Thermal stability of frictional surface layer and wear debris of epoxy nanocomposites in relation to the mechanism of tribological performance improvement

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To enhance service performance of polymeric materials for tribological applications, micrometer inorganic particulates are generally incorporated [1], which increases load-bearing capacity and thermal conductivity of the matrices, promotes adhesion of the transferred film to the counterface, etc. However, these micron particulate composites have some inherent disadvantages. The detached particles, for instance, tend to be entrapped within the rubbing interface, leading to severe abrasion of the composites [2]. Besides, the fraction of the particles needed to achieve sufficient improvement of the tribological properties of the composites is relatively high, which remarkably decreases the processability of the polymers.

To solve the problems, employment of particles of reduced size, i.e., nanoparticles, proves to be an effective method. By either improving dispersion of nanoparticles in matrices [3] or enhancing their affinity to the surrounding polymers [4], the defects of the micro-sized particulate composites can be overcome. As shown by our previous works [4, 5], nano-silica filled epoxy has significantly low frictional coefficient and wear rate at rather low filler loading ($\sim$2 vol%) in comparison with unfilled epoxy. Besides, the above positive effect can be further strengthened when the nanoparticles are pre-grafted by some polymer chains that can take part in curing reaction of epoxy.

Considering that friction and wear are involved mostly in the top layer of a rubbing surface when a bulk material serves in tribological environment, mechanophysically and mechanochemically induced changes in the surface layer would certainly in turn influence the tribological performance of the material [6, 7]. Therefore, post-mortem characterization of frictional surface is able to yield valuable information about the wear processes that cannot be obtained by other techniques.

On the basis of the above analysis, the present communication is focused on the thermal stability of the worn surface layer and wear debris of treated and untreated nano-silica/epoxy composites. It is expected that the friction reducing and wear resisting behaviors of the composites with grafted nano-silica [4, 5] can be understood from another aspect, which would benefit the further development of the materials.

Bisphenol-A epoxy resin (type E-51) and 4,4'-diaminodiphenylsulfone (DDS) were provided by Guangzhou Dongfeng Chemical Co., China. The nano-SiO_2 with an average primary particle size of 9 nm was purchased from Zhoushan Nanomaterials Co., China. Acrylamide was supplied by Guangzhou Chemical Agent Factory, China.

The typical grafting of SiO_2 proceeded as follows. The nanoparticles were preheated at 120 °C in vacuum for 24 hr to eliminate possibly absorbed water on the surface of the particles. Then, the particles were mixed with a solution of acrylamide in acetone by sonication. The mixture was irradiated by ^{60}Co γ-ray at a dose rate of 1 Mrad/hr at room temperature. After being exposed to a dose of 4 Mrad, the solvent was recovered and the dried residual powder could be directly compounded with the epoxy. By using thermogravimetric analysis (TGA, Shimadzu TA-50 thermogravimeter), it was known that the percent grafting and the grafting efficiency of the irradiation products were 10.3 and 53.7%, respectively. In the following text, the polyacrylamide (PAAM) grafted nano-SiO_2 is denoted by SiO_2-g-PAAM.

The composite materials were prepared according to the procedures described in Ref. [4]. Unlubricated sliding wear tests were carried out on a pin-on-ring apparatus of a constant velocity of 0.4 m/s and pressures of 3 and 5 MPa, respectively. The carbon steel ring (0.42–0.45 wt% C, 0.17–0.37 wt% Si and 0.5–0.8 wt% Mn,

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TABLE I Frictional coefficient, μ, and specific wear rate, $\dot{w}_s$, of epoxy and its composites[a]

Materials	Epoxy	SiO₂/Epoxy	SiO₂-g-PAAM/Epoxy	Epoxy	SiO₂/Epoxy	SiO₂-g-PAAM/Epoxy
Pressure (MPa)	3	3	3	5	5	5
μ	0.58 ± 0.01	0.50 ± 0.04	0.39 ± 0.09	0.57 ± 0.05	0.28 ± 0.01	0.25 ± 0.05
$\dot{w}_s (\times 10^{-6} \text{ mm}^3/\text{Nm})$	207.6 ± 32.8	44.7 ± 13.6	11.0 ± 3.3	951.3 ± 32.1	10.4 ± 0.9	2.4 ± 0.3

[a]Nano-silica content: 2.17 vol%; sliding velocity: 0.4 m/s.

HRC 50) had a diameter of 40 mm and an initial surface roughness of 0.1 μm. The specimens for wear tests were machined with a geometry of $5 \times 10 \times 15$ mm³, resulting in an apparent contact area of about 5×10 mm². Prior to wear testing, all the samples were pre-worn to average surface conditions and to shorten the running-in period. The actual steady-state test period was set to 3 hr. Morphologies of the worn surfaces of the samples were observed with a HITACHI S-520 scanning electron microscope (SEM). Thermal decomposition behaviors of the materials were evaluated by the above-mentioned thermogravimeter in N₂ at a heating rate of 10 °C/min.

For the convenience of discussion, the results of sliding wear tests conducted on nano-silica/epoxy composites at given silica content [4, 5] are briefly summarized in Table I. Evidently, the wear rate of the composites can be lowered by 1–2 order of magnitude using a small amount of the grafted nanoparticles, which is difficult to be achieved in micro-particles filled composites. Fig. 1 shows the typical morphologies of the wear particles from different materials. Compared to the case of un-filled epoxy, the wear debris of SiO₂/epoxy and SiO₂-g-PAAM/epoxy has much smaller size and coarser appearance. It has been known that wear debris acts as a medium-carrying extensive information on the wear process. The fractal dimension of the boundary texture of wear debris is directly correlated to the wear performance of materials [8]. Therefore, it is worth analyzing the microphotos in Fig. 1 in detail.

Fatigue-delamination mechanism is usually considered to be responsible for the debris in the form of sheets

[9]. The sheet-like debris produced from unfilled epoxy (Fig. 1a) evidences the mechanism assignment based on morphological study of the worn surfaces [5]. For the composites incorporated with nano-silica, the significantly reduced sizes of the wear debris manifest that the surface failure was restricted to rather small region and hence the amount of material removal due to wearing is also decreased accordingly (Fig. 1b and c, Table I). In addition, the extensive cracks on the wear particles might be indicative of fatigue crack propagation. That is, the contribution of the fatigue element to the sliding wear of the composites becomes more prominent when strong interfacial interaction between the nanoparticles and matrix resin has been built up through the grafting treatment.

To understand the structural variations in the composites during the sliding wear tests, pyrolytic behaviors of the wear debris and the surface layers sliced from the tops of the worn specimens were examined using the unworn bulk materials as reference. In fact, many studies about thermal degradation of epoxy resin have been reported. For example, Grassie and co-workers proposed that the thermal degradation mechanism from the viewpoint of bond energy [10]. They suggested that because oxygen and nitrogen atoms have greater negative inductive effect than other atoms, the scission of epoxy would take place at O—CH₂ and C—N bonds to form phenol, amine, and other small molecules. As seen from Fig. 2, pyrolysis of epoxy and its composites, which have either experienced wear tests or not, is still a one-stage reaction suggesting that the basic decomposition processes are not changed. The decrease
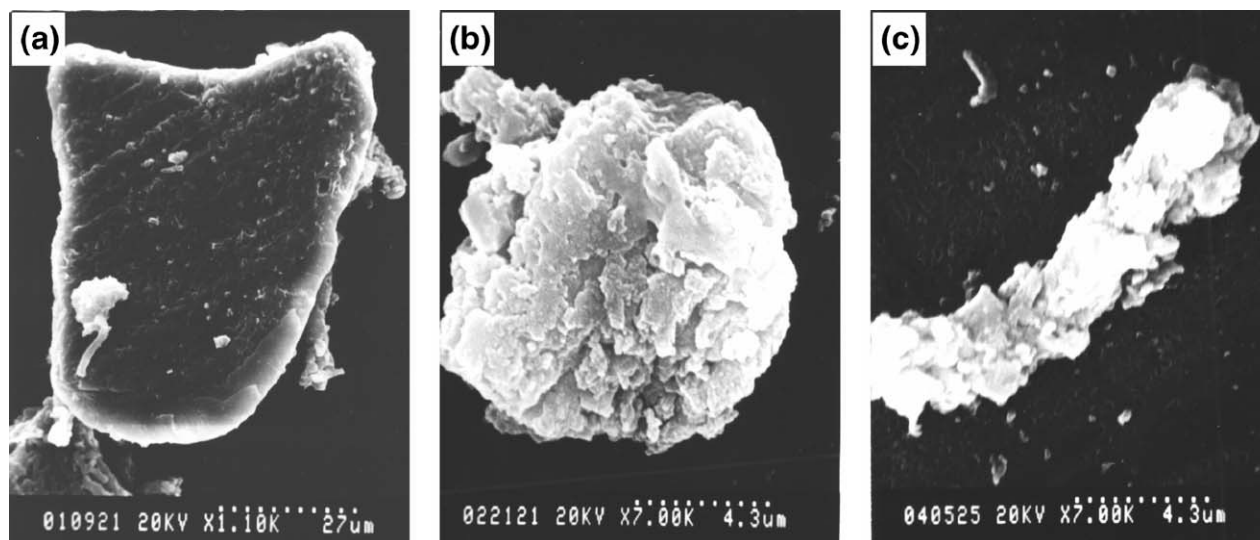

Figure 1 SEM micrographs of the wear debris of: (a) unfilled epoxy, (b) SiO₂/epoxy composites (SiO₂ content = 2.17 vol%) and (c) SiO₂-g-PAAM/epoxy composites (SiO₂ content = 2.17 vol%) produced during sliding at 3 MPa and 0.4 m/s.
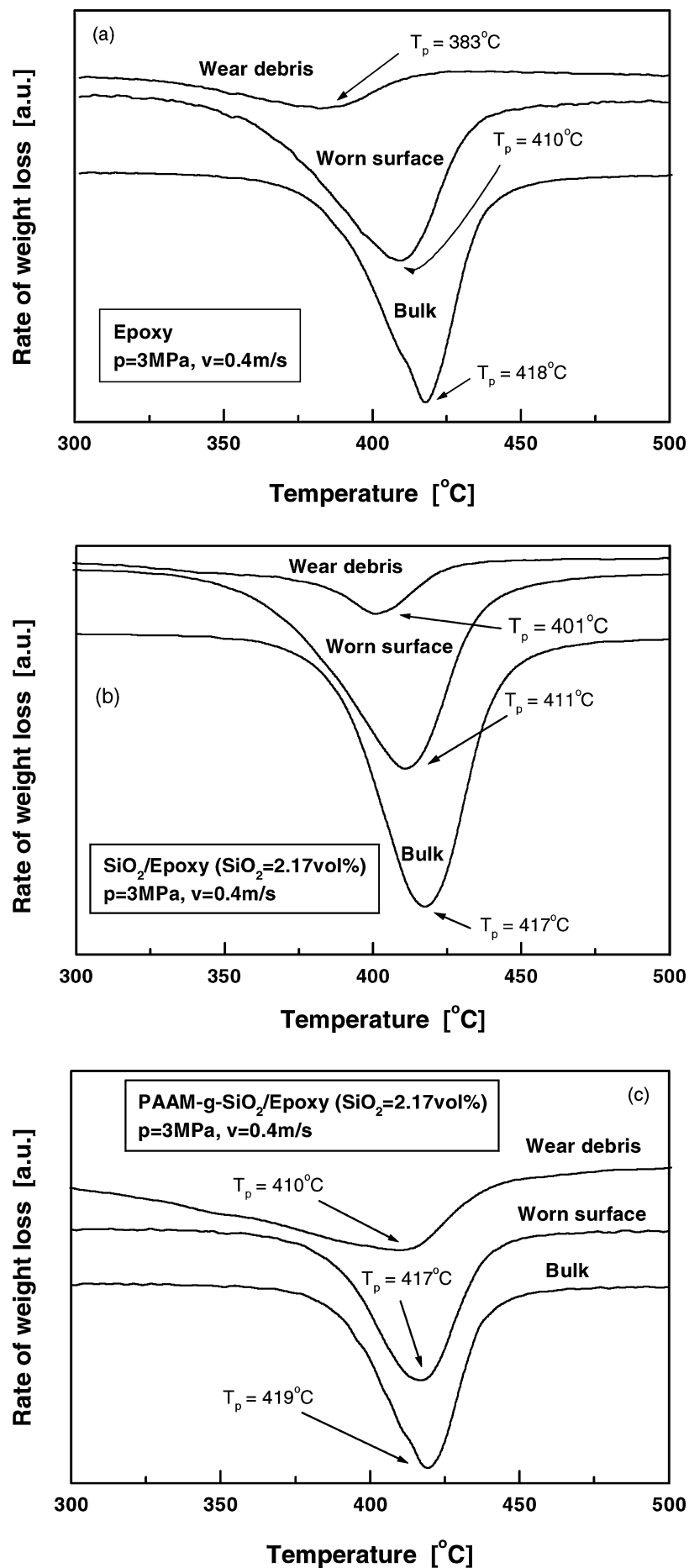
Figure 2 Temperature dependences of rate of thermal decomposition of the materials from: (a) unfilled epoxy, (b) SiO_2/epoxy composites and (c) SiO_2-g-PAAM/epoxy composites. T_p represents the peak temperature on the curve.

in the temperature corresponding to the maximum rate of pyrolysis, T_p, of the wear debris and the worn pin surface (relative to the bulk materials) must be indicative of structural degradation of the materials. Our previous X-ray photoelectron spectroscopic studies of epoxy demonstrated that oxidation and carbonization are the main mechanochemical processes that had occurred on the specimen surfaces during wearing due to the high frictional temperature and contact pressure [11]. Partial chain scission has to take place inevitably. Therefore, it can be deduced from the T_p values in Fig. 2 that the epoxy in the wear debris and on the top layer of the specimens had been somewhat degraded in the course of wear tests. Moreover, the former had received severer damage of the molecular structure. This is reasonable because after detachment of the pin surface the wear debris might often be captured and travel in the rubbing contact for a while as sliding goes on prior to their escape from the contact [8]. On one hand, the duration of the wear particles in the rubbing zone accelerates their mechanochemical degradation; on the other, the wear particles shield the specimen surface from the high frictional heat to a certain extent leading to less significant reduction of T_p of the top layer.

By comparing Fig. 2a, b and c, much more interesting information can be found. That is, the differences between the T_p values of the unworn specimens (i.e., the bulk materials) and the worn surface layers, T_p (bulk) − T_p (worn surface), are arranged in the following order: epoxy > SiO$_2$/epoxy > SiO$_2$-g-PAAM/epoxy. Besides, the differences T_p (bulk) − T_p (wear debris) also exhibit the same dependence on the materials species. According to the analysis in the last section, the smaller difference between T_p (bulk) and T_p (worn surface) or T_p (wear debris) should be interpreted as less severe structural damage of epoxy. It means that either the worn surface or the wear debris of the nano-silica filled composites, especially of the grafted nano-silica/epoxy composites, has higher thermal stability than that of unfilled epoxy. Since the sliding wear test time of the materials is identical, the possible reason accounting for the above-stated phenomena must be related to the difference in the frictional heat. It is believed that the effects of physical crosslinking generated by nano-silica and the additional chemical crosslinking by the grafted nano-silica (which is stronger than the former) decrease the possibility of surface failure of the composites and the amounts of wear splinters. As a result, the transition from severer wear of unfilled epoxy to milder wear of the composites takes place (Table I). With the aid of the lubricating effect [3, 4] and thermal conductivity of the nanoparticles, both wear rate and frictional coefficient of the composites are lowered, which would certainly lead to lower friction interfacial temperature. Therefore, the wear debris and the worn surface of SiO$_2$-g-PAAM/epoxy have the highest T_p as compared with the cases of unfilled epoxy (Fig. 2a) and SiO$_2$/epoxy (Fig. 2b).

On the basis of above discussion, it can be concluded that the fatigue-delamination effect responsible for the sliding wear of epoxy is accelerated by the surface structural deterioration induced by the rather high friction temperature. The unfilled epoxy is thus characterized by poor tribological performance. When nanosilica is added, the flash temperature is reduced, resulting in less significant fatigue driven surface failure and improved wear resistance of SiO$_2$/epoxy composites. In the case of SiO$_2$-g-PAAM/epoxy, the covalent bonding between the grafting polymers on the nanoparticles and the matrix greatly increases the composites integrity. The reduced amount and size of wear debris weaken the abrasive effect of the wear debris as the third body in the contact area [12]. This in turn lowers the frictional temperature to a much greater extent, and the fatigue-induced material removal of the composites becomes even less than SiO$_2$/epoxy consequently.

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