
3. I. C. VISCONTI, A. LANGELLA and M. DURANTE, *Appl. Comp. Mater.* **8** (2001) 179.
4. C. J. SCHWARTZ and S. BAHADUR, *Wear* **237** (2000) 261.
5. Y. M. CAO, J. SUN and D. H. YU, *J. Appl. Polym. Sci.* **83** (2002) 70.
6. H. Y. WANG, Y. L. BAI, S. LIU, J. L. WU and C. P. WONG, *Acta Mater.* **50** (2002) 4369.
7. V. P. PERMINOV, A. G. MODYANOVA, Y. I. RYABKOV, O. A. SEVBO, I. A. GAILYUNAS and A. V. KUCHIN, *Russ. J. Appl. Chem.* **75** (2002) 636.
8. KISHORE and K. KUMAR, *High Temp. Mater. Proc.* **17** (1998) 271.
9. M. Q. ZHANG, M. Z. RONG, S. L. YU, B. WETZEL and K. FREIDRICH, *Macromol. Mater. Eng.* **287** (2002) 111.
10. M. Z. RONG, Q. L. JI, M. Q. ZHANG and K. FREIDRICH, *Eur. Polym. J.* **38** (2002) 1573.
11. S. PAZ-ABUIN, A. LOPEZ-QUINTELA, M. P. PELLIN, M. VARELA and P. PRENDES, *J. Polym. Sci. Polym. Chem.* **36** (1998) 1001.
12. N. ALTMANN, P. J. HALLY, J. COOPER-WHITE and J. LANGE, *Macromol. Symp.* **169** (2001) 171.
13. J. SPANOUDAKIS and R. J. YOUNG, *J. Mater. Sci.* **19** (1984) 487.
14. L. NICHOLAIS and L. NICODEMO, *Polym. Eng. Sci.* **13** (1973) 469.
15. R. P. SINGH, M. ZHANG and D. CHAN, *J. Mater. Sci.* **37** (2002) 781.
16. M. Z. RONG, M. Q. ZHANG, H. LIU, H. M. ZENG, B. WETZEL and K. FRIEDRICH, *Ind. Lubr. Tribology* **53** (2001) 72.

Received 19 August 2003

and accepted 23 June 2004