

Tribological Behavior of Epoxy Composites Containing Reactive SiC Nanoparticles

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ABSTRACT: The present article evaluated the sliding wear behaviors of epoxy and its composites filled with SiC nanoparticles. Polyglycidyl methacrylate (PGMA) and a copolymer of glycidyl methacrylate and styrene were grafted onto the nanoparticles as a measure of surface pretreatment, respectively. The grafted polymers were selected because the epoxide groups on PGMA would take part in the curing reaction of epoxy resin and covalently connect the nanoparticles with the matrix, while styrene acted as a copolymerized monomer to adjust the amount of the reactive groups of the grafted macromolecular chains, and hence the compatibility

between the grafted polymers and the matrix. In comparison to the composites filled with untreated nano-SiC particles, the composites with the grafted nano-SiC exhibit improved sliding wear resistance and reduced frictional coefficient owing to the chemical bonding at the filler/matrix interface. The results were analyzed in terms of structure-properties relationship of the composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2608–2619, 2007

Key words: nanoparticles; surface grafting; nanocomposites; friction and wear; interfaces

INTRODUCTION

Polymers and polymer composites have been used increasingly as engineering materials for technical applications in which tribological properties are of considerable importance. In general, fillers (e.g., glass, carbon, asbestos, oxides, and textile fibers) are incorporated for improving the composites' tribological performance.¹ The reduction in wear rate is mainly due to preferential load support of the reinforcement components, by which the contribution of abrasive mechanism to the wear of the materials is highly suppressed. However, composites filled with micron-size particles usually need quite large amount of fillers to attain an evident improvement of wear resistance.² As a result, some inherent defects have to be inevitably involved. For example, disintegration of the fillers and detached particles were frequently observed for both phenolic and epoxy resin composites when an indenter moved

over the systems, leading to sharp fluctuations in the measured coefficient of friction.³ Furthermore, the high concentration of micro-fillers must be detrimental to the processibility of polymers, especially for thermosetting polymers used as coating materials. Considering the disadvantages imparted by micro-fillers, utilization of nanoparticles or nanofibers would be an optimum alternative to make the most of the technique based on filler incorporation.^{4–6}

Bulk SiC has been known as a ceramic material with high hardness, wear resistance, high temperature stability, and chemical inertness. Accordingly, SiC nanoparticles were employed in the present work to prepare wear resisting nanocomposites in hopes of providing the excellent tribological performance of SiC to the matrix materials. Xue and Wang found that under either dry or water lubrication, wear rate and frictional coefficient of nano-SiC/polyetheretherketone (PEEK) composites were evidently lower than those of unfilled PEEK.^{7,8} Besides, nanometer SiC was able to reduce the wear of PEEK more effectively than micron SiC.⁷ A thin, uniform, and tenacious transfer film formed on the counterpart surface in the case of carbon steel ring/nano-SiC filled composite block. It was believed that some proportion of nanometer SiC was oxidized into SiO₂ during the rubbing process, existing in the transfer film and the wear trace of the block.⁹ As nano-SiO₂ in PEEK is very effective in decreasing friction and wear,¹⁰ it might partly explain why nano-SiC/PEEK composite exhibited the aforesaid improvement of the tribological properties.

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It is worth noting that nanoparticles are very difficult to be uniformly dispersed in polymers because of the strong attraction between the particles and the limited shear force during compounding. Consequently, nanoparticles filled polymers used to contain a number of loosened clusters of nanoparticles, which would lead to extensive material loss in terms of disintegration and crumbling of the particle agglomerates under tribological conditions. To avoid these drawbacks, a series of methods have been attempted in two aspects: development of new compounding (dispersion) techniques and surface pretreatment approaches for nanoparticles. Comparatively, surface modification of nano-fillers is more effective and easier to be applied.¹¹

In our previous works, graft polymerization onto nanoparticles proved to be feasible in improving tribological behavior of polymer nanocomposites.^{12–17} The grafted polymers changed the hydrophilic surface feature of the particles to hydrophobic and broke apart the nanoparticle agglomerates during polymerization process. Besides, filler/matrix interfacial interaction in the composites was enhanced mainly due to chain entanglement of grafted polymer with matrix polymer.

In fact, the interfacial adhesion can be further increased if a chemical reaction between the filler and matrix could take place. This concept is similar to the reactive compatibilization employed in making polymer blends. So far, however, there are little reports using this approach for manufacturing wear resistant nanocomposites. In this paper, polyglycidyl methacrylate (PGMA) was adhered to SiC nanoparticles through emulsifier-free emulsion graft polymerization, and then the treated nano-SiC particles were mixed with epoxy. The grafted polymer (i.e. PGMA) was selected because the epoxide groups on PGMA would take part in curing reaction of epoxy resin, so that the nano-SiC particles could be covalently connected to the matrix, which is believed to be beneficial to the tribological performance of the composites. In addition, styrene was used as a copolymerized monomer to adjust the amount of the reactive groups of the grafted macromolecular chains, so that the compatibility of the grafted copolymers with the composite matrix can be tuned. Its effect on the composite's properties was also studied.

EXPERIMENTAL

Materials

Nanosized SiC provided by Hua-Tai Co., China, were in its α -phase with a specific surface area of 15.2 m²/g and an averaged diameter of 61 nm, respectively. Prior to use, the particles were dried in an oven at 110°C under vacuum for 24 h to get rid of the physically absorbed and weakly chemically absorbed species. 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. A silane coupling agent (γ -methacryloxypropyl trimethoxy silane, provided by Liao Ning Gaizhou Chemical Industry Co., China) was employed to introduce the reactive double bonds on the surface of the nanoparticles prior to graft polymerization. The grafting monomers glycidyl methacrylate (GMA, Shanghai Yuanji Chemical Engineering Co., China) and styrene (St, Guangzhou Guanghua Chemical Co., China) were distilled under low pressure before use.

Graft polymerization onto SiC nanoparticles

The nanoparticles were grafted with PGMA and GMA/St copolymer in terms of emulsion graft polymerization without or with surfactant, respectively. The details of the surfactant-free emulsion graft polymerization have been described in Ref.¹⁸ After the graft polymerization, the product was extracted with acetone for 50 h to isolate the polymer-grafted SiC (SiC-g-PGMA) from the absorbed homopolymers. Then the grafted nanoparticles were dried under vacuum at 50°C. Some of them were transferred to a Shimadzu TA-50 thermogravimeter to determine the percent grafting, γ_g . In the subsequent procedures of composites manufacturing, the SiC-g-PGMA with a percent grafting of 8 wt % was used as the treated fillers. The number-average molecular weight, M_n , of the ungrafted PGMA is 7.0×10^3 as determined by a Walter 208LC gel permeation chromatograph (GPC). Since nano-SiC is hard to be dissolved, the grafted polymers cannot be isolated by conventional separation methods. It is believed that the grafted PGMA possesses similar molecular weight as the ungrafted one.

For emulsion graft copolymerization of GMA and St onto nano-SiC, a typical procedure is described as follows. Two grams silane-treated nano-SiC was charged into a three-neck flask (~250 cc) that contained 100 mL distilled water. After adding the surfactant (OP-10/SDS (sodium dodecyl sulfonate) 1/1, 5 wt % based on the monomer weight), the solution was ultrasonic agitated for 10 min, and then heated up to 50°C and stirred for 30 min during the drip-feeding of the first monomer St under nitrogen atmosphere. The initiator (potassium persulfate solution, 0.006 mol/L) was added at 60°C, and subsequently the graft reaction proceeded for 1 h at

TABLE I
Molecular Weights of Ungrafted P(GMA-co-St)

St/GMA monomer feed (vol/vol)	M_n	M_w (10^5)	M_w/M_n
1.5:1	3.3×10^4	1.0	3.03
2.5:1	9.6×10^4	2.2	2.34
3.5:1	1.1×10^5	2.6	2.42

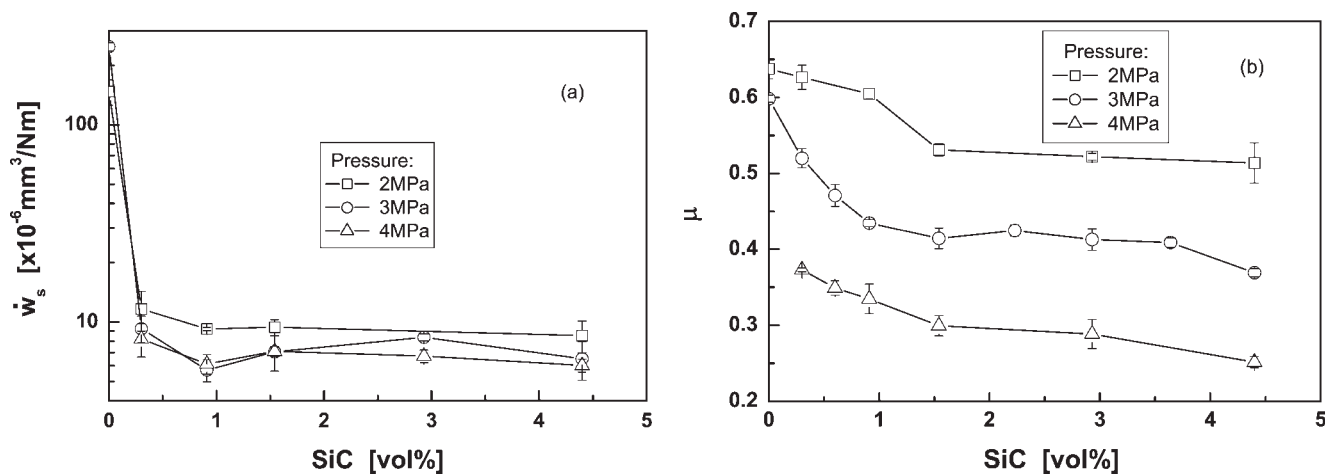


Figure 1 (a) Specific wear rate, \dot{w}_s , and (b) frictional coefficient, μ , of nano-SiC/Ep composites as a function of SiC volume fraction.

82°C. The copolymerization started when the second monomer GMA was added into the solution within 30 min, then the temperature was increased to 90°C and kept for 30 min. Finally, the reaction was stopped by ice cooling, and 20 mL AlCl_3 solution (20%) was used to break the emulsion. The product (SiC-g-P(GMA-co-St))

was obtained by filtrating, washing with distilled water for several times, and drying at 50°C for 24 h under vacuum. The dried mixture was extracted with toluene for 50 h to remove the homopolymer, and then dried again under vacuum at 80°C for 24 h. Similarly, the percent grafting, γ_{gr} , was determined by TGA. Table I shows the

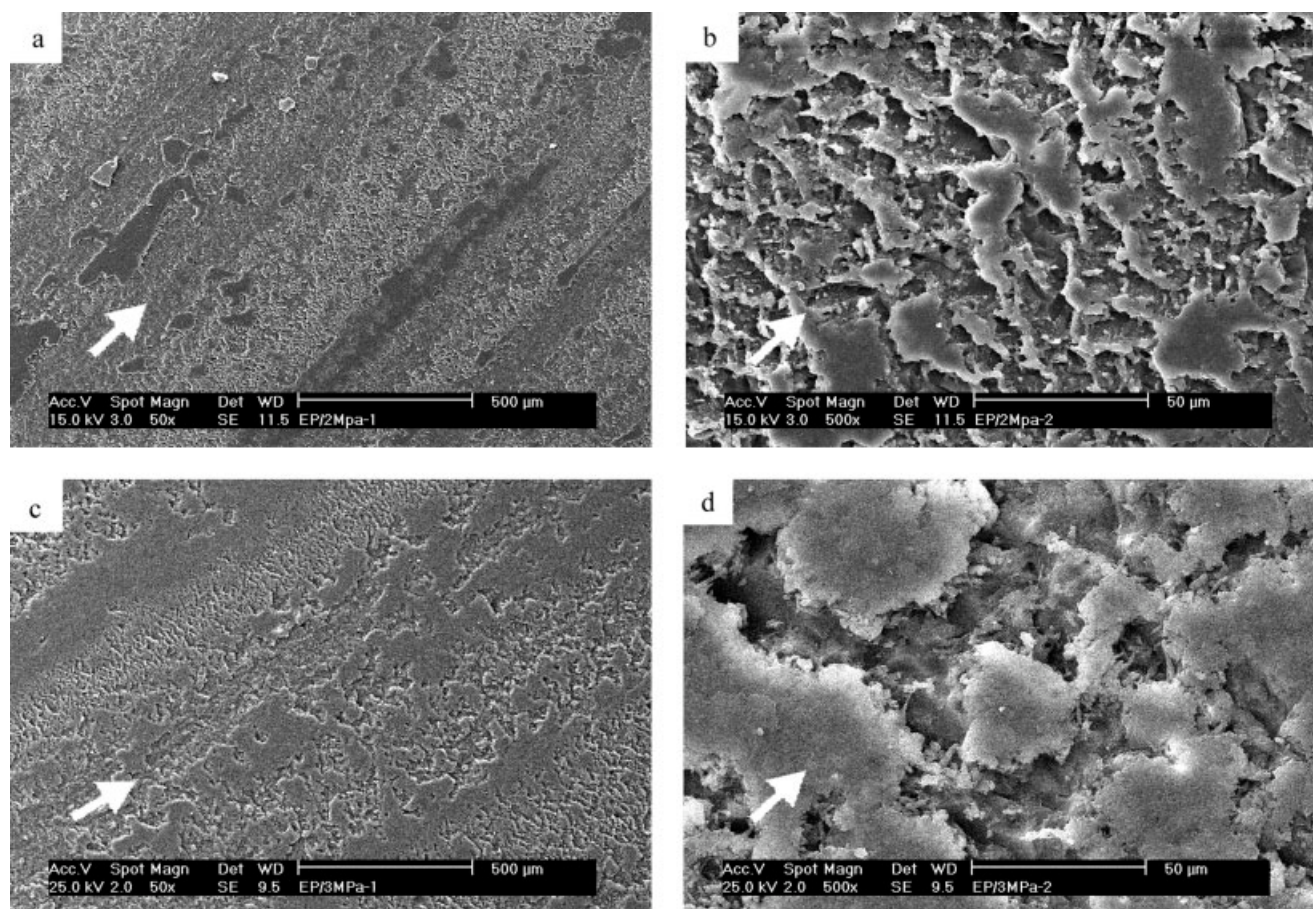


Figure 2 SEM micrographs of the worn surfaces of epoxy experienced wear tests under pressures of (a, b) 2 MPa and (c, d) 3 MPa. The arrows indicate the sliding direction.

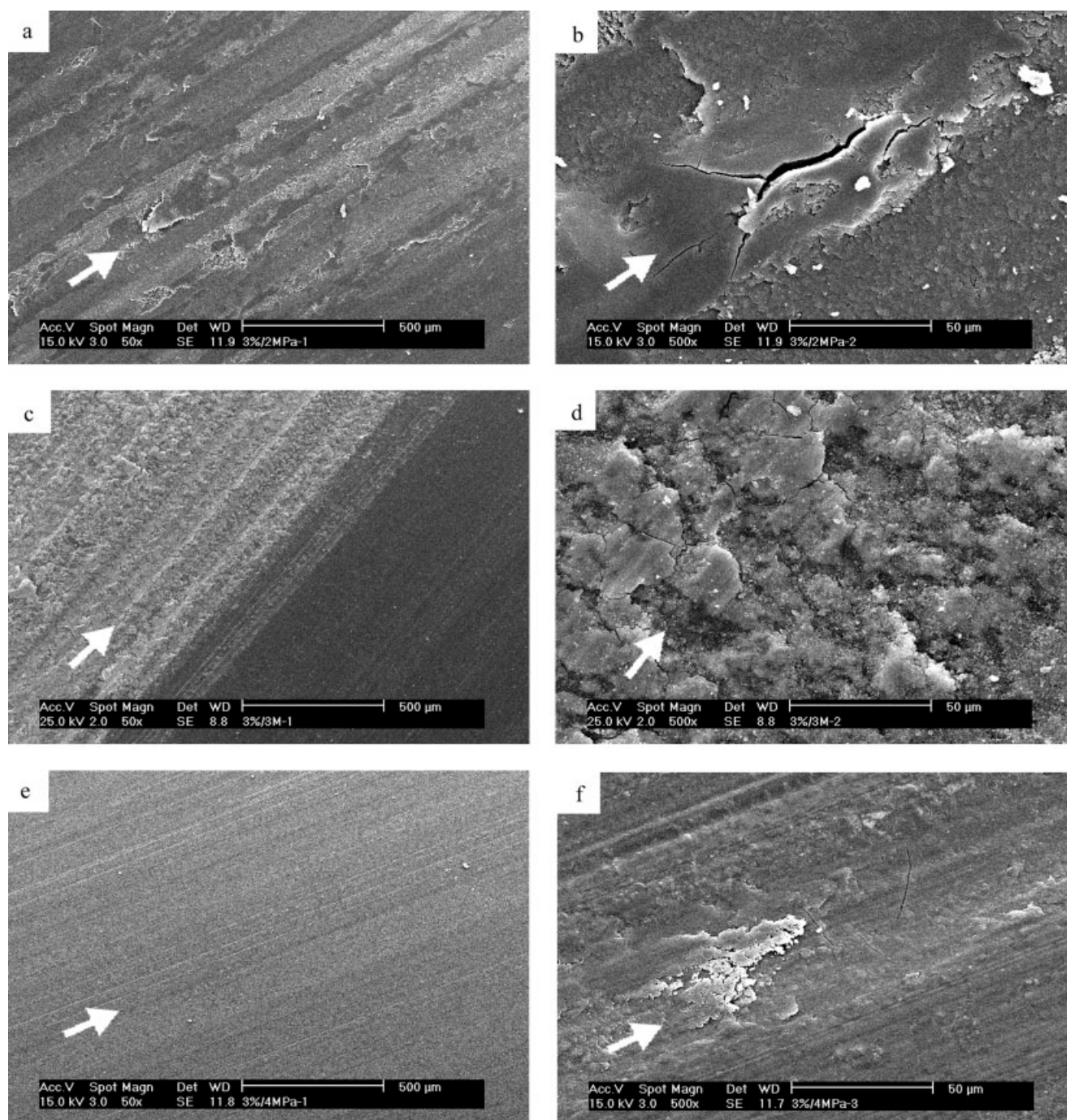


Figure 3 SEM micrographs of the worn surfaces of SiC/Ep composites (SiC = 0.91 vol %) experienced wear tests under pressures of (a, b) 2 MPa, (c, d) 3 MPa, and (e, f) 4 MPa. The arrows indicate the sliding direction.

average molecular weights (M_n and M_w) of ungrafted St-GMA copolymer determined by GPC. It is noted that the molecular weights of the copolymer change with the ratio of St/GMA in monomer feed. Besides, Fourier transform infrared (FTIR) spectroscopy was used to determine the grafted copolymer composition, while a TA MDSC2910 differential scanning calorimeter was employed to evaluate the reactivity of SiC-g-PGMA with the curing agent DDS.

Manufacturing of epoxy based nanocomposites

The composite materials were fabricated by mixing the (untreated or treated) SiC nanoparticles and epoxy (Ep) together with a fast stirring for 3 h under vacuum, and then ultrasonic agitation for 1 h. 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 mold and the curing pro-

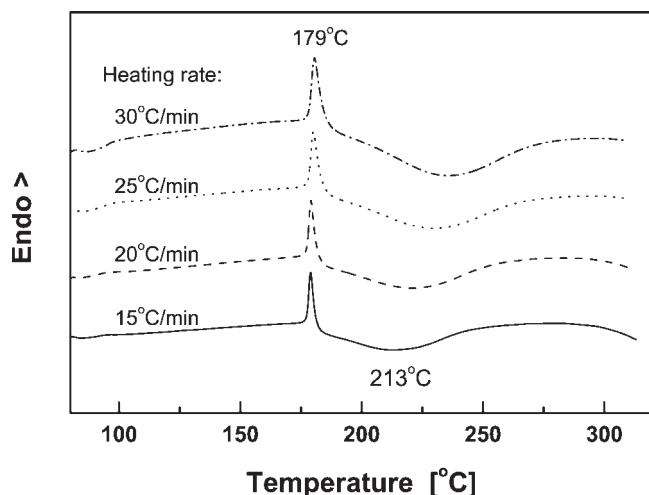


Figure 4 DSC traces of SiC-g-PGMA/Ep system (2/1 by mole) recorded at various heating rates.

cedure began after extraction of possible air bubbles for 45 min. 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.

Characterization

Unlubricated sliding wear tests were carried out using a pin-on-ring configuration at a constant velocity of 0.42 m/s and different pressures to obtain specific wear rate, \dot{w}_s , and friction coefficient, μ . The specimens for wear tests were machined with a geometry of $5 \times 10 \times 15 \text{ mm}^3$. Prior to wear testing, all the samples were preworn to average surface conditions and to reduce the running-in period. The actual steady-state test was conducted for 3 h using the same steel ring as that used for the preworn procedure. After that, a weight measurement of the specimens was conducted. The worn surfaces of the specimens were observed by a Philips XL-30FEG scanning electron microscope (SEM).

Composites' microhardness was measured by a Shimadzu DUH-W201S dynamic microhardness tester under a load of 50 mN and a depth of 10 μm . For each sample 10 points were measured. The roughness of the worn surface was measured by SPM-9500J3 atomic force microscope (AFM). X-ray energy distribution spectra (EDS) of the counterpart steel rings were collected with a LINK-ISIS 300 apparatus at an accelerating voltage of 20 kV. X-ray photoelectron spectra (XPS) of the composites' surfaces were recorded by means of a Vacuum Generators Escalab MK II X-ray photoelectron spectrometer with a resolution of 0.8 eV at 240 W (Mg K α 12 kV). Dynamic mechanical analysis (DMA) was made with a TA Instruments (2980 dynamic mechanical analyzer) under 1 Hz from -130°C to 250°C at a heating rate of $5^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Friction and wear performance of SiC/Ep composites

Friction and wear properties of SiC/Ep composites are plotted as a function of nano-SiC content in Figure 1. Incorporation of the nanoparticles can drastically decrease wear rate and frictional coefficient of epoxy. Under a pressure 3 MPa, for example, the wear rate of epoxy is decreased from $\sim 200 \times 10^{-6}$ to $\sim 6 \times 10^{-6} \text{ mm}^3/\text{Nm}$ by the addition of 0.6 vol % of untreated nano-SiC. It means that the nanoparticles are very effective to improve the tribological performance of epoxy. These effects can be related with the enhancement of epoxy surface stiffness and wear resistance by addition of nanoparticle. With a rise in the nanoparticles concentration, the declining trend of both wear rate and frictional coefficient is gradually subsiding or replaced by a slight increase. It might be due to the fact that the increased amount of the nanoparticles is unfavorable to

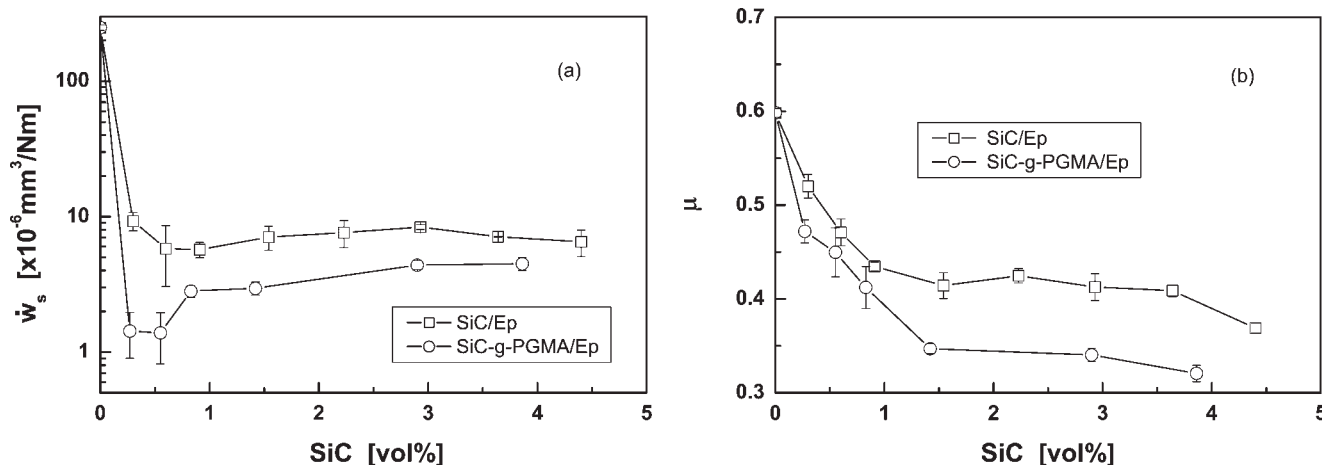


Figure 5 Specific wear rate (a) and friction coefficient (b) of SiC/Ep and SiC-g-PGMA/Ep composites ($\gamma_g = 8 \text{ wt } \%$) as a function of SiC volume fraction.

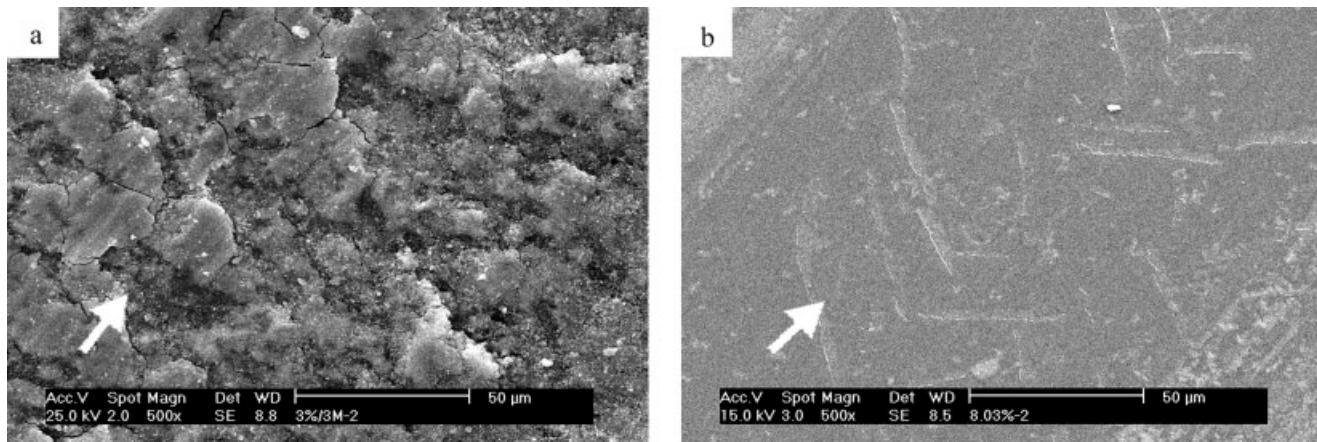


Figure 6 SEM micrographs of the worn surfaces of (a) SiC/Ep (SiC = 0.91 vol %) and (b) SiC-g-PGMA/Ep (SiC = 0.83 vol %, $\gamma_g = 8$ wt %) composites. The arrows indicate the sliding direction.

filler dispersion.¹⁹ Agglomeration of the nanoparticles deteriorates their lubricating effect. On the other hand, when the contact pressure increases from 2 to 3 MPa, the wear rate of SiC/Ep composites decreases and remains nearly unchanged as the pressure is further raised from 3 to 4 MPa, while the friction coefficient keeps continuously decreasing tendency.

It is well known that load carrying capacity of unfilled epoxy is poor. When the wear pressure increases from 1 to 3 MPa, the wear rate of unfilled epoxy increases for two orders of magnitude. At a pressure of 5 MPa, the sample failed and the test had to be terminated abnormally.¹⁷ However, in this work, it seems that the higher pressure facilitates the nanoparticles to take effects. To have more information about the variation in wear behaviors of bulk epoxy under different pressures due to the addition of the nano-SiC, morphologies of the worn pins' surfaces were examined by SEM (Figs. 2 and 3). Severe damages characterized by disintegration of the top layer are observed in

unfilled epoxy [Fig. 2(a, b)]. The higher contact pressure leads to more substantial material loss [Fig. 2(c, d)], revealing that the adhesive wear mechanism plays the main role. Usually higher pressure would cause higher frictional temperature at the surface, and hence more serious adhesive wear occurs.

In the case of nano-SiC filled composites, the worn appearances are completely different and become rather smooth (Fig. 3). The lowering grooves and cracks across the wear tracks are perceivable on the composites' worn surfaces. The former corresponds to the abrasive wear, while the latter is related to the fatigue-delamination process. The cracks might be nucleated at subsurface layer as a result of shear deformation induced by the traction of the harder asperities, and then coalesce and cause the scale-like damage patterns. It can thus be concluded that the adhesive wear of unfilled epoxy is replaced by a mixed mode of abrasive wear and fatigue wear when the untreated nano-SiC particles are incorporated. Under higher pressure, the

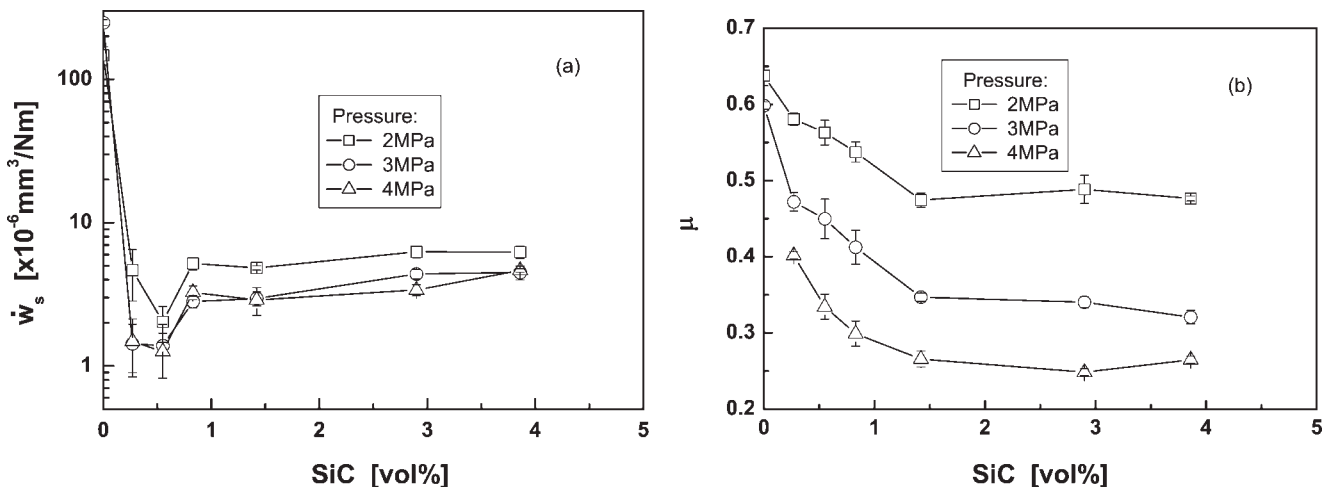


Figure 7 (a) Specific wear rate, \dot{w}_s , and (b) frictional coefficient, μ , of SiC-g-PGMA/Ep composites as a function of SiC volume fraction.

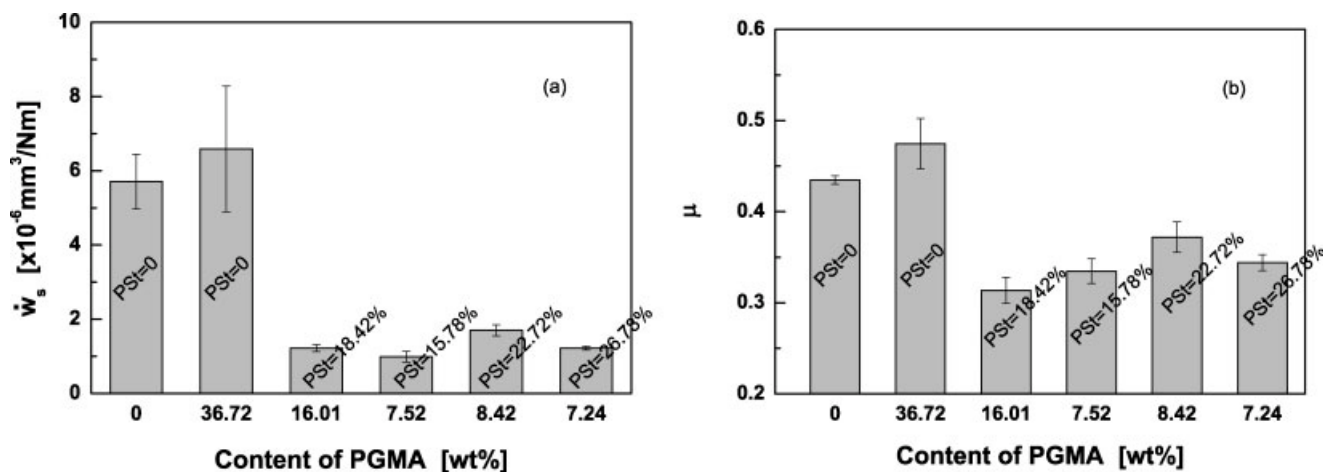


Figure 8 Effect of PGMA/PS ratio of P(GMA-co-St) attached to SiC nanoparticles on (a) specific wear rate, \dot{w}_s , and (b) frictional coefficient, μ , of SiC-g-P(GMA-co-St)/Ep composites (SiC = 0.68 vol %).

higher frictional temperature certainly arouses large-scale plastic deformation, which consequently merges the cracks or debris and even helps to form a transferred film on the counterpart surface. All these factors bring about a smooth surface and smaller cracks on the worn surfaces [Fig. 3(e,f)].

Friction and wear performance of SiC-g-PGMA/Ep and SiC-g-P(GMA-co-St)/Ep composites

The purpose of grafting PGA onto nano-SiC is to introduce chemical bonding between particles and matrix. Therefore, the reactivity of SiC-g-PGMA with curing agent DDS should be first explored even though the possible reaction has been proved in our previous work.²⁰ Accordingly, a model mixture consisting of stoichiometrical SiC-g-PGMA and DDS was heated and monitored by a DSC at different heating rates (Fig. 4). It is seen that the melting peaks of DDS appear at about 179°C, while the exothermic peaks at 213°C should be

ascribed to the reaction between PGMA and DDS. By using the well-known Kissinger equation,²¹ the activation energy was estimated at 58.5 kJ/mol, which is much lower than the value of epoxy/DDS system (62.5 kJ/mol). It means that the epoxide groups on the grafted PGMA should easily take part in the curing reaction.

The advantages of the grafted nanoparticles in tribological performance of epoxy composites are revealed in Figure 5. It is seen that within the entire range of filler content of interests, the wear resistance of SiC-g-PGMA/epoxy composites is higher than that of SiC/epoxy. Meanwhile, the grafted nanoparticles also lead to more significant reduction in frictional coefficient of epoxy as compared with the untreated version. The difference in improving the wear resisting and friction reducing ability of epoxy between the composites with untreated and treated SiC nanoparticles should mainly result from the filler/matrix adhesion strength. As stated before, the grafted PGMA employed in the present work can build up chemical bonding between the

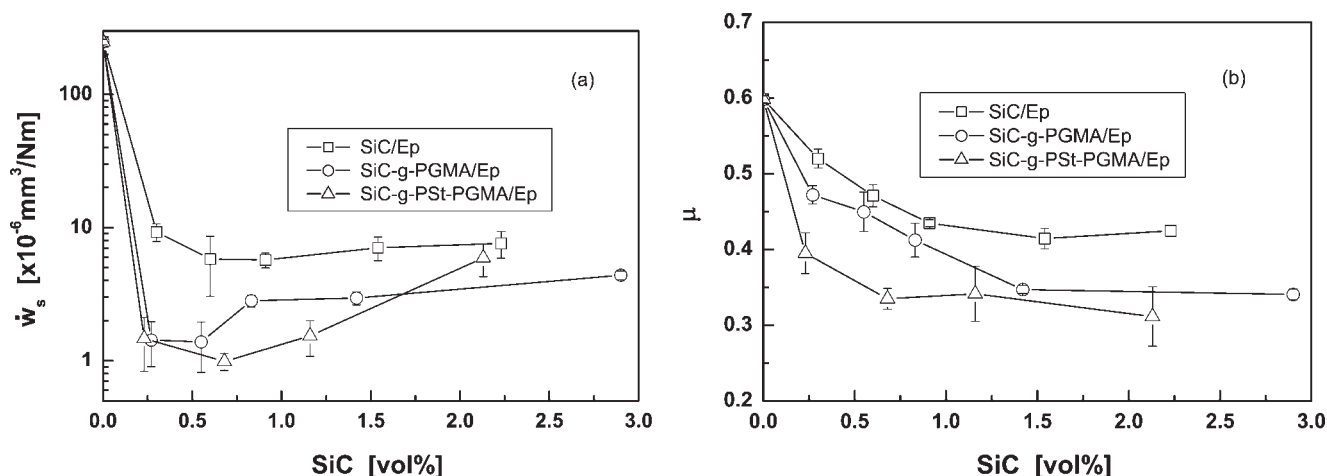


Figure 9 (a) Specific wear rate, \dot{w}_s , and (b) frictional coefficient, μ , of SiC/Ep, SiC-g-PGMA/Ep ($\gamma_g = 8$ wt %) and SiC-g-P(GMA-co-St)/Ep ($\gamma_g = 23.3$ wt %, PS/P(GMA-co-St) = 15.78/7.52) composites as a function of SiC volume fraction.

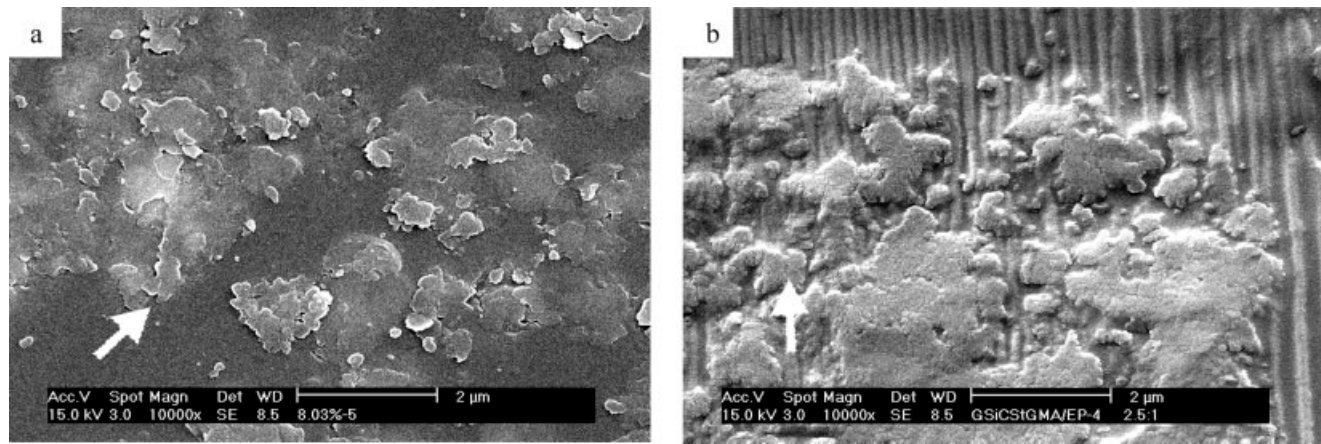


Figure 10 SEM micrographs of the worn surfaces of (a) SiC-g-PGMA/Ep (SiC = 0.83 vol %, γ_g = 8 wt %) and (b) SiC-g-P(GMA-co-St)/Ep (SiC = 0.68 vol %, γ_g = 23.3 wt %, PS/PGMA = 15.78/7.52) composites. The arrows indicate the sliding direction.

nanoparticles and epoxy resin, which should be responsible for the higher resistance to periodic frictional stress. As a result, the strong interfacial adhesion is able to prevent the friction induced crack initiation, coalescence, and propagation. Accordingly, the composites with grafted nano-SiC show higher wear resistance and lower frictional coefficient than those with untreated nano-SiC.

Figure 6 compares the worn surfaces of the composites. Clearly, SiC/epoxy shows a much rougher appearance accompanying by many cracks, while SiC-g-PGMA/epoxy possesses rather smooth surface without obvious cracking. It suggests that polishing effect predominate the wear process of the latter composites, evidencing the change in wear mode described earlier.

The influence of contact pressure on the tribological performance of SiC-g-PGMA/epoxy composites presents similar trend as SiC/epoxy (Fig. 7), further demonstrating that fatigue wear mechanism takes effect in this system. Because of the stronger bonding at the interface, the treated nanoparticles perform better in the composites (cf. Figs. 1 and 7).

In our preliminary study, it was found that SiC nanoparticles with a moderate percent grafting (γ_g = 8 wt %) gave the best tribological performance for SiC-g-PGMA/epoxy composites.²⁰ That means only suitable amount of GMA groups is required for establishing the interfacial adhesion, while excessive GMA groups might interfere with the dispersion of particles by the possible reaction inside the particle agglomerates. To confirm this estimation, styrene was used as a copolymerized monomer to adjust the amount of the reactive groups of the grafted macromolecular chains, and hence the compatibility of the grafted copolymers with the matrix epoxy. Its effect on the composite's properties is shown in Figure 8. When the percent grafting of PGMA is 36.72 wt %, the specific wear rate and frictional coefficient of SiC-g-PGMA/epoxy are even higher than those of untreated SiC/Ep. However, with the introduction of polystyrene (PSt) into the grafted

polymer, both specific wear rate and frictional coefficient of the composites are evidently lowered in the case of similar percent grafting. The results strongly suggest that excessive GMA groups are detrimental to enhancement of the composites' wear resistance. Figure 9 further compares the tribological behaviors of SiC/Ep, SiC-g-PGMA/Ep, and SiC-g-P(GMA-co-St)/Ep composites as a function of nano-SiC content. Within the filler loading range of interests, the composites containing copolymer-grafted nanoparticles are superior to the others despite the fact that they possess higher percent grafting.

The morphologies of the worn pin surfaces were collected in Figure 10. In comparison with the flake-like wear failures on the surface of SiC-g-PGMA/Ep, the wear scars on the surface of SiC-g-P(GMA-co-St)/Ep composites are characterized by tiny scratches without any detached flakes. It can be attributed to the fact that the treatment via graft copolymerization onto the nanoparticles further improves the miscibility between the

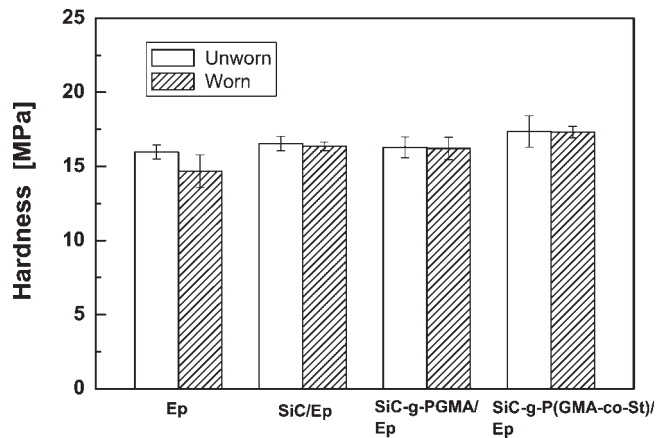


Figure 11 Microhardness of epoxy, SiC/Ep (SiC = 0.3 vol %), SiC-g-PGMA/Ep (SiC = 0.27 vol %, γ_g = 8 wt %), and SiC-g-P(GMA-co-St)/Ep (SiC = 0.68 vol %, γ_g = 23.3 wt %, PS/PGMA = 15.78/7.52) composites before and after the wear tests.

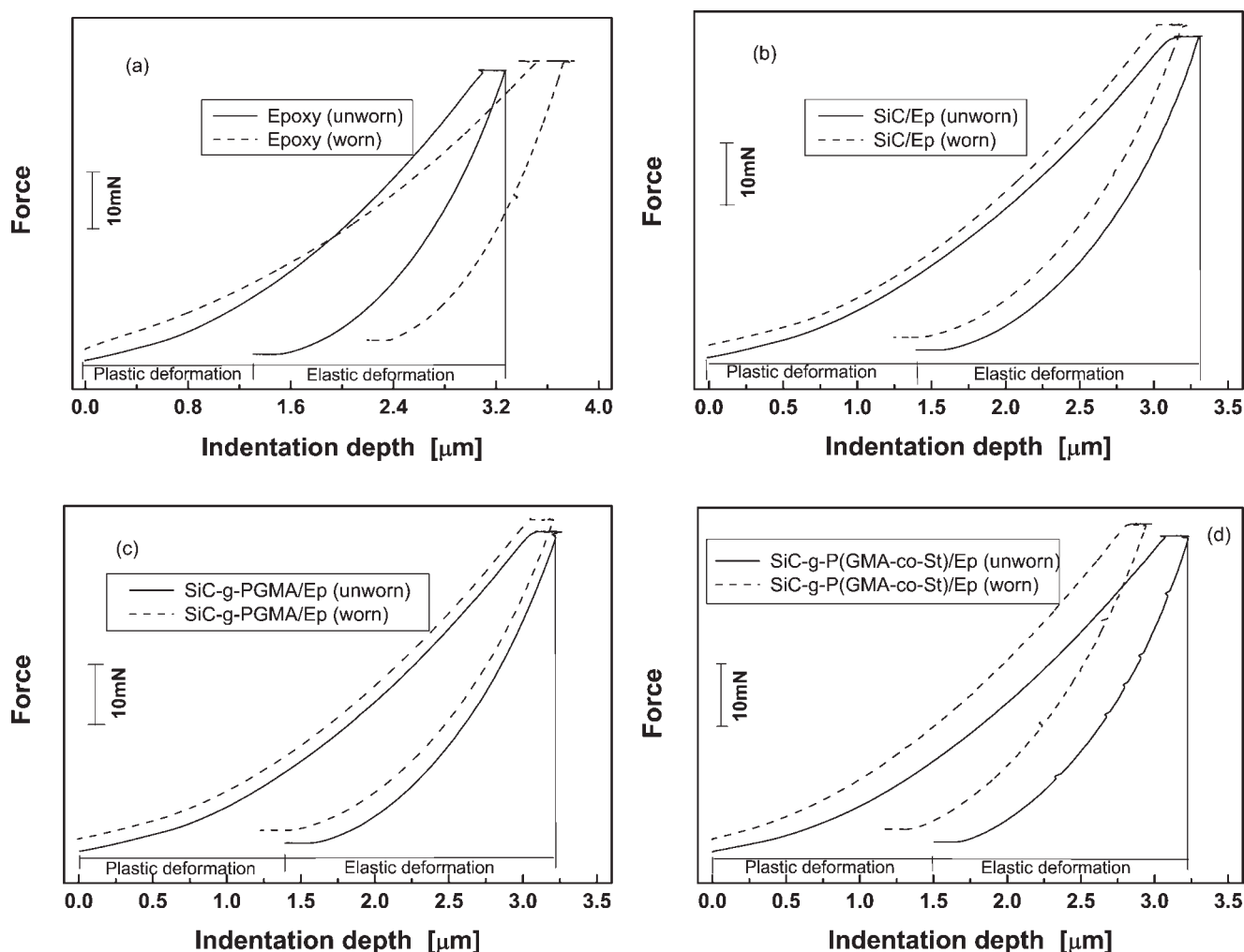


Figure 12 Load-unload curves measured during microhardness tests of (a) epoxy, (b) SiC/Ep (SiC = 0.91 vol %), (c) SiC-g-PGMA/Ep (SiC = 0.83 vol %, $\gamma_g = 8$ wt %), and (d) SiC-g-P(GMA-co-St)/Ep (SiC = 0.68 vol %, $\gamma_g = 23.3$ wt %, PS/PGMA = 15.78/7.52) before and after the wear tests.

grafted polymer and matrix epoxy. It should be beneficial to the dispersion of SiC nanoparticles, and improve the composites' integrity. As a result, the composites' wear resistance was raised accordingly.

Effect of the reaction between grafted polymer and epoxy matrix on the composites' surface feature

The aforementioned results have demonstrated the efficiency of surface grafting treatment of SiC nanoparticles in improving sliding wear properties of epoxy composites. Nevertheless, some details of the role of the chemical bonding on the composites' surface characteristics should be further investigated. Figure 11 shows the microhardness of the materials' surfaces before and after the sliding wear tests. For unfilled epoxy, the microhardness of the worn pin surface is remarkably lowered than the value of the unworn one. It means that the repeated frictional force and high frictional temperature have deteriorated the microstructure of epoxy. When nano-SiC is added, the microhard-

ness of the worn pin surface of the composites is almost the same as that of the unworn one. Besides, it is noted that SiC-g-P(GMA-co-St)/Ep composite possesses a higher hardness, which is indicative of the strong interfacial interaction (chemical bonding) and coincides with its tribological behavior.

On the other hand, the surface feature of epoxy and its composites was also characterized by load-unload curves recorded during the microhardness measurements (Fig. 12). In the case of unfilled epoxy, the worn surface exhibits greater portion of plastic deformation as compared with the unworn one. This reflects destruction of the epoxy network due to the high frictional temperature. However, the addition of SiC nanoparticles exerts restraint effect on the plastic deformation, and even results in a rise in the elastic deformation after the wear test, proving that the interaction between SiC nanoparticles and epoxy is rather strong. When the SiC had been grafted with PGMA or P(GMA-co-St), the elastic deformation of the composites is further improved due

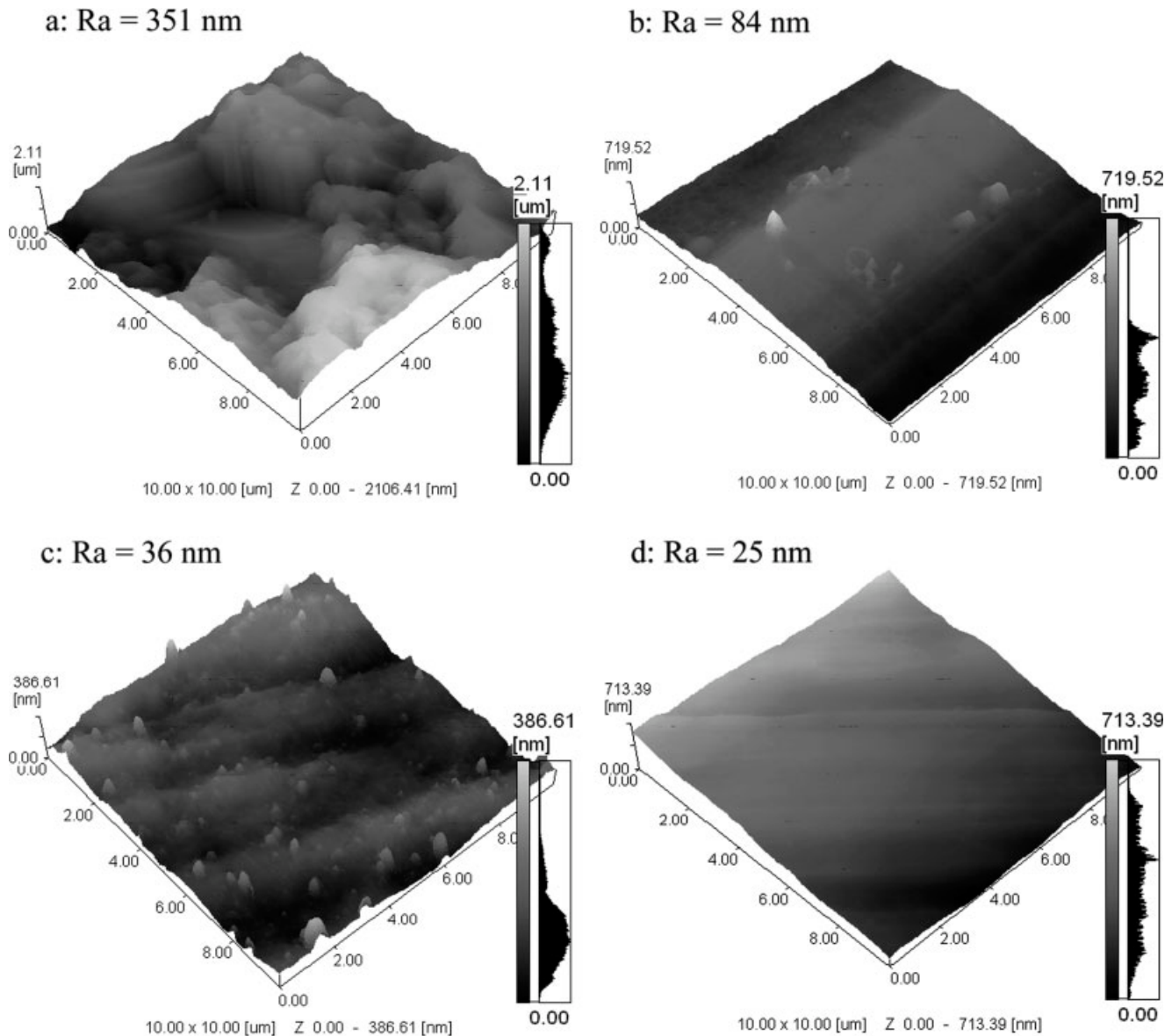


Figure 13 AFM 3D height trace images and average roughness, R_a , of the worn surfaces of (a) epoxy, (b) SiC/Ep (SiC = 0.91 vol %), (c) SiC-g-PGMA/Ep (SiC = 0.83 vol %, γ_g = 8 wt %), and (d) SiC-g(PGMA-co-St)/Ep (SiC = 0.68 vol %, γ_g = 23.3 wt %, PS/PGMA = 15.78/7.52) composites.

to the chemical bonding at the interface. In this sense, the nanoparticles might act as crosslinking sites.

Quantitative description of the worn pin surface profile by AFM presents information about the improvement of the composites' resistance to surface shearing due to the incorporation of SiC nanoparticles from another angle (Fig. 13). Clearly, the wear processes in the SiC filled nanocomposites are dominated by polishing and the worn pin surfaces appear rather smooth. When the particles were grafted with PGMA or P(GMA-co-St), the average roughness of the composites is further reduced by two to three times. The results agree with the aforesaid enhanced integrity and higher wear resistance of the composites.

To illuminate the influence of the chemical bonding on the materials transfer from the specimens to the steel counterpart during wear tests, elements on the steel ring surface were examined (Table II). It is seen that having rubbed against either the unfilled epoxy or the epoxy based composites, element S was detected on the steel counterface. Besides, the amount of Si on the steel ring surface rubbing against the composites is higher than that on the steel ring rubbing against unfilled epoxy. These data prove that the grafted polymer facilitates the adhesion of SiC particles on the steel ring, and strengthens the transferred film. Besides, the low resolution XPS spectra of the pin surfaces of epoxy and nano-SiC/epoxy composites before and after the wear

TABLE II
EDS Analysis of the Steel Counterpart Surface ($p = 3$ MPa, $v = 0.42$ m/s, $t = 3$ h)

	Elements and contents (wt %)		
	Fe	Si	S
Steel ring before wear	98.76	0.48	0
Steel ring rubbed against unfilled epoxy	98.55	0.42	0.21
Steel ring rubbed against SiC/Ep (SiC = 0.6 vol %)	98.02	0.87	0.42
Steel ring rubbed against SiC-g-PGMA/Ep (SiC = 0.55 vol %, $\gamma_g = 8.03$ wt %)	98.37	0.51	0.28
Steel ring rubbed against SiC-g-P(GMA-co-PS)/Ep (SiC = 0.68 vol %, $\gamma_g = 23.3$ wt %, PS/PGMA = 15.78/7.52)	97.91	1.08	0.33

tests reveal that the atomic ratios of C/O have changed (Fig. 14). The decrease of C/O ratios is indicative of oxidation of epoxy surface during wearing process. Incorporation of nano-SiC increases the resistance of epoxy against oxidation, while the grafted nanoparticles are able to bring about more prominent improvement. For SiC-g-P(GMA-co-St)/Ep system, the C/O ratios keep unchanged after wearing.

Dynamic mechanical spectroscopy has long been used as a sensitive method to identify the interfacial

interaction in composites. Generally, the strong interaction between nanoparticle and matrix might restrict the movement of polymer segments nearby the particulate fillers, resulting in a rise of α -peak temperature and intensity.^{22,23} Figure 15 shows temperature dependence of storage modulus and mechanical loss of epoxy and its composites. As expected, the addition of either untreated nano-SiC or grafted nano-SiC enhances the storage modulus of epoxy, especially at low temperature range [Fig. 15(a)]. The composite with SiC-g-PGMA

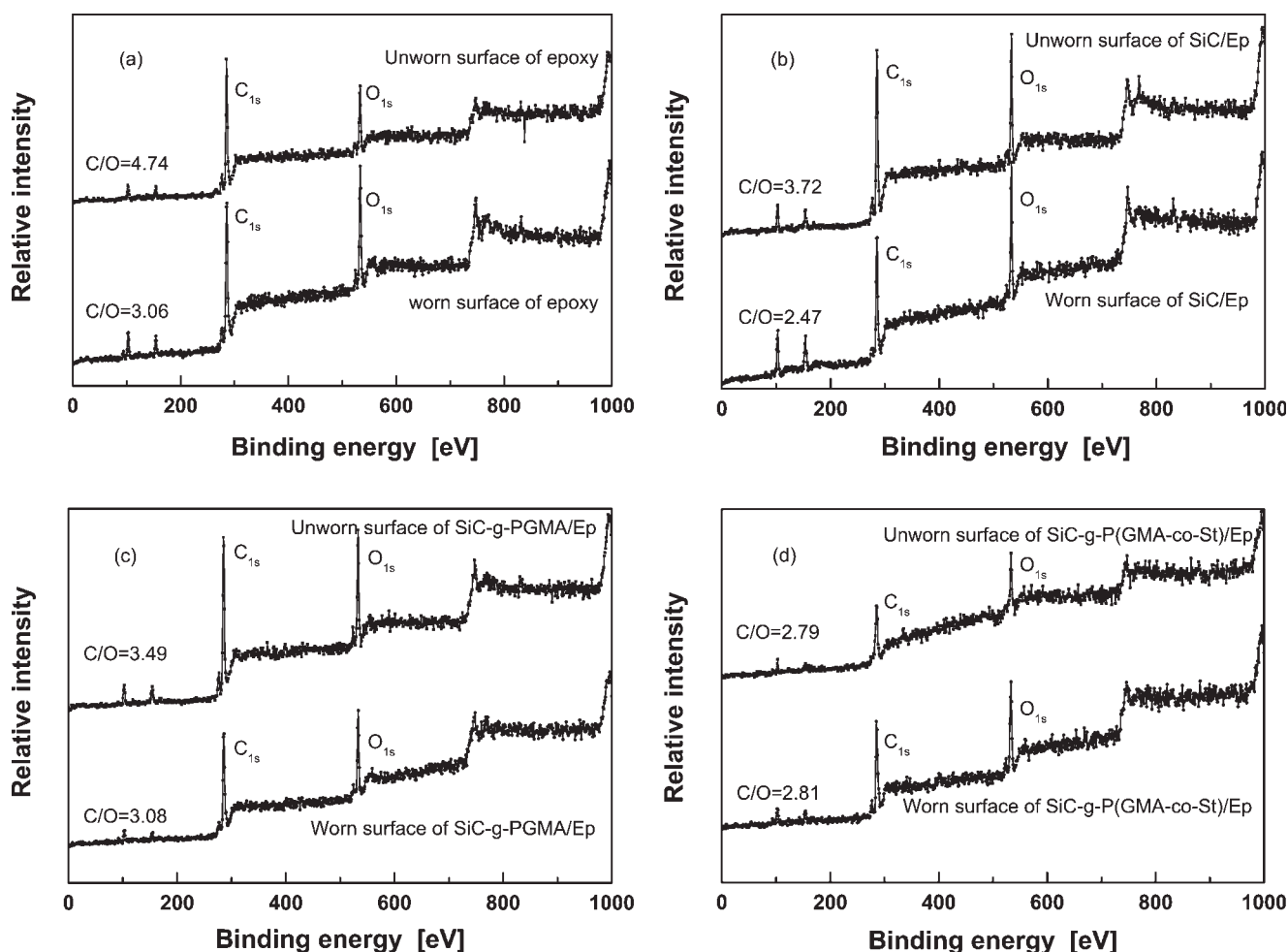


Figure 14 Low resolution XPS spectra of pin surfaces of (a) epoxy, (b) SiC/Ep (SiC = 0.91 vol %), (c) SiC-g-PGMA/Ep (SiC = 0.83 vol %, $\gamma_g = 8$ wt %), and (d) SiC-g-P(GMA-co-St)/Ep (SiC = 0.68 vol %, $\gamma_g = 23.3$ wt %, PS/PGMA = 15.78/7.52) composites before and after the wear tests.

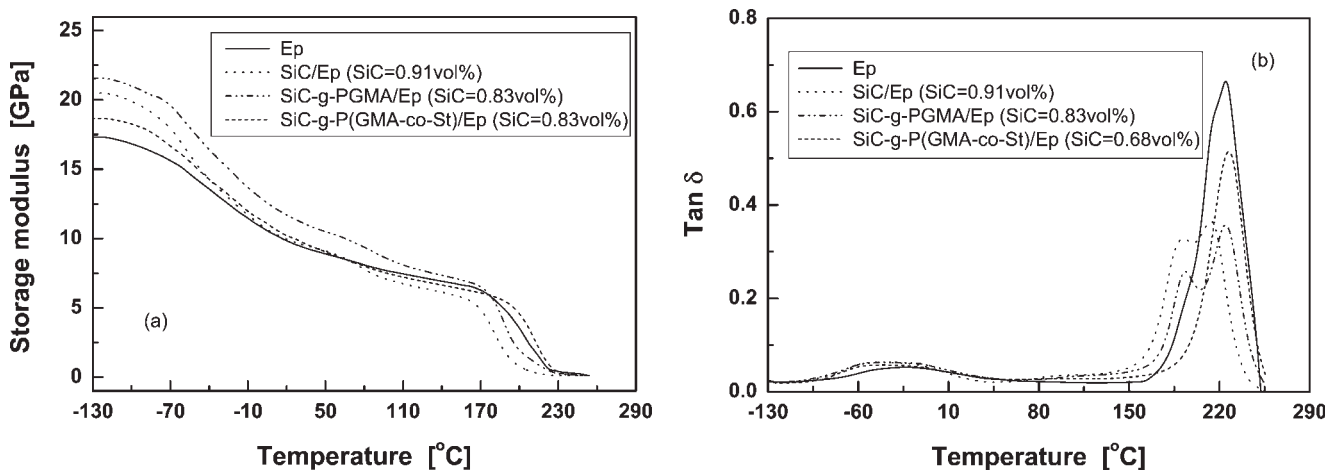


Figure 15 (a) Storage modulus and (b) mechanical loss spectra of epoxy, SiC/Ep (SiC = 0.91 vol %), SiC-g-PGMA/Ep (SiC = 0.83 vol %, $\gamma_g = 8$ wt %), and SiC-g-P(GMA-co-St)/Ep (SiC = 0.83 vol %, $\gamma_g = 23.3$ wt %, PS/PGMA = 15.78/7.52) composites.

shows the highest storage modulus because the particles contain higher content of GMA groups. In contrast to conventional composites, however, incorporation of either the untreated or treated nanoparticles results in reduction of both peak temperatures and intensities of glass transition of the matrix epoxy [Fig. 15(b)]. For the composites with untreated SiC and SiC-g-PGMA, the α -peaks were split into two parts, while SiC-g-P(GMA-co-St)/Ep composite still exhibits single α -peak. These phenomena should be related with the change of crosslinking density at the interface rather than the effect of the nanoparticles. The extra epoxide groups due to the grafted PGMA might lead to lower crosslinking density at the interface and hence decreased peak temperature and height of α -transition. This means that the looseness of epoxy at the interface is so serious that the reinforcing effect of the fillers has been counteracted. When styrene was copolymerized into the grafted polymer, compatibility between the grafted polymer and matrix epoxy would be increased, while the amount of GMA groups was decreased. As a result, only a single α -peak with lower intensity is observed.

CONCLUSIONS

SiC nanoparticles are capable of reducing frictional coefficient and wear rate of epoxy at low filler concentration. Graft of PGMA onto the nanoparticles, which helps to establish chemical bonding with matrix epoxy during the subsequent composites manufacturing, proves to be an effective way to produce nano-SiC/epoxy composites with improved tribological performance. However, excessive GMA groups are detrimental to the enhancement of wear resistance of the composites. Therefore, when PGMA is replaced by the copolymer of GMA and St to adjust the amount of the reactive groups on the grafted polymer, the filler/matrix interfacial compatibility and interaction are optimized. As a

result, the epoxy based nanocomposites acquire much lower frictional coefficient and wear rate.

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