Effect of nano-Si₃N₄ surface treatment on the tribological performance of epoxy composite

Y. Luo^{1,2*}, X. Y. Yu¹, X. M. Dong^{1,2}, M. Z. Rong², M. Q. Zhang²

¹Department of Applied Chemistry, College of Science, South China Agricultural University, Guangzhou 510642, People's Republic of China

²Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou 510275, People's Republic of China

Received 18 October 2009; accepted in revised form 15 December 2009

Abstract. To overcome the disadvantages generated by the loose nano-particle agglomerates dispersed in polymer composites, a chemical grafting method was applied to modify nano-Si₃N₄ by covalently bonding glycidyl methacrylate (GMA) onto the particles. The tribological behavior of the epoxy composite filled with nano-Si₃N₄ or GMA treated Si₃N₄ (Si₃N₄-g-PGMA) was studied using a ring-on-block wear tester under dry sliding, and the worn surface of the filled epoxy composite and the surface roughness of the composites after the sliding wear test were investigated by SEM (scanning electron microscopy) and AFM (atomic force microscopy), respectively. In comparison to the composites filled with untreated nano-Si₃N₄ particles, the composites with the grafted nano-Si₃N₄ exhibit improved sliding wear resistance and reduced friction coefficient owing to the chemical bonding at the filler/matrix interface.

Keywords: nanocomposites, nano-Si₃N₄ particles, surface grafting, friction and wear

1. Introduction

Polymers and polymer composites have been used increasingly as engineering materials for technical applications in which tribological properties are of considerable importance. Recent investigations on inorganic nanoparticles filled polymers demonstrate their significant potential in producing composites with low friction and high wear resistance [1–5]. Compared with the composites incorporated with micro-particles, which are characterized by severe wear resulting from abrasion and particles pull-out, nanocomposites exhibit rather mild wear with fine individual debris acting as lubricant and contributing to material removal by polishing. Evidently, a uniform dispersion of nanoparticles and strong filler/matrix interfacial interaction in the composites are the prerequisites for the aforesaid performance improvement.

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, nano-particle filled polymers used to contain a number of loose 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. Similar to the case of micro-size particles, surface treatment of inorganic nanoparticles can be conducted by either physical or chemical method. The former

*Corresponding author, e-mail: luoying@scau.edu.cn

© BME-PT

deals with surfactant treatment [6] and polymer encapsulation [7], while the later is related to coupling agent treatment [8–9] and graft polymerization [10–14]. Comparatively, the effect of surface modification based on chemical interaction is more significant, as it provides stronger interaction between modifiers and nanoparticles.

In our previous works, graft polymerization onto nanoparticles proved to be feasible in improving tribological behavior of polymer nanocomposites [15–19]. 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. Actually, 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.

In this work, nano-Si₃N₄ particles grafted by polyglycidyl methacrylate (PGMA) were mixed with epoxy. The grafted polymer PGMA was selected because the epoxide groups on PGMA would take part in curing reaction of epoxy resin, so that the nano-Si₃N₄ particles could be covalently connected to the matrix. The technical route is believed to be beneficial to the tribological performance of the composites.

2. Materials and methods

2.1. Materials

The nano-size Si₃N₄ particles supplied by the Hua-Tai, China, have a specific surface area of 52 m²/g and an averaged diameter of 17 nm, respectively. Prior to use, the particles were dried in an oven at 110°C 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 poly-

merization. The grafting monomer glycidyl methacrylate (GMA, Shanghai Yuanji Chemical Engineering Co., China) was distilled under low pressure before use.

2.2. Graft polymerization onto Si₃N₄ nanoparticles

The nanoparticles were grafted with PGMA by surfactant-free emulsion graft polymerization. The details of the surfactant-free emulsion graft polymerization have been described in Reference [20]. After the graft polymerization, the resultant suspension was filtered, washed, and extracted with methanol for 8 h to remove the residual monomer. The dried mixture was extracted with acetone for 50 h to isolate the polymer-grafted Si₃N₄ (Si₃N₄-g-PGMA) from the absorbed homopolymers. Then the grafted nanoparticles were dried under vacuum at 50°C. Some of them were transferred to Shimadzu TA-50 thermogravimeter to determine the percent grafting, γ_g . In the subsequent procedures of composites manufacturing, the Si₃N₄-g-PGMA with a percent grafting of 7.25 wt% was used as the treated fillers. Besides, Fourier transform infrared (FTIR) spectroscopy was used to evaluate the reactivity of Si₃N₄-g-PGMA with the curing agent DDS.

2.3. Manufacturing of epoxy based nanocomposites

The composite materials were fabricated by mixing the (untreated or treated) Si₃N₄ 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 (DDS) was added under continuous stirring. Then the composite system was poured into a preheated mold and the curing procedure 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.

2.4. Characterization

Unlubricated sliding wear tests were carried out on a pin-on-ring configuration at a constant velocity of 0.42 m/s and pressure of 3 MPa to obtain specific wear rate, w_s , and friction coefficient, μ . The con-

Figure 1. Contact schematic diagram for the friction couple

tact schematic diagram of the frictional couple is shown in Figure 1. 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) 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 mm $\times$ 10 mm $\times$ 15 mm, resulting in an apparent contact area of about 5 mm $\times$ 10 mm. 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 was conducted for 3 h using the same steel ring as that used for the pre-worn procedure. After that, a weight measure of the specimens was conducted.

The worn surfaces of the specimens were observed by a Philips XL-30FEG scanning electron microscope (SEM). Transmission electron microscopic (TEM) observation was performed with a Philips EM400 on the sample prepared from acetone dispersion of the particles (0.1 g in 50 ml), which were sonicated for 45 min and then deposited on copper grids covered by carbon film. 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' surface 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). Three-point bending tests of the compos-

ites specimens were carried out in a Hounsfield universal tester in accordance with GB/T1039-92 standard at a deformation rate of 5 mm/min.

3. Results and discussion

3.1. Surfactant-free emulsion graft polymerization of GMA and its characterization

When nanoparticles are mixed with epoxy, whether a stationary suspension state can be kept is of the first importance for producing homogeneous composites. To check the effect of surface treatment qualitatively, the dispersibility of PGMA grafted Si_3N_4 in acetone was compared with that of the untreated nano- Si_3N_4 (Figure 2). The results clearly show that a remarkable improvement of dispersibility of the former particles originating from the surface grafting. Untreated nano- Si_3N_4 completely precipitates after a few hours. On the contrary, Si_3N_4 -g-PGMA gives a stable colloidal dispersion in the solvent. In addition, the grafted nano- Si_3N_4 particles with higher percent grafting (48%) tend to be less stable than that with lower percent grafting (7%) within 25 h, indicating that excessive graft polymer chains interfere with the dispersion of nano- Si_3N_4 particles due to molecular entanglement.

Figure 3 shows the TEM morphologies of the nano- Si_3N_4 particles before and after the grafting treatment in acetone. Due to the serious aggregation resulting from the high specific surface area, the untreated nano- Si_3N_4 particles get together forming clusters larger than 500 nm. When the particles are grafted by PGMA, they can be well dispersed in the

Figure 2. Dispersibility of nano- Si_3N_4 particles and Si_3N_4 -g-PGMA particles with different grafting percent in acetone at room temperature

Figure 3. TEM photos of (a) nano-Si₃N₄ particles and (b) Si₃N₄-g-PGMA particles (γ_g : 7.25%)

solvent and most of them have sizes smaller than 100 nm. A comparison between Figures 3a and 3b obviously demonstrates that the graft treatment is rather effective in separating the agglomerated nanoparticles, which would benefit the subsequent composites manufacturing.

Since the surface treatment of the particles aims at increasing the reactive compatibilization in the nanocomposites by grafting polymers with reactive groups onto the nanoparticles, the reactivity of the grafted polymer should be of interests. Firstly, it is needed to confirm whether the epoxide groups of PGMA grafted on the nano-Si₃N₄ particles will react with the amine groups of DDS. To prove the reaction, a model system consisting of stoichiometrical Si₃N₄-g-PGMA and the curing agent 4,4'-diamino-diphenylsulfone (DDS) was thermally treated following the same curing sequence as that applied for epoxy/DDS compound, and then evaluated by FTIR. It is seen from Figure 4 that the double bands at 3332 and 3369 cm⁻¹ corresponding to the primary amine groups (–NH₂) disappear after curing. Instead, a single band at 3365 cm⁻¹ representing the secondary amine groups (–NH) is perceived, evidencing the above deduction. Therefore, it is known that PGMA is able to take part in the curing reaction of epoxy. Such a chemical bonding between the PGMA chains grafted onto nano-Si₃N₄ particles and the surrounding epoxy networks would certainly enhance the filler/matrix adhesion in the composites.

Figure 4. FTIR spectra of the mixture of Si₃N₄-g-PGMA/DDS before and after curing

3.2. Friction and wear performance of Si₃N₄/EP nanocomposites

To illuminate the effect of the grafting polymer on the tribological performance of the epoxy composites, Figure 5 presents the specific wear rate, w_s , and frictional coefficient, μ , as a function of the amount of the grafting polymers attached to nano-Si₃N₄ particles. It is found that the particles with a medium grafting percentage ($\gamma_g = 7.25\%$) give the lowest w_s and μ . It can thus be estimated that the molecular chains of the grafted PGMA with a medium grafting percentage might present themselves in an extended conformation, which is beneficial to the dispersion of the grafted particles and

Figure 5. (a) Specific wear rate, w_s , and (b) friction coefficient, μ , of epoxy composites filled with Si_3N_4 -g-PGMA (0.79 vol%) with different grafting percentage

the establishment of chemical bonding between the particles and the matrix. The typical steady-state friction coefficients and specific wear rates of the unfilled and filled epoxy composites under 3 MPa and at 0.42 m/s are shown in Table 1. It can be seen that Si_3N_4 and Si_3N_4 -g-PGMA can reduce the friction coefficient and specific wear rate of the epoxy composites significantly. Comparatively, 0.52 vol% Si_3N_4 -g-PGMA is more effective than untreated Si_3N_4 in improving the tribological performance of the composites. Furthermore, when the composites are mixed with the help of acetone solvent (wet mixed), it holds the lowest friction coefficient and specific wear rate under a pressure of 3 MPa. Effect of the content of Si_3N_4 and Si_3N_4 -g-PGMA on the friction coefficient and specific wear rate of

Figure 6. (a) Specific wear rate and (b) friction coefficient of $\text{Si}_3\text{N}_4/\text{EP}$ and Si_3N_4 -g-PGMA/EP (γ_g : 7.25%) composites as a function of filler content

the epoxy composite sliding against the steel ring is revealed in Figure 6 under dry sliding. It is seen that within the entire range of filler content of interests, both frictional coefficient and specific wear rate of the composites incorporated with nano- Si_3N_4 particles show a drastical decrease as compared with the values of unfilled epoxy. For example, the wear rate of epoxy is decreased from $\sim 200 \cdot 10^{-6}$ to $\sim 2.6 \cdot 10^{-6}$ and $0.96 \cdot 10^{-6} \text{ mm}^3/\text{Nm}$ by the addition of 0.8 vol% of untreated nano- Si_3N_4 and treated nano- Si_3N_4 , respectively. Comparatively, Si_3N_4 -g-PGMA is more effective than untreated Si_3N_4 in improving the tribological performance of the composites. The difference in improving the wear resistance of epoxy between the composites with untreated and treated nano- Si_3N_4 particles should mainly result from the filler/

Table 1. Typical friction coefficient and specific wear rate of epoxy composites under dry sliding (3 MPa, 0.42 m/s)

Composites	Friction coefficient	Specific wear rate [$\cdot 10^{-6} \text{ mm}^3/\text{Nm}$]
Epoxy+DDS	0.598	248.75
Epoxy+DDS+0.52 vol% Si_3N_4	0.441	2.95
Epoxy+DDS+0.52 vol% Si_3N_4 -g-PGMA (dry mixed)	0.433	2.33
Epoxy+DDS+0.52 vol% Si_3N_4 -g-PGMA (wet mixed)	0.428	1.55

matrix adhesion strength. As stated before, the grafted PGMA employed in the present work can build up chemical bonding between the nanoparticles and epoxy resin, which should be responsible for the higher resistance to periodic frictional stress. With a rise in the nanoparticles concentration, both the wear rate and the friction coefficient increase slightly. It might be due to the fact that the increased amount of the nanoparticles is unfavorable to filler dispersion [21]. Meanwhile, the grafted nanoparticles also lead to more significant

reduction on specific wear rate of epoxy as compared with the friction coefficient.

Figure 7 compares the worn surface of unfilled epoxy with those of the composites. Clearly, the severe wear associated with the detachment of bulk materials for unfilled epoxy (Figure 7a, 7b) is replaced by the mild wear for untreated Si_3N_4 filled composites (Figure 7c, 7d). In comparison with the flake-like wear failures on the surface of $\text{Si}_3\text{N}_4/\text{EP}$, the wear scars on the surface of $\text{Si}_3\text{N}_4\text{-g-PGMA}/\text{EP}$ composites (Figure 7e, 7f) are characterized by tiny

Figure 7. SEM micrographs of the worn surface of (a, b) epoxy, (c, d) Si_3N_4 /epoxy composites (0.79 vol%), and (e, f) ‘dry mixed’ $\text{Si}_3\text{N}_4\text{-g-PGMA}$ /epoxy composites (0.79 vol%, γ_g : 7.25%) (arrows indicate the sliding direction)

scratches without any detached flakes. It can be attributed to the fact that the treatment via graft polymerization onto the nanoparticles further improves the miscibility between the grafted polymer and matrix epoxy. It should be beneficial to the dispersion of nano-Si₃N₄ particles, and improve the composites' integrity. As a result, the composites' wear resistance was raised accordingly. On the other hand, it suggests that polishing effect predominates the wear process of the latter composites, evidencing the change in wear mode.

3.3. 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 Si₃N₄ 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 8 shows the surface feature of epoxy and its composites characterized by load-unload curves recorded during the micro-hardness measurements. 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 nano-Si₃N₄ particles exerts restraining effect on the plastic deformation, and even results in a rise in the elastic deformation after the wear test, proving that the interaction between nano-Si₃N₄ particles and epoxy is rather strong. When the Si₃N₄ had been grafted with PGMA, the elastic deformation of the composites is further improved due to the chemical bonding at the interface.

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 nano-Si₃N₄ particles from another angle (Figure 9). Clearly, the wear process in the Si₃N₄ filled nanocomposites are dominated by polishing and the worn pin surface appears rather smooth. When the particles were grafted with PGMA, the average roughness of the composites is further reduced by three to four times. The results agree with the afore-

Figure 8. Load-unload test results of (a) epoxy, (b) Si₃N₄/EP (0.26 vol%) and (c) Si₃N₄-g-PGMA/EP (0.26 vol%, γ_g : 7.25%) composites before and after the wear test

said 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 test, elements on the steel ring surface were examined in Table 2. It is seen that having rubbed against either the unfilled epoxy or the epoxy composites, element Si was detected on the steel counter face. Besides, the amount of Si on the steel ring surface rubbing against the composites is higher than that on the

Figure 9. AFM 3D height trace images of worn surface of (a) epoxy, (b) Si₃N₄/EP (0.26 vol%) and (c) Si₃N₄-g-PGMA/EP (0.26 vol%, γ_g : 7.25%) composites

steel ring rubbing against neat epoxy. These data prove that the grafted polymer facilitates the adhesion of Si₃N₄ particles on the steel ring, and strengthens the transferred film. Besides, the low resolution XPS spectra of the pin surfaces of epoxy

Table 2. EDS analysis of the surface of the steel counter-part before and after the wear test

Samples	Elements and contents [wt %]		
	Fe	Si	S
Steel ring before wearing	98.76	0.48	0.00
Steel ring worn against EP	98.55	0.42	0.21
Steel ring worn against nano-Si ₃ N ₄ /EP (0.52 vol%)	96.77	2.46	0.42
Steel ring worn against Si ₃ N ₄ -g-PGMA/EP (0.52 vol%, γ_g : 7.25%)	98.73	0.51	0.54

Figure 10. Low resolution XPS spectra of pin surface of (a) epoxy, (b) Si₃N₄/EP (0.79 vol%) and (c) Si₃N₄-g-PGMA/EP (0.79 vol%, γ_g : 7.25%)

Figure 11. Flexural strengths and modulus of (a) $\text{Si}_3\text{N}_4/\text{EP}$ and (b) $\text{Si}_3\text{N}_4\text{-g-PGMA}/\text{EP}$ ($\gamma_g: 7.25\%$) composites as a function of filler concentration

and nano- $\text{Si}_3\text{N}_4/\text{epoxy}$ composites before and after the wear tests reveal that the atomic ratios of C/O have changed (Figure 10). The decrease of C/O ratios is indicative of oxidation of epoxy surface during wearing process. Incorporation of nano- Si_3N_4 and $\text{Si}_3\text{N}_4\text{-g-PGMA}$ particles increases the resistance of epoxy against oxidation.

The addition of either untreated nano- Si_3N_4 or grafted nano- Si_3N_4 could enhance the flexural strength and modulus of epoxy (Figure 11), which can be easily explained by the high hardness of the particles. The composites with $\text{Si}_3\text{N}_4\text{-g-PGMA}$ particles possess high flexural performance, especially at low filler content. The graft treatment of the nano- Si_3N_4 particles by PGMA ensures good filler-matrix bonding and favors stress transfer across interface.

4. Conclusions

1. Grafting of GMA onto nano- Si_3N_4 increased the interfacial interaction between the particles and

the epoxy matrix through chemical bonding. It proved to be an effective way to further enhance the nano-effect of the nanoparticles on the improvements of the tribological performance. However, excessive GMA groups are detrimental to the enhancement of wear resistance of the composites due to molecule entanglement.

2. Compared with the unfilled and nano- Si_3N_4 filled epoxy, the epoxy filled with low content $\text{Si}_3\text{N}_4\text{-g-PGMA}$ exhibited lower friction coefficient and higher wear rate. However, the friction and wear of the filled epoxy composites deteriorated with further increasing content of nano- Si_3N_4 and $\text{Si}_3\text{N}_4\text{-g-PGMA}$ particles.
3. The technical route proposed by the authors is not limited to the system made of Si_3N_4 nanoparticles and epoxy resin. In fact, the surface treatment method presented in this paper is also feasible for various inorganic/polymer composites aiming at improving particle dispersion and interface interaction.

References

- [1] Ng C. B., Schadler L. S., Siegel R. W.: Synthesis and mechanical properties of TiO_2 -epoxy nanocomposites. *Nanostructured Materials*, **12**, 507–510 (1999). DOI: [10.1016/S0965-9773\(99\)00170-1](https://doi.org/10.1016/S0965-9773(99)00170-1)
- [2] Wetzel B., Hauptert F., Zhang M. Q.: Epoxy nanocomposites with high mechanical and tribological performance. *Composites Science and Technology*, **63**, 2055–2067 (2003). DOI: [10.1016/S0266-3538\(03\)00115-5](https://doi.org/10.1016/S0266-3538(03)00115-5)
- [3] Sawyer W. G., Freudenberg K. D., Bhimaraj P.: A study on the friction and wear behavior of PTFE filled with alumina nanoparticles. *Wear*, **254**, 573–580 (2003). DOI: [10.1016/S0043-1648\(03\)00252-7](https://doi.org/10.1016/S0043-1648(03)00252-7)
- [4] Chang L., Zhang Z., Breidt C., Friedrich K.: Tribological properties of epoxy nanocomposites: I. Enhancement of the wear resistance by nano- TiO_2 particles. *Wear*, **258**, 141–148 (2005). DOI: [10.1016/j.wear.2004.09.005](https://doi.org/10.1016/j.wear.2004.09.005)
- [5] Chang L., Zhang Z., Ye L., Friedrich K.: Tribological properties of epoxy nanocomposites III. Characteristics of transfer films. *Wear*, **262**, 699–706 (2007). DOI: [10.1016/j.wear.2006.08.002](https://doi.org/10.1016/j.wear.2006.08.002)
- [6] Geng Y., Liu M. Y., Li J., Shi X. M., Kim J. K.: Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites. *Composites Part A: Applied Science and Manufacturing*, **12**, 1876–1883 (2008). DOI: [10.1016/j.compositesa.2008.09.009](https://doi.org/10.1016/j.compositesa.2008.09.009)

- [7] Rosa M. C., Peter A. L., Parnia N.: Polymer encapsulation of surface-modified carbon blacks using surfactant-free emulsion polymerization. *Polymer*, **48**, 2554–2563 (2007).
DOI: [10.1016/j.polymer.2007.02.063](https://doi.org/10.1016/j.polymer.2007.02.063)
- [8] Vassileva E., Friedrich K.: Epoxy/alumina nanoparticle composites. II. Influence of silane coupling agent treatment on mechanical performance and wear resistance. *Journal of Applied Polymer Science*, **101**, 4410–4417 (2006).
DOI: [10.1002/app.23297](https://doi.org/10.1002/app.23297)
- [9] Chand N., Dwivedi U. K.: Effect of coupling agent on abrasive wear behaviour of chopped jute fiber-reinforced polypropylene composites. *Wear*, **261**, 1057–1063 (2006).
DOI: [10.1016/j.wear.2006.01.039](https://doi.org/10.1016/j.wear.2006.01.039)
- [10] Espiard Ph., Guyot A.: Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 2. Grafting process onto silica. *Polymer*, **23**, 4391–4395 (1995).
DOI: [10.1016/0032-3861\(95\)96844-X](https://doi.org/10.1016/0032-3861(95)96844-X)
- [11] Sondi I.: Encapsulation of nanosized silica by in situ polymerization of *tert*-butyl acrylate monomer. *Langmuir*, **16**, 9031–9034 (2000).
DOI: [10.1021/la000618m](https://doi.org/10.1021/la000618m)
- [12] Rong M. Z., Zhang M. Q., Zheng Y. X., Zeng H. M., Walter R., Friedrich K.: Structure-property relationship of irradiation grafted nano-inorganic particle filled polypropylene composites. *Polymer*, **42**, 167–183 (2001).
DOI: [10.1016/S0032-3861\(00\)00325-6](https://doi.org/10.1016/S0032-3861(00)00325-6)
- [13] Zhang M. Q., Rong M. Z., Yu S. L.: Effect of particle surface treatment on the tribological performance of epoxy based nanocomposites. *Wear*, **253**, 1086–1093 (2002).
DOI: [10.1016/S0043-1648\(02\)00252-1](https://doi.org/10.1016/S0043-1648(02)00252-1)
- [14] Ueda J., Yamaguchi H., Yamaguchi T., Tsubokawa N.: Radical graft polymerization of vinyl monomers onto nanoparticles in ionic liquid initiated by azo groups introduced onto the surface. *Journal of Polymer Science Part A: Polymer Chemistry*, **6**, 1143–1149 (2007).
DOI: [10.1002/pola.21879](https://doi.org/10.1002/pola.21879)
- [15] Rong M. Z., Zhang M. Q., Shi G.: Graft polymerization onto inorganic nanoparticles and its effect on tribological performance improvement of polymer composites. *Tribology International*, **36**, 697–707 (2003).
DOI: [10.1016/S0301-679X\(03\)00029-X](https://doi.org/10.1016/S0301-679X(03)00029-X)
- [16] Ji Q. L., Zhang M. Q., Rong M. Z., Wetzel B., Friedrich K.: Tribological properties of surface modified nano-alumina/epoxy composites. *Journal of Materials Science*, **39**, 6487–6493 (2004).
DOI: [10.1023/B:JMSC.0000044887.27884.1e](https://doi.org/10.1023/B:JMSC.0000044887.27884.1e)
- [17] Luo Y., Rong M. Z., Zhang M. Q.: Covalently connecting nanoparticles with epoxy matrix and its effect on the improvement of tribological performance of the composites. *Polymers and Polymer Composites*, **13**, 245–252 (2005).
- [18] Luo Y., Rong M. Z., Zhang M. Q.: Tribological behavior of epoxy composites containing reactive SiC nanoparticles. *Journal of Applied Polymer Science*, **104**, 2608–2619 (2007).
DOI: [10.1002/app.24414](https://doi.org/10.1002/app.24414)
- [19] Guo Q. B., Rong M. Z., Jia G. L., Lauc K. T., Zhang M. Q.: Sliding wear performance of nano-SiO₂/short carbon fiber/epoxy hybrid composites. *Wear*, **266**, 658–665 (2009).
DOI: [10.1016/j.wear.2008.08.005](https://doi.org/10.1016/j.wear.2008.08.005)
- [20] Luo Y., Rong M. Z., Zhang M. Q., Friedrich K.: Surface functionalization of Si₃N₄ nanoparticles by graft polymerization of glycidyl methacrylate and styrene. *Journal of Applied Polymer Science*, **102**, 992–999 (2006).
DOI: [10.1002/app.24011](https://doi.org/10.1002/app.24011)
- [21] Wu C. L., Zhang M. Q., Rong M. Z., Friedrich K.: Tensile performance improvement of low nanoparticles filled-polypropylene composites. *Composites Science and Technology*, **62**, 10–11 (2002).
DOI: [10.1016/S0266-3538\(02\)00079-9](https://doi.org/10.1016/S0266-3538(02)00079-9)