Polymer Journal, Vol. 37, No. 9, pp. 677–685 (2005)

Grafting of Poly(glycidyl methacrylate) onto Nano-SiO_2 and Its Reactivity in Polymers

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(Received January 24, 2005; Accepted June 9, 2005; Published September 15, 2005)

ABSTRACT: In order to introduce reactive groups onto the surface of inorganic nanoparticles, which can take part in the *in-situ* reaction when being compounded with matrix polymers to produce nanocomposites, poly(glycidyl methacrylate) (PGMA) was grafted onto silane pretreated nano-SiO_2 by free-radical polymerization. This paper mainly studied the factors that influence the graft polymerization, including monomer concentration, initiator consumption, reaction temperature and reaction time. The reactive kinetics of the PGMA grafted on the nanoparticles with 4,4′-diaminodiphenylsulfone (DDS) in polypropylene (PP) or polystyrene (PS) matrices were evaluated by differential scanning calorimetry (DSC). It was shown that the appearance of PP or PS in the model composites did not change the overall curing reaction mechanism and the grafted nanoparticles gave a stable dispersion in the good solvent for the grafting chains. [DOI 10.1295/polymj.37.677]

KEY WORDS Glycidyl Methacrylate / Silica Nanoparticles / Graft Polymerization / Reactive Kinetics /

Nano-sized inorganic particles have been widely used in recent years as fillers in polymers to improve toughness[1,2] and tribological performance[3,4] of the composites. However, a homogeneous dispersion of nanoparticles in polymer matrices is very difficult because the particles with high surface energy are easy to agglomerate. In addition, the hydrophilic nanoparticles and the hydrophobic polymers are not compatible in nature, which has to result in poor interfacial bonding. All of these deficiencies obstruct effective utilization of inorganic nanoparticles in polymer composites. To lower surface energy of nanoparticles, surface treatment that aims at improving dispersibility of the powders in polymers and tailoring the interfacial interaction is highly desired. Many approaches have been proposed so far, including coupling agents[5,6] and grafting modification,[7–10] whereas most of them do not consider the possibility of reactive compatibilization. As a result, physical interaction generally predominates the interfacial interaction between these treated nanoparticles and polymer matrices.

In our previous works, graft polymerization of polystyrene, poly(methyl methacrylate), poly(ethyl acrylate) and poly(butyl acrylate) was employed to modify non-layered nanoparticles like silica and calcium carbonate, which were then mechanically compounded with polypropylene as usual. Mechanical testing of polypropylene filled with nano-SiO_2[2,11] and nano-$CaCO_3$[8,12] demonstrated that only a small amount of the treated nanoparticles (typically less than 3 vol. %) could simultaneously improve stiffness, strength, toughness and thermal deformation temperature of the matrix polymer. The interface in these grafted nanoparticles/polypropylene composites is believed to be enhanced by the chain entanglement between the grafted polymers and the matrix. Moreover, the inherently friable structure of nanoparticle agglomerates that is detrimental to the mechanical properties of polymeric composites can be amended so that they are provided with load bearing ability.

Actually, the graft treatment of nanoparticles leads to specific structures that can be tailored by changing graft monomers and graft conditions. To further bring the positive effects of nanoparticles into play in the very area, the authors of the present work plan to introduce grafted polymers containing reactive groups onto nanoparticles so as to build up chemical bonding at the filler/matrix interface during the subsequent composites manufacturing. In this context, a fine adjustment of the interfacial interaction in the subsequent composites can be completed by controlling the amount and species of the reactive groups. The technical route belongs to reactive compatibilization, which means blending process accompanied by chemical reaction and is capable of generating strong polymer/polymer or filler/polymer interactions at

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the interface.[13–15]

In this work, the authors try to graft glycidyl methacrylate onto nano-silica particles. The monomer has an unsaturated vinyl group and an epoxide functional group. Its double bond can be used to construct grafted polymer, and the pendant oxirane ring might be opened to react with a series of functional groups like carboxyl, amino, hydroxyl, etc., which can be either introduced onto matrix macromolecules beforehand or pre-incorporated to the matrix along with compatibilizers like maleic anhydride grafted polypropylene.

The present work is a continuation of the program dealing with fabrication of thermoplastics based nanocomposites that are supposed to have excellent mechanical properties than the micro-counterparts. It is expected that a controllable bonding can thus be established between the deliberately grafted nanoparticles and the matrix, enabling effective stress transfer across the interface. In addition, network structure formed throughout the composites in terms of the aforesaid reaction of the epoxide groups on the grafted polymers with the third components would further improve the nanocomposites properties. Aiming at this ultimate target, the current paper investigated the preparation of poly(glycidyl methacrylate) grafted nano-SiO_2 to obtain differently modified nanoparticles. Effects of polymerization conditions were carefully considered. Besides, 4,4′-diaminodiphenylsulfone was added to the model blends consisting of the treated nanoparticles and polypropylene or polystyrene as a functional component to evaluate the reactivity of epoxide groups on the grafted polymer molecules with amino terminals.

EXPERIMENTAL

Materials

Nano-SiO_2 particles (Aerosol 200, Degussa Co., Germany) with an average primary particle size of 12 nm, a specific surface area of $200\,m^2/g$ and a specific gravity of $2.2\,g/cm^3$ were dried in vacuum at 120 °C for 24 h to get rid of the physically absorbed and weakly chemically absorbed species before use. The coupling agent, γ-methacryloxypropyl trimethoxy silane (KH570, provided by Liao Ning Gaizhou Chemical Industry Co. Ltd., China), was used as received. Glycidyl methacrylate (GMA) monomer was distilled under low pressure prior to the graft polymerization. The initiator, azobisisobutyronitrile (AIBN) was recrystallized from methanol and water and dried in vacuum at room temperature. Powdered isotactic polypropylene (PP) homopolymer F401 was supplied by Guangzhou Petroleum Chemical Company, China. Amorphous PS (Type SG-23) was provided by Shan Tou Sea First Polystyrene Resin Co. Ltd., China.

Chemical Grafting onto Nano-SiO_2

To chemically attach polymer chains onto nano-SiO_2 by free-radical graft polymerization, the particles have to be pretreated to introduce double bonds to the surfaces. This was achieved by the reaction of silane with the hydroxyl groups of SiO_2. A typical procedure for the coupling agent treatment is described as follows. An excess of KH570 was added to a suspension of SiO_2 in 300 mL of toluene (weight ratio = 1/30). Then, the suspension was ultrasonically agitated for 30 min and refluxed for 10 h at 110 °C under the protection of nitrogen. Afterward, the particles were collected by filtration, and extracted with alcohol for 24 h to remove the excessively absorbed silane. The silane treated SiO_2 (named SiO_2-g-KH570) was dried for 24 h at 50 °C under vacuum. The content of the silane attached to the silica surface was detected by thermogravimetric analysis (TGA).

To graft GMA monomer onto nano-SiO_2, the silane pretreated particles were mixed with toluene under sonication for 30 min. Then, the initiator, AIBN, was added with stirring into the reactor that was kept at certain temperature and protected with N_2. The monomer, GMA (weight W_1), was charged into the system 5 min later, and the reaction kept several hours. Figure 1 schematically shows the procedure of the surface grafting through radical polymerization. The products were precipitated by pouring them into a large amount of methanol. The precipitated products were then filtrated and washed with methanol for several times to remove the residual monomer. The dried mixture (weight W_2) was extracted with acetone for 48 h to separate the grafted SiO_2 (named SiO_2-g-PGMA) and the homopolymerized poly(glycidyl

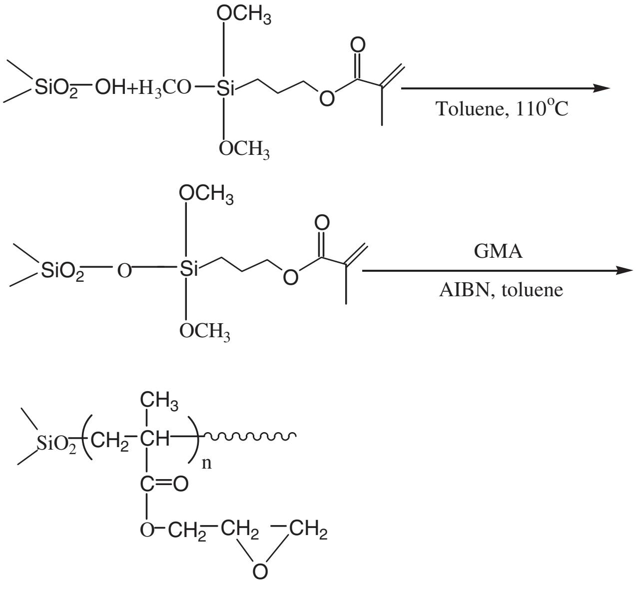

Figure 1. Schematic illustration of surface grafting of PGMA onto nano-SiO_2.

methacrylate) (PGMA) that were generated during the graft polymerization of the monomer. Finally, the SiO_2-g-PGMA was dried at 50 °C for 24 h. Some of them were transferred to a Shimadzu TA-50 thermogravimeter to determine the grafting percentage, γ_g. Here, the weight fraction of the attached silane was deducted from the values of γ_g. Monomer conversion, γ_c, and grafting efficiency, γ_e, were calculated as follows:

$$\gamma_c = (W_2 - W_o - W_{AIBN})/W_1 \quad (1)$$

$$\gamma_e = \gamma_g W_o/\gamma_c W_1 \quad (2)$$

where W_{AIBN} is the weight of the initiator AIBN and W_o denotes the weight of SiO_2 nanoparticles. The average area taken up by one grafted PGMA molecule on the surface of nano-SiO_2, S, can be estimated using eq. 3:

$$S = 200 \times 10^{20}/(\gamma_g N_{av}/M_n) \quad (3)$$

where S is expressed in $Å^2$, M_n denotes the number average molecular weight of the grafted polymer and N_{av} is Avogadro's number. The numeral 200 is the value of specific surface area of the nano-silica in terms of m^2/g. The value of $\gamma_g N_{av}/M_n$ is equal to the molecular number of the grafted polymer on the surfaces per gram of nano-silica. The number of the grafted PGMA chains attached to one silica particle, G_d, can be calculated by eq. 4:

$$G_d = (\gamma_g N_{av} \rho V)/M_n \quad (4)$$

where ρ denotes the specific gravity of silica and V is the volume of one primary silica particle.

Characterization

The infrared spectra of the polymer-grafted and untreated silica were recorded on a Nicolet 5DX Fourier-transform infrared (FT IR) spectroscope. The molecular weight of the grafted and homopolymerized PGMA were determined with a Walter 208LC gel chromatograph (GPC) at 40 °C with THF as the solvent (chromatography column: Ultrastyragel 10^3 A; flowing speed of THF: 1 mL/min). The grafted polymer was obtained by removing silica from the grafted particles with a 20% HF solution, and the homopolymerized PGMA was isolated from extraction.

To study the reactive kinetics of epoxide groups on the grafted polymer molecules with amino terminal components, the SiO_2-g-PGMA powder was mixed with required amount of 4,4′-diaminodiphenylsulfone (DDS) powder in a mortar box at room temperature. Then, the mixture was mixed with PP or PS powder in the same mortar (weight ratio = 1:3). The reaction between epoxide groups and amine groups was monitored directly using small amount of these compounds. A MDSC 2910 differential scanning calorimeter (DSC) was used for the inspection up to 300 °C under a dry nitrogen flow of 40 mL/min at different heating rates from 15 to 30 °C/min. The DSC runs were made in duplicate and the reproducibility of kinetic data was very good.

The dispersibility of SiO_2-g-PGMA in acetone was compared with that of untreated and SiO_2-e-PGMA (*i.e.*, PGMA encapsulated SiO_2). A typical procedure is described as follows. SiO_2-g-PGMA (0.5 g) was dispersed in 100 mL of acetone, and the suspension was sonicated for 30 min to attain a uniform dispersion of the particles in the solvent. Similarly, several glass vessels of the same size were filled with the samples for comparison. After a definite time, 5.0 mL of the liquid were taken out from each suspension at the same position and weighted. The amount of the suspending particles was determined by the difference between the weight of this liquid and the weight of the pure solvent having the same volume.

RESULTS AND DISCUSSION

Influence of Reaction Conditions on Graft Polymerization

Since the present work aims at bringing a fine adjustment of interfacial interaction in the subsequent nanocomposites by controlling the amount and species of the reactive groups on the grafted polymer, the effects of reactive conditions on the grafting onto the nanoparticles should be known at the very beginning of the discussion. In fact, the treated nano-silica particles containing double bonds can be initiated as conventional monomers, leading to chain propagation to generate grafted polymers from the particles. Besides, the grafted polymers can also be obtained through bimolecular termination between the surface radicals of the nanoparticles and the propagating radicals in the solution. Meanwhile, the formation of homopolymers in the solution follows the general radical polymerization law. It is worth noting that the nanoparticles possess higher mobility in the solution due to their very small size, which might influence the grafting reaction. The grafted polymers covering the nanoparticles would hinder the contacts between the components.

Table I lists the influence of coupling agent concentration on the degree of reaction. It is seen that the amount of the silane coupling agent attached to the particles tends to increase with the concentration of the coupling agent used in the pre-treatment. On the whole, however, only a small portion of silane can be chemically attached onto the nanoparticles. With a rise in the concentration of KH570, the ratio of the amount of the attached silane over the precursor amount decreases from 18 to 12%. This might be

Table I. Nano-SiO_2 treated with coupling agent KH570

Concentration of KH570[a] (wt %)	Precursor amount[b] (μmol/m^2)	Amount of the grafted KH570 (μmol/m^2)	Grafting percent (%)
40	9.09	1.63	6.20
50	11.36	1.92	7.79
80	18.18	2.15	8.60

[a] Weight percent based on the particle weight. [b] Precursor amount = Moles of KH570/Surface area of SiO_2 used.

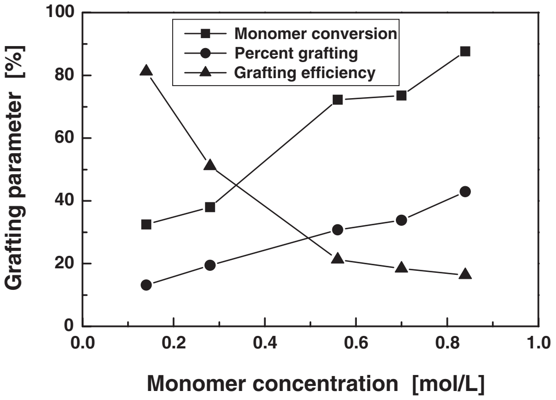

Figure 2. Effect of monomer concentration on the grafting polymerization of GMA onto nano-SiO_2. Rreaction conditions: nano-SiO_2 = 2 g, initiator concentration = 0.018 mol/L, reaction time = 6 h, reaction temperature = 80 °C.

related to the rapid establishment of the three-dimensional siloxane multilayer in the case of high coupling agent concentration, which hinders the subsequent reaction of silane with the nanoparticles staying inside the agglomerates. In consideration of effective utilization of silane and the requirement of double bonds on the nanoparticles surface, the silane treated SiO_2 nanoparticles containing 6.2 wt % KH570 was used in the following grafting reaction.

The effect of monomer concentration on the graft polymerization is given in Figure 2. It is found that both the grafting percentage and the monomer conversion tend to increase linearly with the monomer concentration. This phenomenon can be attributed to the fact that the polymerization rate increases with monomer concentration. As a result, there is a greater possibility for the monomers to react with the double bonds on the nanoparticles surfaces at the beginning of the reaction. It means that the grafting degree of the nano-SiO_2 can be controlled by monomer concentration. In contrast, the grafting efficiency shows a sharp decrease with the monomer concentration and then declines slightly when the concentration is greater than 0.56 mol/L. This implies that the growth of the grafted polymer is more significant in the case of low monomer concentration, and homopolymerization covers the growth of the grafted polymer under high monomer concentration. Since the experimental data indicated that when the monomer concentration exceeded 1 mol/L, the reaction system became too viscous to be stirred by a magnetic stirrer. Accordingly, a suitable monomer concentration of 0.56 mol/L was chosen in the subsequent chemical grafting modification of nano-SiO_2.

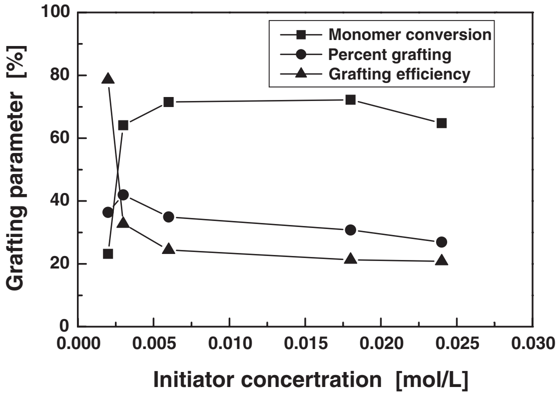

Figure 3. Effect of initiator concentration on the grafting polymerization of GMA onto nano-SiO_2. Reaction conditions: nano-SiO_2 = 2 g, monomer concentration = 0.56 mol/L, reaction time = 6 h, reaction temperature = 80 °C.

Figure 3 illustrates the dependence of γ_g, γ_c and γ_e on the initiator concentration. It is seen that γ_c shows a drastic increase at rather low initiator concentration and then keeps almost unchanged when the concentration is over 0.005 mol/L. In contrast, γ_e shows a drastic decrease with initiator concentration and then is also independent of the initiator concentration. These results coincide with the above-mentioned influence of monomer concentration. That is, growth of the grafted polymer mostly occurs at the beginning of the reaction, while homopolymerization predominates the rest of the reaction. Consequently, the higher the initiator concentration, the higher the amount of the homopolymerized PGMA, which leads to higher γ_c but lower γ_e.

With respect to γ_g, it is not significantly influenced by initiator concentration (Figure 3). This is understandable if the grafting polymerization is supposed to proceed at the beginning of the reaction as demonstrated by the variation tendencies of γ_c and γ_e. Higher initiator concentration would promote the formation of homopolymer rather than grafted polymer.

The dependences of γ_g, γ_c and γ_e on reaction temperature further evidence that the graft polymerization mostly takes place at the beginning of the reaction (Figure 4). With increasing reaction temperature, the polymerization rate has to increase and γ_c increases within the temperature range from 60 to 70 °C accordingly. The slight increase in γ_g and remarkable decrease in γ_e suggests that higher temperature favors

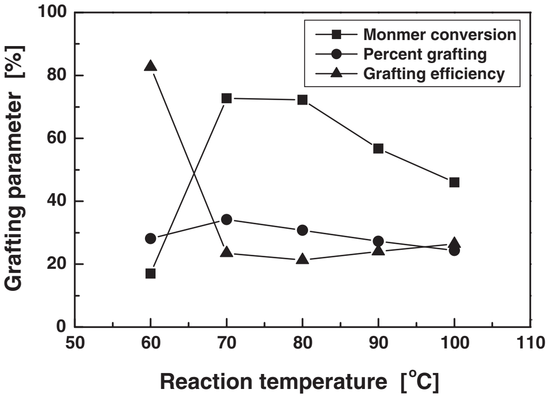

Figure 4. Effect of reaction temperature on the grafting polymerization of GMA onto nano-SiO_2. Reaction conditions: nano-$SiO_2 = 2$ g, monomer concentration $= 0.56$ mol/L, initiator concentration $= 0.018$ mol/L, reaction time $= 6$ h.

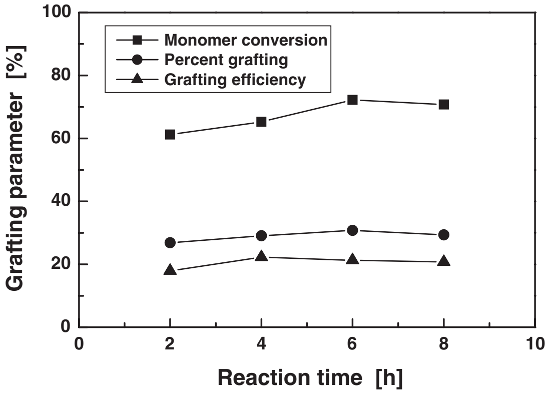

Figure 5. Effect of reaction time on the grafting polymerization of GMA onto nano-SiO_2. Reaction conditions: nano-$SiO_2 =$ 2 g, initiator concentration $= 0.018$ mol/L, monomer concentration $= 0.56$ mol/L, reaction temperature $= 80$ °C.

homopolymerization. When the reaction temperature is over 80 °C, the temperature dependences of γ_g, γ_c and γ_e are reversed. This is because an elevated temperature would lead to higher initiation rate, and hence higher rate of radical recombination and termination of the propagating polymer chains, which accounts for the reduction in γ_c.

As shown in Figure 5, the reaction time nearly has no influence on γ_g and γ_e from 2 to 8 h. In spite of the moderate increase in γ_c with time up to 6 h, γ_c can be basically considered as a constant. In other words, the reaction was nearly completed within 2 h in the given system. It is worth noting that the highest γ_c in Figure 5 is about 70%, while prolonged reaction time could not further increase the value. In fact, higher γ_c might be obtained under higher monomer concentration (Figure 2).

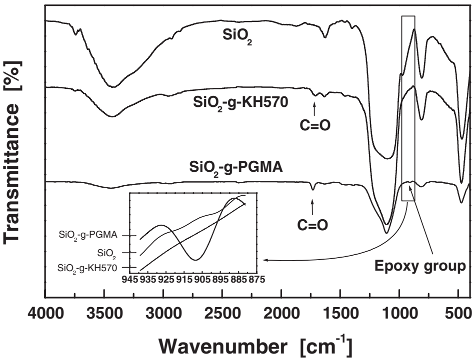

Figure 6. FT IR spectra of untreated and treated nano-SiO_2. The excess silane or non-grafted polymers were extracted before the measurements.

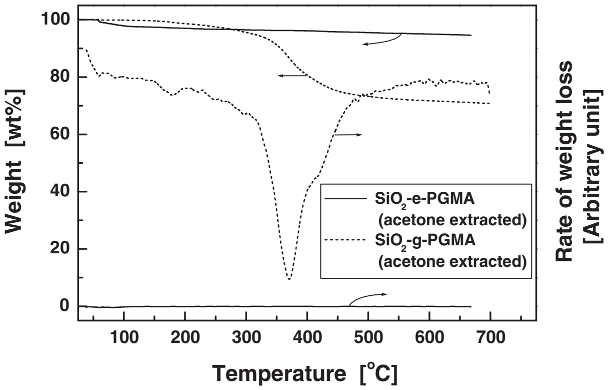

Figure 7. Thermogravimetric analyses of SiO_2-g-PGMA in comparison with SiO_2 encapsulated by PGMA. Both the samples were thoroughly extracted before the measurements.

Characterization of the Grafted Nano-SiO_2

FT IR spectra of the untreated silica, SiO_2-g-KH570 and SiO_2-g-PGMA are shown in Figure 6. The absorption at 1730 cm^{-1} in the spectrum of SiO_2-g-KH570 represents stretching mode of carboxyl groups and reveals the existence of silane on the surface of nano-silica. For the spectrum of SiO_2-g-PGMA, the peak at 910 cm^{-1} can be assigned to epoxide groups besides the peak of carboxyl groups. This proves that PGMA chains have been chemically connected to the surface of nano-silica, and the grafted polymer cannot be removed by the extraction procedure.

For purposes of confirming that PGMA is chemically bonded to the nano-silica but not physically absorbed on the particles, SiO_2 nanoparticles as-received were encapsulated by PGMA, and then extracted by acetone. The remainder was examined by TGA to check whether the coated polymer can still be adhered to the particles surface due to physical interaction. The pyrolytic behaviors of the materials shown in Figure 7 demonstrate that the encapsulated polymer had been completely removed by acetone extraction, while the grafted polymer remains. It proves that PGMA has been successfully attached to the nano-silica surface through the chemical bonding.

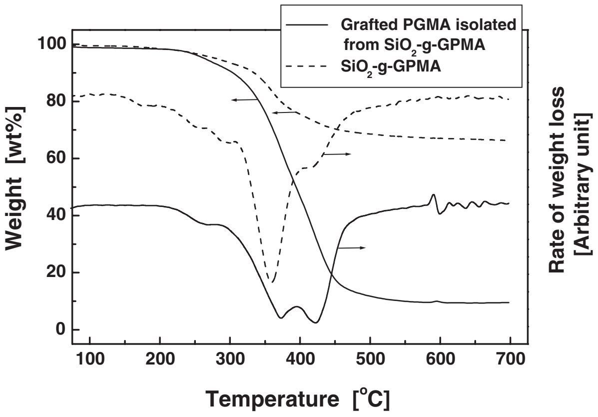

Figure 8. Thermogravimetric analyses of SiO_2-g-PGMA and grafted PGMA isolated from SiO_2-g-PGMA. The homopolymerized PGMA was extracted from SiO_2-g-PGMA before the measurement.

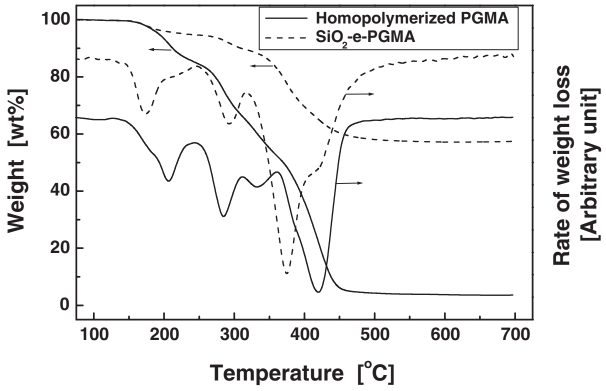

Figure 9. Thermogravimetric analyses of homopolymerized PGMA and SiO_2 encapsulated by PGMA.

The strong interaction between nano-silica and the grafted PGMA can be roughly evaluated from the considerably higher thermal stability of SiO_2-g-PGMA than that of grafted PGMA isolated from SiO_2-g-PGMA. As seen in Figure 8, the temperature corresponding to the peak rate of weight loss at the first thermal decomposition stage of SiO_2-g-PGMA is 295 °C, which is higher than that of grafted PGMA isolated from the grafted nanoparticles (~270 °C). On the contrary, the same temperature of the SiO_2 encapsulated by PGMA (*i.e.*, SiO_2-e-PGMA) is lower than that of PGMA homopolymer (Figure 9). It reveals that physical interaction between SiO_2 particles and PGMA cannot enhance the thermal stability of PGMA. The result also evidences that PGMA is chemically bonded to silica nanoparticles in the case of SiO_2-g-PGMA.

Number average molecular weight, M_n, and weight average molecular weight, M_w, of both grafted and homopolymerized PGMA are shown in Table II as a function of percentage grafting. Clearly, the grafted polymers collected from the grafted nano-SiO_2 under different percentage grafting have similar molecular weights. That is, the aforesaid increase in the amount of grafted polymer with increasing monomer concentration originates predominately from the increase in grafting density per surface area of the nanoparticles but not from the increase in the molecular length of the grafted polymer. Accordingly, both the number of grafted PGMA chains per gram of nano-SiO_2 and the number of grafted PGMA chains attached to one silica particle increase with the percentage grafting. Since the G_d values are quite high while the particles are very small, it is suggested that grafted PGMA possibly exhibits a standing up conformation, which should be beneficial to the contact and reaction of epoxide groups of PGMA with other components during composites manufacturing. It is seen that the molecular weights of both grafted and ungrafted PGMA are lower than those synthesized in emulsion solution.[16] It might be related to the chain-transfer reaction, the premature termination of a growing polymer by the transfer of a hydrogen or another atom or species to it from some compound present in the system—the monomer, initiator, and especially the nano-silica particles, as the case may be. On the other hand, the homopolymerized PGMA has higher molecular weight than that of the grafted PGMA. It can be ascribed to the higher mobility of the nanoparticles that makes chain termination between the radicals easier.

Table II. Molecular weights of grafted and homopolymerized PGMA in SiO_2-g-PGMA

γ_g (%)	Materials	M_n	M_w	M_w/M_n	S (Å^2)	G_n ($\times 10^{20}$/g)	G_d
19.42	Grafted PGMA	867	887	1.02	5.51	1.35	265
	Homopolymerized PGMA	3960	4654	1.17			
34.20	Grafted PGMA	891	919	1.03	3.22	2.31	473
	Homopolymerized PGMA	7025	11692	1.70			

M_n: Number average molecular weight. M_w: Weight average molecular weight. S: Average area taken up by one grafted PGMA molecule on nano-SiO_2 surface. G_n: Number of grafted PGMA chains per gram of nano-SiO_2. G_d: Number of grafted PGMA chains attached to one silica particle.

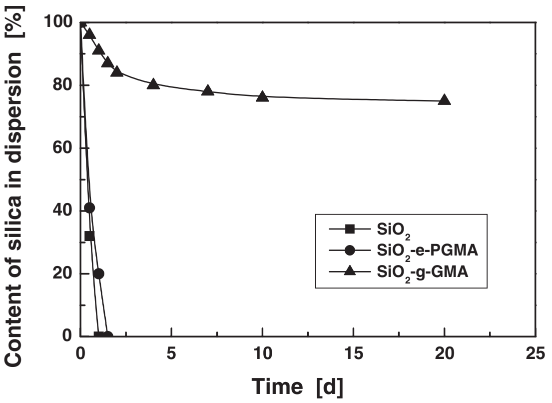

Figure 10. Stability of dispersion of untreated and treated nano-SiO_2 in acetone at room temperature.

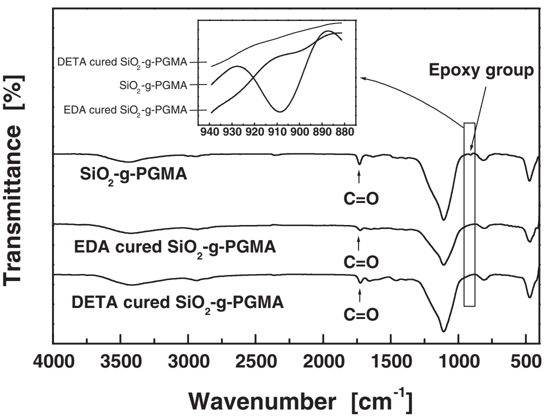

Figure 11. FT IR spectra of SiO_2-g-PGMA and its cured versions.

It is interesting to note that the molecular weights of PGMA homopolymer increases with γ_g. In fact, the monomer concentration, which was used to control percent grafting, was rather high to yield high γ_g value (Figure 2). It means that the degree of polymerization (*i.e.* kinetic chain length) for the homopolymerization increases with increasing polymerization rate and monomer concentration, which follows the same law as general radical polymerization. Besides, both grafted and homopolymerized PGMA exhibit quite narrow molecular distribution, probably due to the fact that chain transfer was not severe in the systems. Therefore, percentage grafting might exert more significant influence on interfacial interaction in the subsequent composites.

The stability of the dispersion of PGMA-grafted silica in acetone, which is a good solvent for PGMA, was compared with that of PGMA encapsulated silica and untreated silica, respectively (Figure 10). The untreated silica particles cannot give a stable dispersion in the solvent and the particles completely precipitated within 1 d. The physical adsorption of PGMA onto the nano-silica particles can scarcely improve the dispersibility in spite of the fact the suspension was stirred by sonication. In contrast, PGMA grafted nano-silica exhibits a good dispersion in acetone. About 70% of the treated particles remain in the suspension even after 20 d. This can be ascribed to that the grafted PGMA chains on the nanoparticles surface interfere with the agglomeration of the particles.

Reactivity of SiO_2-g-PGMA in Polymers

Since the present work aims at inducing 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 reactivity of the epoxide groups of glycidyl methacrylate is still kept when PGMA was grafted onto nano-silica. Accordingly, SiO_2-g-PGMA was treated with excessive amine components, *i.e.* ethylene diamine (EDA) and diethylene triamine (DETA), at room temperature for 16 h, rinsed thoroughly with absolute ethanol to remove the physically adsorbed EDA and DETA, and then dried at 100 °C under vacuum. Figure 11 gives the FT IR spectra of SiO_2-g-PGMA before and after the amine treatment. In comparison with the original SiO_2-g-PGMA, the absorption band at $910\,cm^{-1}$ representing the epoxide groups has disappeared after curing by EDA and DETA, suggesting that the reactivity of epoxide groups in the SiO_2-g-PGMA remains.

In order to quantitatively check the reactivity of the epoxide groups, reactivity kinetics of SiO_2-g-PGMA cured with DDS was studied by DSC analysis using various heating rates. Figure 12 shows the typical thermograms, from which one might collect the maximum exothermic temperature, T_p, and the overall exothermic heat, ΔH. As exhibited in Table III, T_p of all the materials increases with a rise in heating rate, while the addition of PP or PS into SiO_2-g-PGMA/DDS has slightly increased T_p. On the other

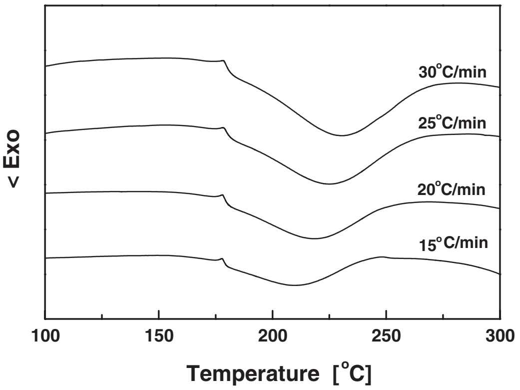

Figure 12. DSC thermograms of SiO_2-g-PGMA/DDS recorded at various heating rates.

Table III. DSC characterization of the curing reactions in different model composites

Model composites	Φ (°C/min)	T_p (°C)	ΔH (J/g)
SiO_2-g-PGMA/DDS	15	208.55	74.02
	20	217.64	75.02
	25	224.18	40.90
	30	228.98	50.82
SiO_2-g-PGMA/DDS/PP	15	212.27	38.69
	20	220.31	16.15
	25	227.96	18.71
	30	233.26	15.85
SiO_2-g-PGMA/DDS/PS	15	212.41	56.52
	20	218.31	59.46
	25	223.65	65.10
	30	230.45	58.70

Φ: Heating rate. T_p: Peak exothermic temperature. ΔH: Overall exothermic heat.

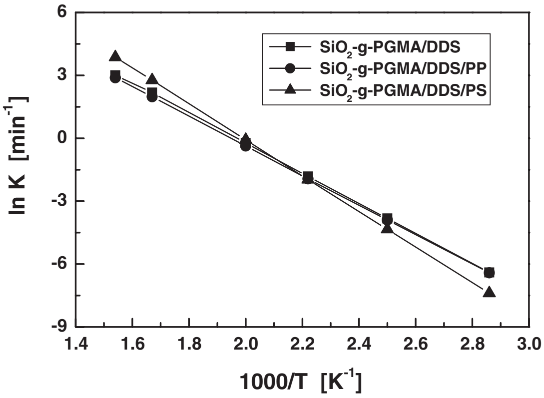

Figure 13. Temperature dependences of rate constant of different model composites.

hand, the values of ΔH change greatly with the heating rates and the incorporation of PP and PS. In general, higher T_p and lower ΔH are observed at a faster heating rate due to diffusion of the reactive components, while this effect is obscured in the systems containing PP and PS. It is noted that the reduction in ΔH is more evident for SiO_2-g-PGMA/DDS/PP than SiO_2-g-PGMA/DDS/PS. This might be related to the melting of PP crystallites during the DSC measurements. The endothermic processes of PP melting should affect the exothermic process of the curing reaction if the two processes take place at similar temperatures. Nevertheless, T_p should not be influence by the melting of PP as it is far away from the melting point of PP (~160 °C).

By applying the well-known Kissinger,[17] Crane[18] and Arrhenius equations to the DSC data, the characteristic parameters of the curing kinetics were yielded (Table IV). The appearance of PP and PS in the model composite systems does not alter the overall reaction mechanism, as the order of reaction, *n*, keeps nearly unchanged. In addition, the addition of PP does not affect the rest kinetics parameters, except a slight decrease in the pre-exponential factor, *A*. The results manifest that the viscosity of the composites was not changed greatly due to the melting of PP. In contrast, the addition of amorphous PS increases the activation energy, *E*, by 20%, which can be ascribed to an increase in the bulk viscosity of the system.

Figure 13 shows the Arrehenius plots of various composites. The rate constant of SiO_2-g-PGMA/DDS is slightly higher than that of SiO_2-g-PGMA/DDS/PP within the experimental temperature range of 50–380 °C. For SiO_2-g-PGMA/DDS/PS, its rate constant is lower than that of SiO_2-g-PGMA/DDS when temperature is below 200 °C, while the trend is reversed in the case of a temperature higher than 200 °C.

CONCLUSIONS

For inducing reactive compatibilization between nanoparticles and polymer matrix in the subsequent nanocomposites preparation, PGMA was chemically grafted onto the surface of nano-SiO_2 by solution free-radical polymerization. It was found that the grafting percentage and monomer conversion increase linearly with monomer concentration, so that the grafting degree for the nanoparticles can be controlled by changing monomer concentration. The grafting polymerization occurs predominately at the beginning of the reaction.

Due to the chemical bonding between the grafted polymer and the nanoparticles, the thermal stability of the grafted nano-silica became superior to that of PGMA encapsulated nano-SiO_2 and the grafted PGMA itself. Besides, the dispersibility of the treated

Table IV. Kinetics parameters quantifying the curing reactions in different model composites

Model composites	E (kJ/mol)	n	A	K (min^{-1}) 450 K	K (min^{-1}) 570 K
SiO_2-g-PGMA/DDS	59.88	0.88	1.44×10^6	0.162	4.701
SiO_2-g-PGMA/DDS/PP	58.67	0.88	9.30×10^5	0.144	3.903
SiO_2-g-PGMA/DDS/PS	70.94	0.89	2.39×10^7	0.139	7.543

E: Activation energy. n: Order of reaction. A: Pre-exponential factor. K: Rate constant.

particles in solvent was also improved significantly.

Reactivity of the epoxide groups of glycidyl methacrylate remains after the monomers were grafted onto nano-SiO_2 as expected. The presence of PP or PS in SiO_2-g-PGMA/DDS did not change the overall curing reaction mechanism. As a result of the differences in viscosity of PP and PS, the model composites with PP possess nearly the same rate constant as that of SiO_2-g-PGMA/DDS, while the system with PS shows a lower rate constant.

Acknowledgment. The authors are grateful to the support of the Deutsche Forschungsgemeinschaft (DFG FR675/40-4) for the cooperation between the German and Chinese institutes on the topic of nanocomposites. Further thanks are due to the Natural Science Foundation of China (Grant: 50273047), the Key Program of the Science and Technology Department of Guangdong, China (Grants: 2003C50107 and 2004A10702001) and the Program of the Science and Technology Department of Guangzhou, China (Grant: 2004Z3-D2061).

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