

Surface Functionalization of Si₃N₄ Nanoparticles by Graft Polymerization of Glycidyl Methacrylate and Styrene

Ying Luo,^{1,2} Min Zhi Rong,² Ming Qiu Zhang,^{1,2} Klaus Friedrich³

¹Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou 510275, People's Republic of China

²Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China

³Institute for Composite Materials (IVW), University of Kaiserslautern, Kaiserslautern D-67663, Germany

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ABSTRACT: To improve dispersibility and interfacial interaction of nano-Si₃N₄ particles in epoxy-based composites, graft of glycidyl methacrylate (GMA) and styrene (St)/GMA onto the nanoparticles' surface was carried out in terms of emulsion polymerization method. The grafting polymers proved to be chemically attached to the nanoparticles via the double bonds introduced during the coupling agent pretreatment. The factors affecting the graft parameters, such as monomer concentration, initiator consumption, reaction time, etc., were investigated. It was shown that higher con-

centrations of monomer and initiator are favorable for the graft polymerization. When St/GMA was employed as the grafting monomer, the nanoparticles were found to play the role of polymerization loci. The grafted nanoparticles exhibit greatly improved dispersibility in cured epoxy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 992–999, 2006

Key words: emulsion polymerization; graft polymerization; nanocomposites; nanoparticles

INTRODUCTION

The importance of nanocomposites is growing from industrial and research point of view. These composites exhibit new and improved properties derived from the ultra fine phase dimension of the filler when compared to their micro- and macrocomposite counterparts.¹ However, unmodified inorganic particles tend to agglomerate in polymeric matrices independent of their species and sizes when being compounded into polymers. The particle agglomeration would weaken mechanical or optical properties of the polymer nanocomposites, which is often observed in a variety of hybrid systems in which clusters and particles are involved. In addition, the hydrophilic nanoparticles and the hydrophobic polymers are not compatible in nature, which has to result in poor interfacial interaction. To avoid these drawbacks, a series of methods have been tried in two aspects: development

of new compounding (dispersion) techniques and surface pretreatment approaches for nanoparticles. Comparatively, surface modification of the nano-fillers is more effective and easier to be applied, which is attracting the attention of material scientists.²

In microparticulates/polymer composites, surface modification of the fillers has already proved to be a widely applicable technique to minimize particle/particle interaction and to enhance particle/matrix interaction.³ With the recent developments in nanoscience and nanotechnology, the correlation between polymer nanocomposites' properties and surface modification of nanoparticles is also becoming an issue of great interests.^{4–6} Our previous works demonstrated that graft treatment of nanoparticles is capable of toughening plastics^{7,8} and reducing wear rate of polymers.^{9,10} In comparison with low molecular surfactants or coupling agents, grafting macromolecules onto inorganic nanoparticles has some advantages. The polymer-grafted nanoparticles might possess desired properties through a proper selection of the species of graft monomers and the conditions of graft reaction,^{11,12} so that the interfacial characteristics between the treated nanoparticles and the matrix polymer can be tailor-made when manufacturing nanocomposites. Besides, the fragile nanoparticle agglomerates would become much stronger because they turn into a nanocomposite microstructure consisting of the nanoparticles, the grafted, and the ungrafted (homopolymerized) polymer.

Correspondence to: Dr. M. Z. Rong (cesrmz@zsu.edu.cn).

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Recently, the approach of chemical graft was utilized to induce reactive compatibilization in nanocomposites preparation.¹³ That is, the reactive groups (such as epoxide or amine groups) were first introduced onto nanoparticles by graft polymerization, which might then result in the chemical bonding between the fillers and epoxy matrix through reaction between the epoxide groups and the curing agent.^{14,15} Owing to the greatly enhanced compatibility, the epoxy composites filled with poly(glycidyl methacrylate)-grafted nano-SiC particles have rather high sliding wear resistance and low frictional coefficient at low filler loading, which cannot be observed in untreated SiC nanoparticles/epoxy system.

As a part of our serial works dealing with epoxy nanocomposites that are supposed to have excellent tribological properties, the present article investigates graft polymerization of glycidyl methacrylate (GMA) and graft copolymerization of GMA/styrene (St) on the surface of nano-sized silicon nitride using an emulsion technique. Aiming at this ultimate target, the current report is focused on the preparation of PGMA and PGMA/St-grafted nano-Si₃N₄ to obtain differently modified nanoparticles.

It is worth noting that copolymerization was applied to tailor content of epoxide groups on the grafted macromolecular chains, and hence the compatibility of the grafted copolymers with the composites matrix can also be tuned accordingly. For this purpose, effects of polymerization conditions have to be carefully considered. Various factors that affect the grafting reaction were investigated, including monomer concentration, initiator consumption, reaction time, and emulsion agent content as well.

EXPERIMENTAL

Materials

The nano-sized 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 usage, the particles were dried in an oven at 110°C under vacuum for 24 h to get rid of the physically absorbed water. A KH570 silane coupling agent (γ -methacryloxypropyl trimethoxy silane, provided by Liao Ning Gaizhou Chemical Industry, China) was employed to introduce the reactive double bonds on the surface of the nanoparticles as follows. A certain amount of KH570 was added to a suspension of Si₃N₄ in butanol (weight ratio 1/10), which was then treated with ultrasonic for 30 min. The reaction proceeded for 10 h under refluxing. After filtration and extraction with butanol for 12 h to remove the excess silane absorbed on the Si₃N₄ nanoparticles, the KH570-treated nano-Si₃N₄ (called Si₃N₄-KH570) was dried in vacuum at 50°C for 24 h. The content of the KH570

introduced onto the Si₃N₄ surface was determined by thermogravimetric analysis (TGA) on a Shimadzu TA-50 machine.

The grafting monomers glycidyl methacrylate (GMA) (Shanghai Yuanji Chemical Engineering, China) and styrene (St) (Guangzhou Guanghua Chemical, China) were distilled under low pressure prior to the graft polymerization.

Surfactant-free emulsion graft polymerization of GMA onto nano-Si₃N₄

Si₃N₄-KH570 (4 g) and 200 mL ammonia (pH = 7–8, containing 0.4% isobutanol) were charged into a four-neck flask (~250 cc). The nonionic surfactant (OP-10, polyoxyethylene nonyl phenyl ether) was incorporated with a dosage lower than the critical micelle concentration (CMC). Having been ultrasonically agitated for 30 min, the above mixture was stirred for additional 5.5 h under argon atmosphere. The reaction temperature was increased up to 60°C and then the initiator (potassium persulfate in 30 mL water) was added. After 35 min, the graft polymerization was started when the monomer (weight W_1) was filled by drip-feeding within 1 h. The reaction had to proceed for a period of time (usually 16 h) and was stopped by ice cooling.

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 (weight W_2) 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 a Shimadzu TA-50 thermogravimeter to determine the percent grafting, γ_g . Accordingly, monomer conversion, γ_c , and grafting efficiency, γ_{er} , were calculated from the following expressions:

$$\gamma_c = (W_2 - W_0) / W_1 \quad (1)$$

$$\gamma_{er} = \gamma_g W_0 / \gamma_c W_1 \quad (2)$$

where W_0 denotes the weight of Si₃N₄ nanoparticles.

Emulsion graft copolymerization of GMA and St onto nano-Si₃N₄

A typical procedure is described as follows. Si₃N₄-KH570 (2 g) was charged into a three-neck flask (~250 cc) containing 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 (weight W_1) un-

TABLE I
Nano-Si₃N₄ Treated with Silane Coupling Agent KH570

Concentration of KH570 (wt %) ^a	Amount of the KH570 attached to nano-Si ₃ N ₄ (wt %) ^a
0.5	0
1	0.51
5	1.31
10	1.81
25	1.58
50	1.26

^a Weight percent based on the particle weight.

der 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 82°C. The copolymerization started when the second monomer GMA (weight W_2) was charged 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 AlCl₃ solution (20%) was used to break the emulsion. The product was obtained by filtrating, washing with distilled water for several times, and drying at 50°C for 24 h under vacuum. The dried mixture (weight W_3) 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_g , was determined by TGA, while monomer conversion, γ_c , and grafting efficiency, γ_e , were calculated from the following expressions:

$$\gamma_c = (W_3 - W_0) / (W_1 + W_2) \quad (3)$$

$$\gamma_e = (W_0 \gamma_g) / [(W_1 + W_2) \gamma_c] \quad (4)$$

Characterization

A Bruker Equinox 55 Fourier transform infrared spectroscope (FTIR) was used to examine the variations in surface structure of the nanoparticles. The molecular weights of the nongrafted PGMA and GMA-St copolymer were measured by using a Walter 208LC gel permeation chromatograph (GPC) at room temperature with THF as the solvent. Since nano-Si₃N₄ is hard to be dissolved, the grafted polymers cannot be isolated by conventional separation methods.

Dispersibility of the nanoparticles in cured epoxy was characterized by transmission electron microscopic (TEM) observation using a Philips EM400. For preparing epoxy composites, both the resin (bisphenol-A epoxy resin, type E-51) and the nanoparticles with certain proportion were carefully mixed by mechanical stirring and ultrasonication before the curing agent (4,4'-diaminodiphenylsulfone, DDS) was added at a stoichiometric ratio in respect to the resin.

RESULTS AND DISCUSSION

Surfactant-free emulsion graft polymerization of GMA and its characterization

According to the authors' previous study,¹⁴ pretreatment of inorganic nanoparticles with coupling agent is a prerequisite for chemical grafting of polymer chains. A monolayer coverage or a relative thin attachment of silane should be beneficial to the subsequent graft polymerization. From Table I, it is seen that the amount of the silane coupling agent attached to the nanoparticles exhibits the highest value at the concentration of 10 wt %. Further increase in the silane concentration leads to reduced amount of the attached silane. The phenomenon might be related with the fact that the higher concentration coupling agent can hardly penetrate the agglomerated nanoparticles due to the rapid establishment of the three-dimensional siloxane multilayer. Considering the requirements of graft polymerization and saving coupling agent, the Si₃N₄ nanoparticles containing 1.31 wt % KH570 was used in the following study.

With respect to the mechanism involved in graft polymerization in surfactant-free emulsion, the authors have already proved that the polymerization loci are located at the surface of silane-treated nanoparticles due to the higher number of nanoparticles and their hydrophobic surface feature.¹⁴ This reaction mechanism is particularly important to ensure effective encapsulation and graft of polymer surrounding the nanoparticles. Small amount of surfactant is helpful to absorb the monomers on the nanoparticles but has no effect on the subsequent grafting reaction. Figure 1 shows the effect of surfactant concentration on the graft polymerization. The CMC value of OP-10 in water is about 0.00035 mol/L. When the surfactant concentration is lower than its CMC value, it is found

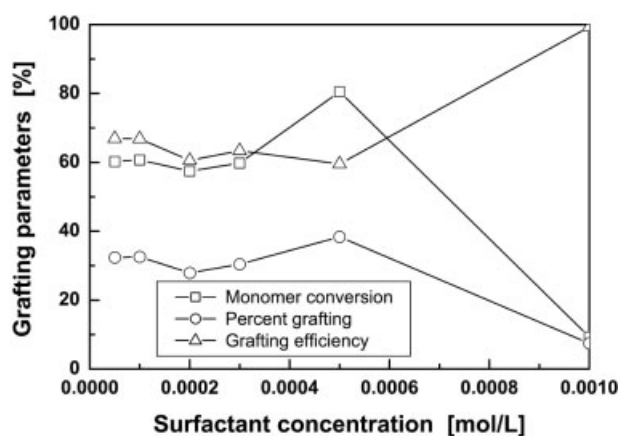


Figure 1 Effect of surfactant concentration on the grafting polymerization of GMA onto nano-Si₃N₄. Reaction conditions: monomer concentration, 0.11 mol/L; initiator concentration, 0.003 mol/L; and reaction time, 8 h.

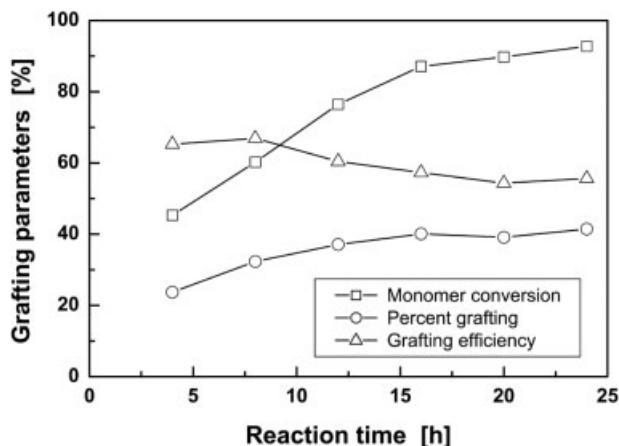


Figure 2 Effect of reaction time on the grafting polymerization of GMA onto nano- Si_3N_4 . Reaction conditions: monomer concentration, 0.11 mol/L; initiator concentration, 0.003 mol/L; and surfactant concentration, 0.00005 mol/L.

that the surfactant is useful to slightly improve monomer conversion and percent grafting, while grafting efficiency remains constant. When the amount of the surfactant exceeds its CMC value, partial polymerization should occur in the micelles. However, as indicated by Figure 1, the monomer conversion and percent grafting are reduced, while the grafting efficiency increases, implying that the monomer reacts more likely at the surface of the nanoparticles rather than in the micelles. The higher concentration of the surfactant would obstruct the diffusion of the monomers into the polymer particles (containing Si_3N_4 nanoparticles).

Evolvement of the graft polymerization is presented in Figure 2. The monomer conversion and percent grafting increase with time initially and then level off at about 16 h. On the other hand, the grafting efficiency shows the highest value at the beginning of the reaction, and decreases gradually with increasing time. These phenomena imply that the graft of GMA onto the surface of nano- Si_3N_4 prefers to take place at the beginning of the reaction, owing to the blocking effect of the grafted polymers on the subsequent graft reaction. That is, the surface double bonds cannot be initiated at the latter stage of polymerization as the growing polymer radicals and grafted polymer chains block the diffusion of radicals to the particles' surfaces. Comparatively, the graft reaction on nano- Si_3N_4 proceeded more slowly than that on nano- SiC ,¹⁴ reflecting that the tight agglomeration of Si_3N_4 nanoparticles needed more time to break.

Figure 3 shows that higher monomer concentration facilitates higher percent grafting and monomer conversion, but conversely influences the values of grafting efficiency. These results can be attributed to the fact that the polymerization rate increases with monomer concentration. Consequently, there is a greater

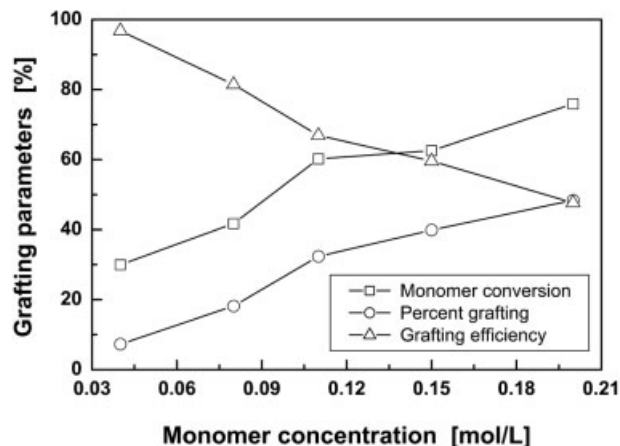


Figure 3 Effect of monomer concentration on the grafting polymerization of GMA onto nano- Si_3N_4 . Reaction conditions: initiator concentration, 0.003 mol/L; surfactant concentration, 0.00005 mol/L; and reaction time, 8 h.

possibility for the monomers to react with the double bonds on the nanoparticle surfaces at the beginning of the reaction. The decreasing tendency of grafting efficiency with monomer concentration is consistent with the above-mentioned blocking effect exerted by the grafted polymer. That is, the faster the reaction, the more severe the blocking effect.

The influence of initiator concentration is given in Figure 4. With an increase in initiator concentration, γ_c and γ_g show complicated trends of variation: rising at the beginning and then descending, but rising again when the initiator concentration exceeds 0.008 mol/L. Nevertheless, γ_e keeps almost unchanged within the range of interests. It is known that higher initiator concentration would lead to higher initiation rate, and hence more double bonds on the particles' surfaces can be initiated. This accounts for the enhancement of

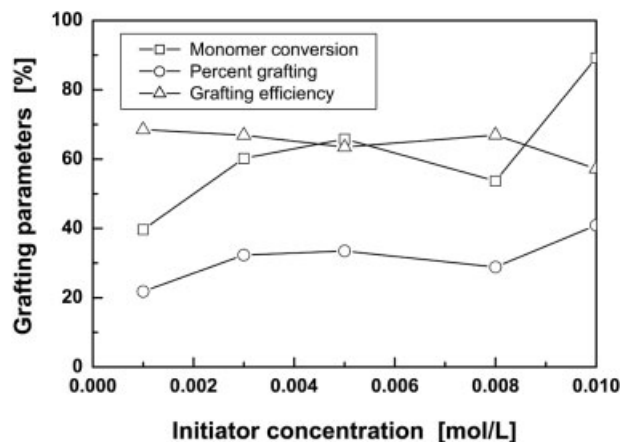


Figure 4 Effect of initiator concentration on the grafting polymerization of GMA onto nano- Si_3N_4 . Reaction conditions: monomer concentration, 0.11 mol/L; surfactant concentration, 0.00005 mol/L; and reaction time, 16 h.

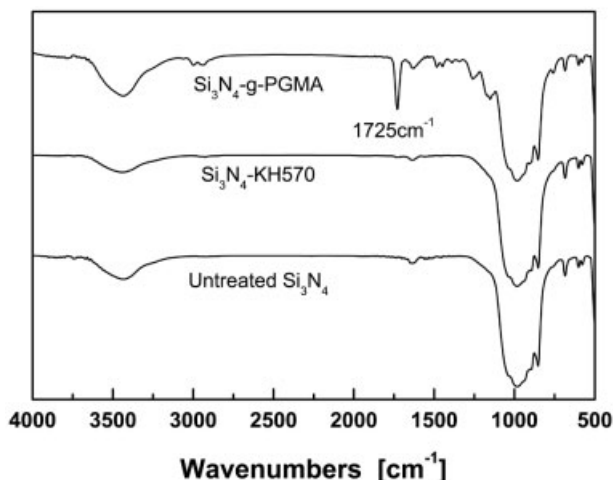


Figure 5 FTIR spectra of untreated nano-Si₃N₄, Si₃N₄-KH570 and Si₃N₄-g-PGMA ($\gamma_g = 7.3\%$). Prior to the measurements, either the excess silane or nongrafted polymers were extracted.

γ_c and γ_g . However, a further increase of initiator concentration may cause the faster bimolecular termination, which is responsible for the decreasing trends of both γ_c and γ_g . Only when the initiator concentration is high enough, the hindering effect becomes inconspicuous.

Figure 5 illustrates the infrared spectra of the nanoparticles before and after the treatments. The spectrum of the KH570-modified nano-Si₃N₄ exhibits similar profile as that of the untreated nanoparticles due to the less amount of the attached KH570 (1.31 wt %). After the graft reaction, the formation of grafted PGMA is confirmed by the strong absorption of carboxyl groups at 1725 cm⁻¹. Besides the variation in the surface chemistry of the nanoparticles, molecular weights of the grafting products are also of interests. As stated in the experimental part, however, the molecular weight of the grafted PGMA is not available due to the difficulty in separating the grafted polymers from the nanoparticles. It can be recalled that, when polystyrene and poly(methyl methacrylate) were grafted onto nano-SiO₂,^{7,16} the molecular weights of both grafted and nongrafted polymers

TABLE II
Molecular Weights of Nongrafted PGMA Measured by GPC^a

γ_g (%)	M_n (10 ⁴)	M_w (10 ⁴)	M_w/M_n
48.39	1.44	3.60	2.49
40.94	1.02	3.28	3.22
27.90	1.22	3.74	3.06
23.72	1.08	3.58	3.32

^a Each reaction was carried out at 70°C for 10 h in 200 mL ammonia (pH = 7–8, containing 0.4% isobutanol). The weight of Si₃N₄-KH570 particles is 4 g and the initiator concentration is 0.003 mol/L.

were reported to be almost the same. Possibly the same conclusion might be valid in the case of PGMA studied here. Table II shows the number-average molecular weight, M_n , and mass-average molecular weight, M_w , of PGMA homopolymer determined by GPC. It is found that the molecular weights of PGMA do not change with percent grafting, implying that the higher γ_g values might result from increased amount of the grafted macromolecules rather than from increased chains' length.

Emulsion graft copolymerization of GMA and St and its characterization

Interfacial interaction has long been realized as a key role in determining composites properties. Therefore, the present work utilizes a copolymerization technique in graft modification of the nanoparticles. It is expected that a controllable bonding can thus be established between the deliberately grafted nanoparticles and the matrix polymer when making composites. Since styrene is compatible with epoxy resin, it was chosen as a copolymerization monomer. In consideration of the fact that styrene is hydrophobic and can hardly be polymerized by surfactant-free emulsion method, emulsion polymerization method has to be used to stabilize polystyrene particles.

The effect of the concentration of surfactant on the γ_c , γ_g , and γ_e is shown in Table III. Evidently, with a rise in surfactant content, γ_c increases but γ_g and γ_e decrease. In this system, there are two types of loci in

TABLE III
Effect of the Surfactant Concentration on the St/GMA Copolymer Grafting onto Nano-Si₃N₄

Weight of Si ₃ N ₄ -KH570 (g)	Surfactant (SDS/OP-10) amount (%) ^a	Initiator concentration (mol/L)	St concentration (mol/L)	GMA concentration (mol/L)	γ_c (%)	γ_g (%)	γ_e (%)
2	2	0.006	0.436	0.075	85.78	44.11	18.35
	3.5				95.98	37.52	13.95
	5				97.71	36.55	13.35
	10				99.22	28.47	10.25

^a Weight percent based on the particle weight.

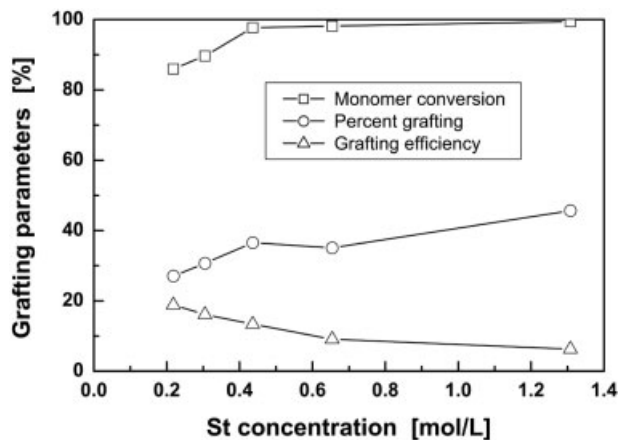


Figure 6 Effect of St concentration on the grafting copolymerization onto nano- Si_3N_4 (GMA concentration is fixed at 0.075 mol/L).

which the polymerization proceeds. One lies in the nanoparticles that absorb small amount of surfactant and another the micelle. The micelle number must increase with increasing the surfactant concentration, implying that more monomer can react inside the micelle. It might explain the aforesaid dependence of γ_{cr} , γ_{gr} , and γ_e on surfactant concentration. It is noted that even when the amount of surfactant is quite high (i.e., 10 wt %), the grafting percentage is still high (i.e., 28 wt %), indicating that the nanoparticles always act as polymerization loci. This is understandable because nanoparticles possess quite large surface areas (the concentration of the particles is $10^{13}/\text{mL}$) if they were uniformly dispersed. Besides, the double bonds on the particles surfaces can take part in the initiation reaction to form particulate nucleation. This process is undoubtedly beneficial to the graft polymerization onto the nanoparticles.

The effect of St concentration on the grafting parameters at a constant amount of GMA (i.e., 0.075 mol/L) is shown in Figure 6. Similar to the case of graft of GMA onto nano- Si_3N_4 , higher St concentration favors higher percent grafting and monomer conversion due to the faster reaction, but reduces grafting efficiency as a result of the blocking effect of the grafted polymer. It is noted that the monomer conversion is quite high and approaches 100% when St concentration is over 0.4 mol/L, indicating that GMA is likely copolymerized with St. On the other hand, when the dosage of St is fixed at 0.44 mol/L, the effect of GMA concentration on the grafting parameters is shown in Figure 7. Although the monomer conversion keeps unchanged at high level, both γ_g and γ_e increase with GMA concentration. This suggests that the GMA is more likely to react with St in the particles containing nano- Si_3N_4 rather than in the micelle.

The FTIR spectrum of Si_3N_4 -g-PS-PGMA is shown in Figure 8. The characteristic peaks at 1729 and 1600

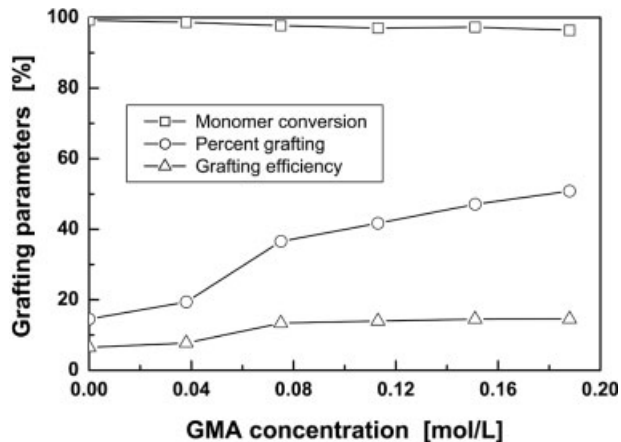


Figure 7 Effect of GMA concentration on the grafting copolymerization onto nano- Si_3N_4 (St concentration is fixed at 0.44 mol/L).

cm^{-1} are ascribed to PGMA and PS, respectively. Besides, the peak at 848 cm^{-1} belongs to the absorption of epoxide groups, while the peaks at 2842, 2925, and 3025 cm^{-1} correspond to the stretching motion of $-\text{CH}_2-$, $-\text{CH}-$, and $\text{C}-\text{H}$ groups, respectively. Owing to the existence of carbonyl groups, the above three peaks are not so evident as those in neat PS.¹⁷ It means that most of the grafted polymers should be the copolymer of PS-PGMA. Otherwise, a evident peak at 3025 cm^{-1} should be perceived.

Table IV shows the average molecular weights (M_n and M_w) of St-GMA ungrafted copolymer determined by GPC. It is interesting to note that the molecular weights of the copolymer change with the ratio of St/GMA in monomer feed. The highest

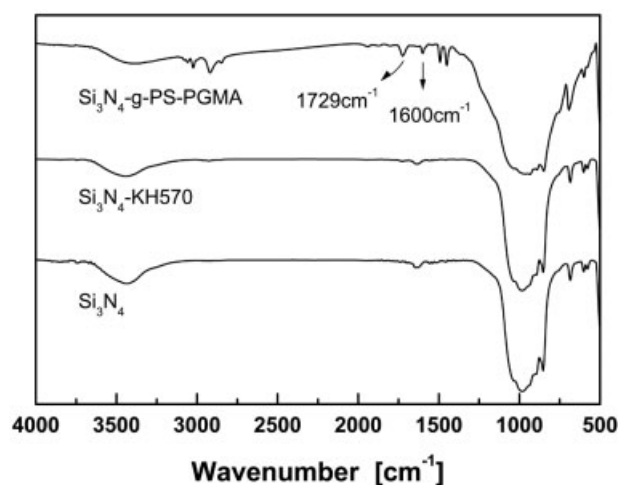


Figure 8 FTIR spectra of untreated nano- Si_3N_4 , Si_3N_4 -KH570 and Si_3N_4 -g-PS-PGMA ($\gamma_g = 36.6\%$, PS/PGMA = 28.8/7.8 weight ratio). Prior to the measurements, either the excess silane or nongrafted polymers were extracted.

TABLE IV
Molecular Weights of Nongrafted St-GMA Copolymers Measured by GPC

Ratio of St/GMA (v/v)	M_n (10^4)	M_w (10^4)	M_w/M_n
1.5:1	5.1	14.7	2.92
2.5:1	6.0	18.3	3.06
3.5:1	9.4	23.1	2.46
5:1	6.5	18.2	2.79

molecular weight is obtained at the St/GMA ratio of 3.5/1 (v/v), which might be related to the change of polymerization rate at different monomer feeds. Detailed mechanism needs to be further explored.

For all the copolymerizations except azeotropic copolymerization, the comonomer feed and copolymer compositions are not identical. The comonomer feed changes in composition as one of the monomers preferentially enters the copolymer. Therefore, there is a drift in the comonomer composition toward the less reactive monomer with a rise in the degree of conversion. This results in a similar variation of copolymer composition with conversion. In the current work, the presence of nanoparticles might exert a more complicated influence on the copolymer's composition. Since the grafted copolymer cannot be isolated by dissolving Si_3N_4 nanoparticle, an indirect method has to be used for analysis of the composition. As shown in Figure 9, the area of the absorption band at 1600 cm^{-1} due to PS becomes larger with increasing St content, while the area of the peak at 1729 cm^{-1} due to PGMA decrease gradually. This clearly demonstrates that a quantitative analysis can be made by examining the areas under the characteristic absorption bands. Figure 10 gives the area ratio of the peaks at 1600 and

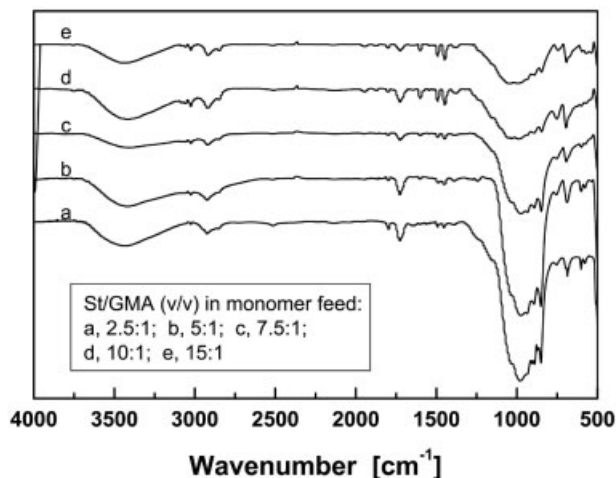


Figure 9 FTIR spectra of various Si_3N_4 -g-PS-PGMA with different monomer feeds.

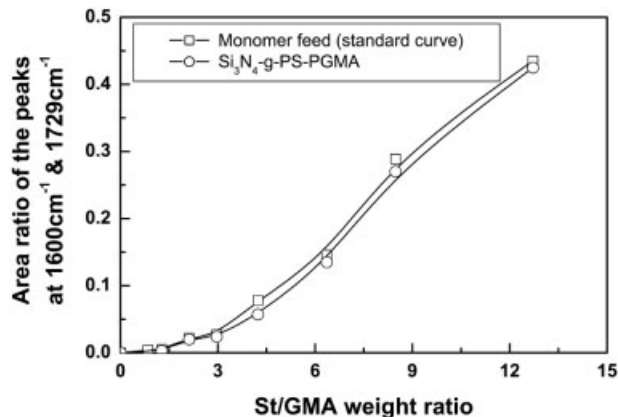


Figure 10 Area ratio of the FTIR peaks at 1600 and 1729 cm^{-1} as a function of St/GMA ratio measured from monomer feed and Si_3N_4 -g-PS-PGMA, respectively.

1729 cm^{-1} as a function of St/GMA monomer ratio, which is taken as an internal standard curve. The same curve measured from the FTIR spectra of Si_3N_4 -g-PS-PGMA (Fig. 9) is also plotted in Figure 10. It shows a similar trend but slightly lower values as compared with the standard curve. The corresponding ratio of St/GMA was presented in Figure 11. It is seen that the amount of St in the grafted copolymer is slightly lower than that in the monomer feed, but the two curves are quite similar on the whole.

CONCLUSIONS

Chemical grafting of PGMA onto the surface of nano-sized silicone nitride particles can be accomplished through surfactant-free emulsion polymerization. In this reaction, the blocking effect exerted by the growing polymer radicals or grafted polymer chains have significant influence on monomer conversion and per-

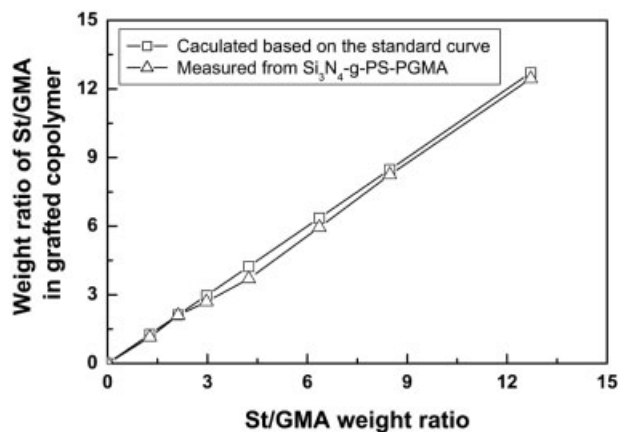


Figure 11 Weight ratio St/GMA in the grafted copolymer as a function of monomer feed.

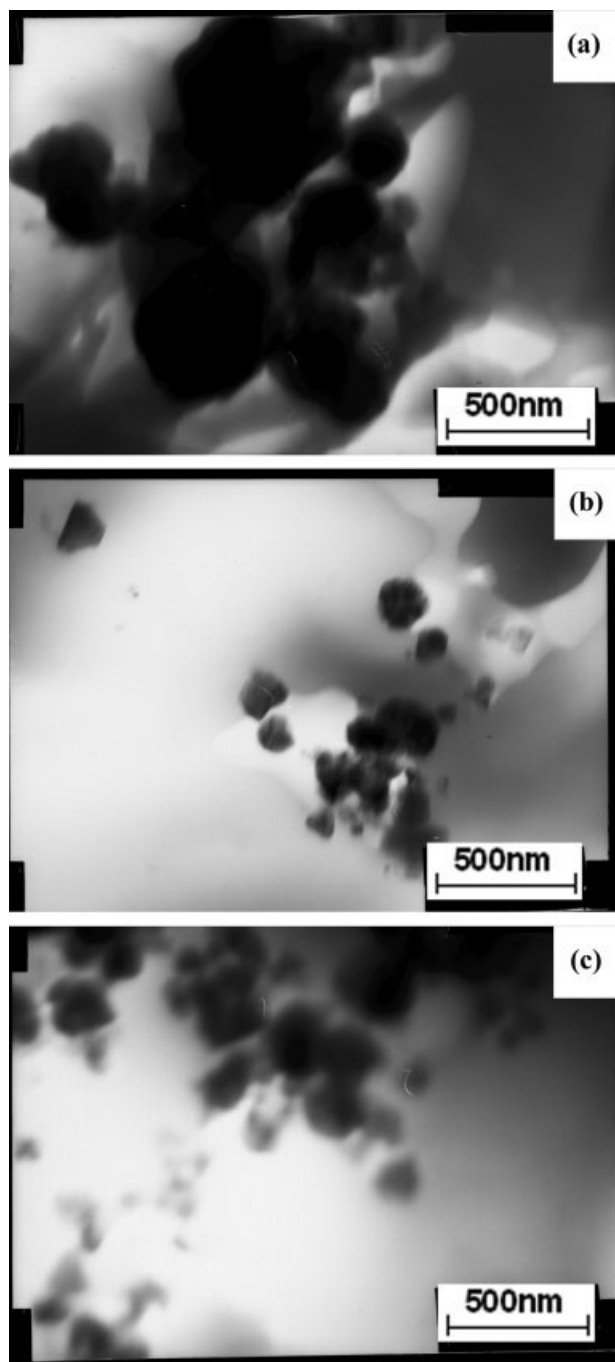


Figure 12 TEM photos of (a) nano- Si_3N_4 , (b) Si_3N_4 -g-PGMA/epoxy composite ($\gamma_g = 7.3\%$), and (c) Si_3N_4 -g-PS-PGMA/epoxy composite ($\gamma_g = 35.1\%$, PS/PGMA = 30.03/5.05).

cent grafting. In this context, higher concentration of monomer and initiator are favorable for the graft reaction.

The copolymer of St/GMA can be grafted onto Si_3N_4 nanoparticles in emulsion solution. The silane-treated nanoparticles always play the role of polymerization loci due to their large surface area and hydrophobic nature. Higher monomer concentration (of either St or GMA) leads to higher percent grafting and monomer conversion because of the faster reaction. Composition of the grafted copolymer can be tailored by changing the monomer feed. Accordingly, the optimal interfacial adhesion in nano- Si_3N_4 particles-filled epoxy composites can be obtained by changing the composition of the grafted copolymer in our future works.

The surface treatment of nano- Si_3N_4 through graft polymerization greatly improves dispersibility of the particles in cured epoxy (Fig. 12). It is thus expected that the nanocomposites performance would be significantly increased, which will be discussed in another paper of the authors.

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