Studies on Preparation of PGMA/Al₂O₃ and its Effect on Impact Strength of Epoxy Resin

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ABSTRACT: In this article, two kinds of methods for grafting polyglycidyl methacrylate (PGMA) onto Al_2O_3 surface by the radical polymerization initiated by peroxide groups and double bond groups, respectively, were investigated. In the first method, peroxide groups, as initiators, were immobilized onto the Al_2O_3 surface. Then, GMA was polymerized on Al_2O_3 under the radicals decomposed by peroxide groups, and PGMA was grafted onto Al_2O_3. But in the second method, 3-methacryloyl-propyl trimethoxysilane was chemically bonded onto the Al_2O_3 surfaces firstly to introduce double bonds. Secondly, the copolymerizations between the immobilized double bonds and the monomer GMA were performed, homopolymerizations of GMA followed, and finally PGMA was grafted to the Al_2O_3 surfaces. The effects of grafting methods on grafting degree were examined mainly. At the same time, the effects of different grafting conditions on the grafting degree were researched. Furthermore, the effect of the grafted particles PGMA/Al_2O_3 on impact strength of the epoxy composites was studied. It was found that the grafting degree achieved by the first method was much higher than that by the second, and the grafting degree can reach about 54%. Moreover, the impact strength of epoxy composites containing PGMA/Al_2O_3 particles were improved largely, and which increased with the grafting degree. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 41–48, 2009

Key words: Al_2O_3 composites; graft polymerization; GMA; peroxide groups; toughness

INTRODUCTION

Epoxy resins are very convenient polymer materials because of their good mechanical, thermal, and electrical properties. Recently, many researchers have focused on improving the mechanical properties of epoxy resins using the modified inorganic particles, to make the epoxy resins applied more widely. At present, the inorganic particles filled in epoxy resins are mainly modified with the silane coupling agent, or are wrapped by polymers without any reactive groups,[1–3] but which result in the limited properties improvement of epoxy resins.

In the present work, the alumina particles are used owing to its high hardness, corrosion resistance and strength. Grafting of polyglycidyl-methacrylate (PGMA) on alumina particles are applied to show the effect of grafting pretreatment on enhancing mechanical performance of the composites. PGMA is selected because the active epoxy groups[4–6] might react with epoxy resins during curing and form three-dimensional networks throughout the composites, so that the particles can be connected with the matrix covalently and take effect desirably. Besides, if only PGMA is grafted onto the inorganic particles, a lot of new characteristics will be given, such as amphiphilic property, biological activity, dispersibility, chelating property and compatibility with organic substance, etc.[7–10] Therefore, to obtain the polyglycidyl-methacrylate(PGMA)/inorganic composite particles which has the higher grafting degree, advantage was taken of covalently attached peroxide groups to initiate the graft polymerization of GMA onto alumina particles. Simultaneously, the effects of various factors on the grafting degree were studied, such as the concentrations of the monomer, polymerizing time and temperature, and so on. Moreover, the effects of the grafted particles PGMA/Al_2O_3 on impact strength of epoxy composites were also researched, and the impact strength was increased largely owing to the PGMA/Al_2O_3 particles which had the higher grafting degree.

EXPERIMENTAL

Materials

Al_2O_3(about 1 μm) was purchased from Ocean Chemical Engineering, Qingdao, China. Thionyl

chloride and *tert*-butyl hydroperoxide were obtained respectively, from FuChen Chemical Reagent, Tientsin and Sinopharm Chemical Reagent, Glycidyl methacrylate (GMA) obtained from Japonic Mitsubishi. was distilled under vacuum before use. Bisphenol-A epoxy resin (type E-39D) and Methyltetrahydrophalic anhydride methpa(MTHPA)as curing agents, was supplied by Wuxi Resin, China. Toluene, DMF, dioxane and all other chemicals were of analytical or chemical purity grades.

Chlorination of hydroxy groups with thionyl chloride

As described by Fery et al.,[11] and confirmed by Wang and Partch the chlorination of hydroxy groups can be achieved using thionyl chloride ($SOCl_2$). Firstly, the Al_2O_3 particles were activated using aqueous solution of methane sulfoacid with a concentration of 5%. The activated Al_2O_3 together with certain amount of $SOCl_2$ and toluene were refluxed for 50 h. Unreacted $SOCl_2$ and solvent were removed by distillation after which the modified Al_2O_3 was dried in vacuum at 100°C. To achieve the higher content of chloride on Al_2O_3 surface, chlorination were performed by using different solvents, including toluene, trichloromethane and benzene.

The chloric groups on Al_2O_3 surface were quantified as follows: 0.2 g of Al_2O_3, 0.01 g of sodium bicarbonate and 25 mL of desionized water were introduced in an Erlenmeyer. Then hydrogen chloride formed by the hydrolysis of chloric groups was titrated with 0.1 mol/L of silver nitrate solution using potassium chromate solution as indicator.[12]

Introduction of peroxide groups onto the Al_2O_3 surface

The introduced chloric groups were reacted with *tert*-butyl hydroperoxide (TBHP) to covalently bond peroxide groups onto the Al_2O_3 surface. Sodium bicarbonate was added to neutralize generated HCl. In the case of the $SOCl_2$ modified Al_2O_3, a slurry of 1 g of these phases in 30 mL of dioxane was mixed with 5 mL of TBHP and 0.10 g of sodium bicarbonate, and the reaction mixture was stirred under dry nitrogen at 20°C in the dark. The reaction was stopped after 12 h and the modified Al_2O_3 was washed with methanol repeatedly and dried overnight in vacuum at room temperature.

The peroxide groups on Al_2O_3 surface were determined as follows: 0.2 g of Al_2O_3 modified with peroxide groups, 10.0 mL of acetic anhydride, and 0.5 g of potassium iodide was added into an Erlenmeyer flask, and the mixture was stirred for 20 min. Then isolated iodide was titrated with 0.1 mol/L of sodium hyposulfite using starch as an indicator.[13]

The graft polymerization of GMA on peroxide bonded phases

In a further reaction step, covalently bonded peroxide groups on Al_2O_3 surfaces were used as initiators for polymerization of GMA. Peroxide bonded Al_2O_3, solvent DMF and monomer GMA were added into a four-necked flask equipped with a thermometer, a mechanical stirrer and an N_2 inlet, and N_2 was purging for 30 min so as to exclude air. The content of flask was firstly placed in the ultrasonic for 1 h to disperse peroxide bonded Al_2O_3 particles fully, then the reaction was performed at 80°C for 10 h under a dry nitrogen atmosphere. After terminating polymerization, the mixture was filtrated, and the product was extracted with acetone in a soxhlet extractor for 20 h until the epoxy groups were not detected in the extracted solution by titration of perchloric acid using crystal violet as an indicator, so as to remove the polymer only physically absorbed on the Al_2O_3 surfaces. The product was dried under vacuum.

The grafting degree (wt %) of the composite particles PGMA/Al_2O_3 was calculated by mensurating epoxy groups on the Al_2O_3 surfaces.[14] The epoxy groups were titrated with 0.1mol/L of perchloric acid using tetraethylammonium bromide as catalyst and crystal violet as an indicator.

$$\text{The grafting degree}\,(\text{wt\%}) = \frac{V \bullet C \bullet M_{\text{GMA}}}{W}$$

In the formula, V (mL), C (mol/L), W (g), and M_{GMA}, respectively, corresponded to the volume of the used perchloric acid, the concentration of perchloric acid, the quantity of PGMA/Al_2O_3, andthe molecular weight of GMA.

To examine the effects of various factors on grafting degree of PGMA on Al_2O_3, the grafting polymerizations were performed under various conditions, including monomer concentrations (the percentage of the solvent weight, wt %), polymerizing time and temperature.

The graft polymerization of GMA by double bond groups on Al_2O_3 surface

According to Ref. 15, firstly, monolayers of γ-methacryloylpropyl trimethoxysilane (MPS) were chemically bonded onto the Al_2O_3 particles surfaces, so double bond groups were immobilized onto the surfaces. Secondly, GMA was grafted onto the Al_2O_3 surfaces modified with MPS by copolymerization of double bond groups with the GMA.

Composites preparation

Typically, a mixture of epoxy resins(20 g), virgin Al_2O_3 or PGMA/Al_2O_3—the fillers and a little of
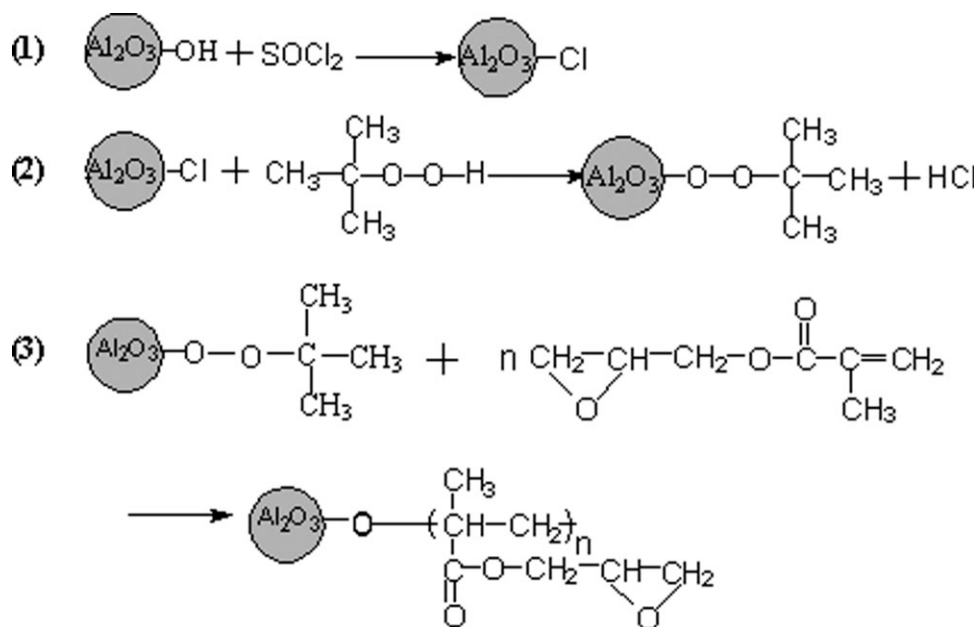
Scheme 1 Reaction process for preparing composite particle PGMA/Al$_2$O$_3$.

acetone was placed in a glass beaker and dispersed with sonication at 30°C for 1 h. The mixture was heated to 60°C for 45 min to remove the acetone completely. Then, the curing agent was added to the beaker slowly for 10 min while being stirred mechanically. The mixture with curing agent was poured into a glass mold and kept in vacuum for 3 h to get rid of air bubbles. After that, for curing the composites, the procedures listed below were followed step by step: 3 h at 50°C, and 4 h at 120°C.

Characterization of the PGMA/Al$_2$O$_3$ particles and composites

The FTIR spectra of Al$_2$O$_3$ and PGMA/Al$_2$O$_3$ were measured on a spectrometer with press piece method. The morphologies of the particles before and after grafting polymer and the impact fracture surfaces of composites containing virgin Al$_2$O$_3$ and PGMA/Al$_2$O$_3$ were observed and compared on a 438VP scanning electron microscope, and typical samples were taken pictures.

The impact strength of the composites according to GB1043 was measured by an XJU-22J impact tester.

RESULTS AND DISCUSSION

Preparation of PGMA/Al$_2$O$_3$

Chlorination of hydroxy groups was achieved by reaction of SOCl$_2$ with the Al$_2$O$_3$. The chloric groups were then treated with TBHP to form immobilized peroxide molecules. In a further reaction step these covalently bonded peroxide groups initiated the graft polymerization of GMA on Al$_2$O$_3$ surfaces, and

finally the composite particles PGMA/Al$_2$O$_3$ were obtained. Scheme 1 shows the reaction process.

Characterization of composite particles PGMA/Al$_2$O$_3$

FTIR spectrum of PGMA/Al$_2$O$_3$

Figure 1 shows the spectra of virgin alumina and polyglycidylmethacrylate-grafted alumina (PGMA/Al$_2$O$_3$) (the grafting degree of GMA of 36%, gained from the first method). After grafting polymerization, the FTIR spectrum of PGMA/Al$_2$O$_3$ shows a sharp peak at 1728 cm^{-1} due to C=O stretching in the GMA. New absorption peaks of the epoxy group and ester group of GMA are observed at 908 and 1257 cm^{-1} respectively.[16] All of these indicate that
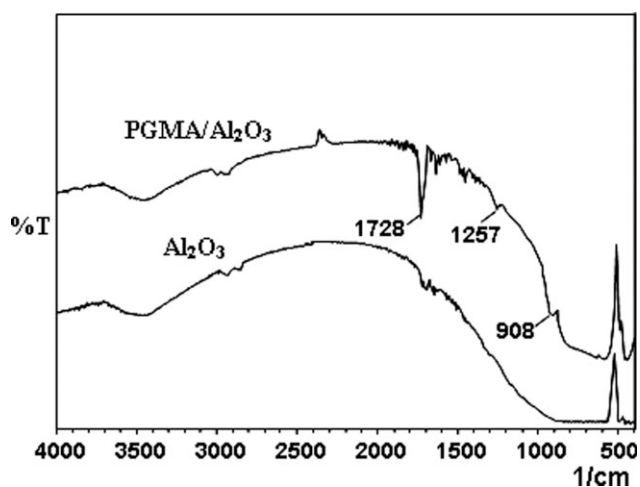

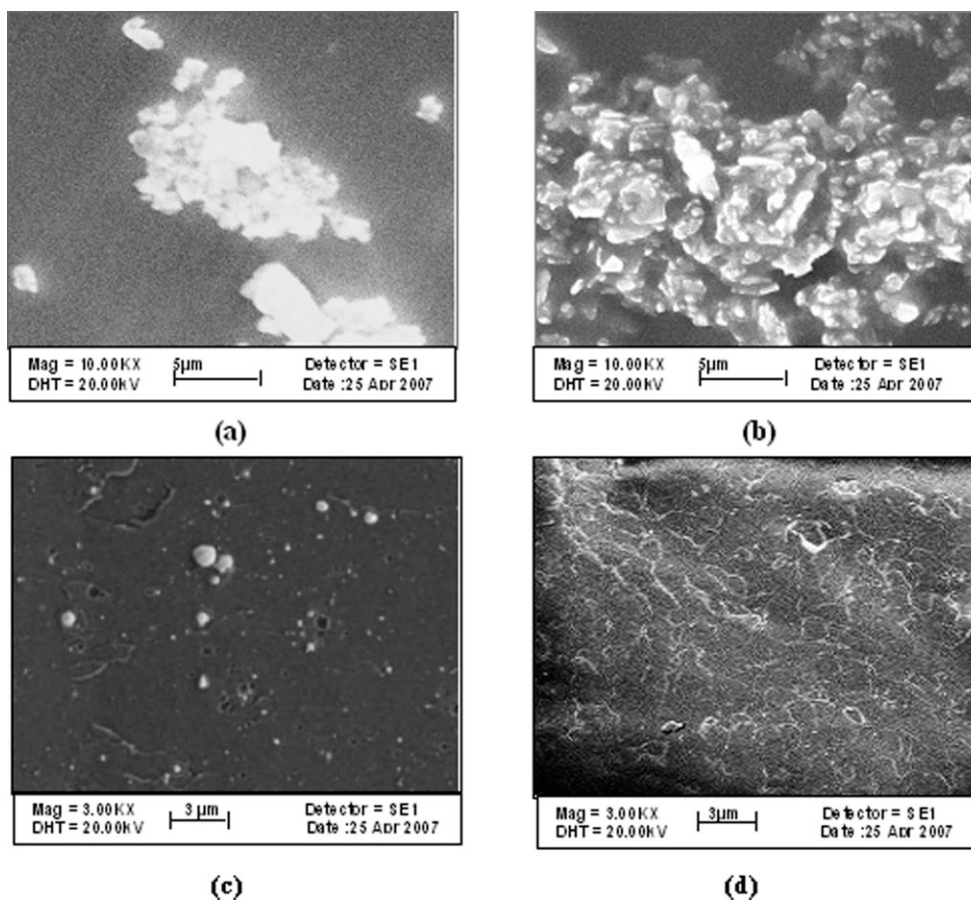**Figure 1** FTIR spectra of Al$_2$O$_3$ and PGMA/Al$_2$O$_3$.

Figure 2 SEM micrographs of Al_2O_3 (a) and PGMA/Al_2O_3 (b), and the impact fracture surfaces of composites containing Al_2O_3 (c), and PGMA/Al_2O_3 (d), respectively.

polyglycidylmethacrylate have been successfully grafted onto the surface of the alumina particles, and the composite particles PGMA/Al_2O_3 have been obtained.

Morphology of PGMA/Al_2O_3 particles

Figure 2(a,b) are the SEM photographs of Al_2O_3 particles and the composite particles (PGMA/Al_2O_3), respectively. It can be found that the sizes of the virgin Al_2O_3 particles [Fig. 2(a)] are much larger than the diameters of the virgin particles given by the company, indicating a serious agglomeration of the particles. After grafting modification, the agglomerates of PGMA/Al_2O_3 seem to be quite fluffy and a number of tiny particles appear in the case of PGMA/Al_2O_3 [Fig. 2(b)]. These imply that grafting PGMA onto the Al_2O_3 surfaces could make the composite particles PGMA/Al_2O_3 dispersed effectively.

Figure 2(c,d) show the typical impact fracture surfaces of epoxy composites containing virgin Al_2O_3 and the grafted particles PGMA/Al_2O_3. The virgin Al_2O_3 particles are severely agglomerated in epoxy composites and even pulled out in several places, thus having little or no interaction with the crack

[Fig. 2(c)], whereas the grafted particles are well separated into tiny aggregates and bond well with the epoxy resin to enhance crack trapping [Fig. 2(d)]. It means that the composites containing the virgin Al_2O_3 particles are provided with heterogeneous microstructure and would exhibit worse reinforcing and toughening effects as compared with those having more homogeneous appearances due to graft pretreatment of the particles. Furthermore, it is also observed that composites with PGMA/Al_2O_3 particles have rougher fracture surfaces, which are indicative of greater resistance to crack propagation, as compared with those with virgin Al_2O_3 particles.

Effect of various factors on grafting process

Effect of monomer concentration

By varying the concentation of monomer and by fixing other conditions, (1) Amount of peroxide and double bond groups on Al_2O_3 surfaces: 0.87 mmol/ g; 2) Temperature: 80 °C; 3) Time: 10 h; 4) Amount of initiator: 0.16 g), the grafting reactions were performed. Figure 3 shows the varying curves of grafting degree with the monomer concentrations achieved by two grafting methods respectively. It
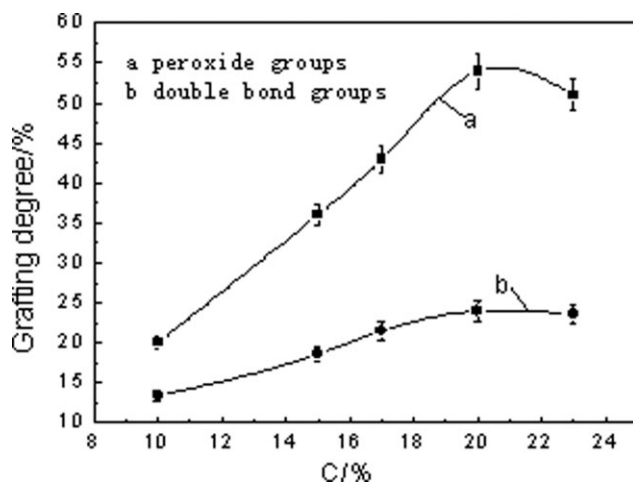
Figure 3 Effect of concentration of monomer ongrafting degree. 1) Amount of peroxide and double bond groups on Al$_2$O$_3$ surfaces: 0.87 mmol/g; 2) Temperature: 80°C; 3) Time: 10 h; and 4) Amount of initiator: 0.16 g.

can be seen clearly from Figure 3: when the concentrations of the monomer are lower, the grafting degree enhances remarkably with the increase of the monomer concentrations; when the concentrations of the monomer go up to a certain value, the grafting degree trends toward decreasing; and the highest grafting degree (54%) achieved by the surface grafting of PGMA onto Al$_2$O$_3$ surface by the radical polymerization initiated by peroxide groups is much higher than that (24%) by double bond groups. The corresponding interpreting for these experiment facts can be given as follows. When the monomer concentrations are lower, the increase of the monomer concentrations will result in obvious acceleration of the grafting reaction, and the increase of the monomer concentrations also is advantageous to forming the grafting polymer with high molecular weight, and so in the same period of time (10 h), the higher the monomer concentration, the greater the grafting degree is. But as the concentration of the monomer exceeds 20%, further increase in the concentration of the monomer will result in a too fast rate of grafting reaction, and will lead to rapid formation of the dense overlapping and enwinding polymer layer, so that the grafting degrees trend to decrease in the same period of time.

It still can be seen from Figure 3 that under the same reaction conditions, the grafting degree in the radical polymerization initiated by peroxide groups is much higher than that by double bond groups, and this should be attributed to the special mechanism of the radical polymerization initiated by peroxide groups. During the grafting polymerization, the primary free radicals on the Al$_2$O$_3$ surface for the first method are more than that for the second method, so the probability of the surface grafting of

GMA onto Al$_2$O$_3$ surface by the radical polymerization initiated by peroxide groups is much higher than that by double bond groups. Besides, the hindrance for grafting reaction is not only from the overlapping and entwisting polymer layer grafted onto the Al$_2$O$_3$ surfaces, but also from the polymers physically absorbed into the layer. But in the second graft polymerization system, the macromolecules (homo-PGMA) with longer chains independent of Al$_2$O$_3$ particles because of all of the primary free radicals fully dissolved in the solvent, are more adsorbed into the overlapping polymer layer on the Al$_2$O$_3$ surface than that in the first graft polymerization system(only half of the primary free radicals dissolved in the solvent), so that in the first graft polymerization systems, the kinetic hindrance caused by the physical adsorption is much weaker than that in the second graft polymerization systems. Besides, in the second graft polymerization system, the increasing viscosity of the reaction medium caused by the macromolecular dissolving is larger than that in the first graft polymerization system, and this caused the larger difficulty for the monomers to diffuse toward the Al$_2$O$_3$ surface.

Based on the above description, the following viewpoint or conclusion is put forward: the polymer chains formed by the free radicals decomposed by peroxide groups on the Al$_2$O$_3$ surface are more than that by double bond groups, and the kinetic hindrance for grafting polymerization onto solid surfaces in the first graft polymerization system is weaker than that in the second graft polymerization system, and so the rate of the grafting reaction in the first graft polymerization system is faster than that in the second graft polymerization system and the former has higher grafting degree than the latter under the same reaction conditions.
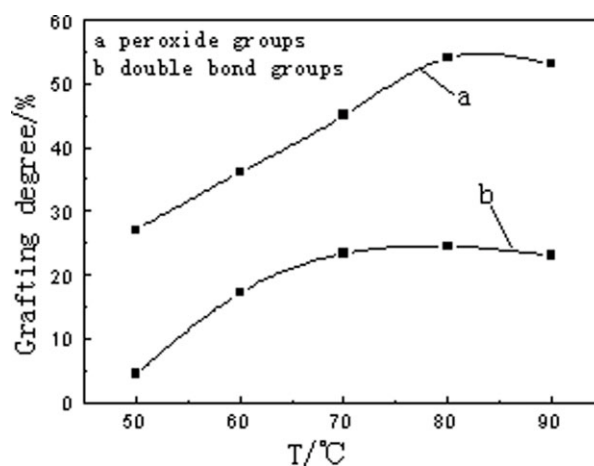

Figure 4 Effect of temperature on grafting degree. 1) Amount of peroxide and double bond groups on Al$_2$O$_3$ surfaces: 0.87mmol/g; 2) Concentration of monomer: 20%; 3) Time: 10 h; and 4) Amount of initiator: 0.16 g.
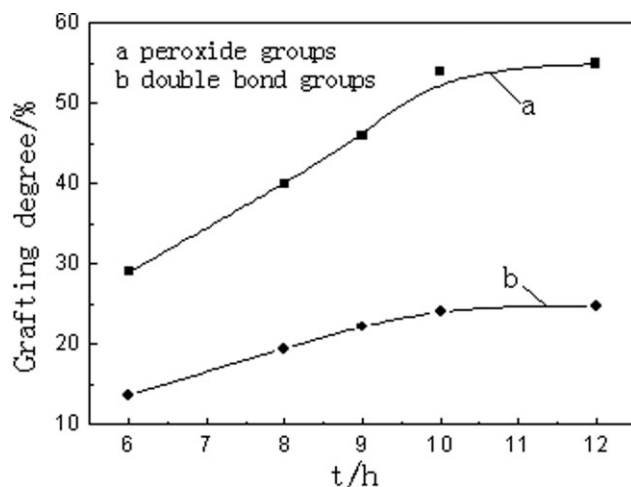
Figure 5 Varying of grafting degree with reaction time. 1) Amount of peroxide and double bond groups on Al$_2$O$_3$ surfaces: 0.87 mmol/g; 2) Temperature: 80°C; 3) Concentration of monomer: 20%; and 4) Amount of initiator: 0.16 g.

Effect of temperature

Fixed other reaction conditions are: (1) Amount of peroxide and double bond groups on Al$_2$O$_3$ surfaces: 0.87 mmol/g; 2) Concentration of monomer: 20%; 3) Time: 10 h; 4) Amount of initiator: 0.16 g), the grafting reactions were performed with different temperature. Figure 4 displays the varying curves of grafting degree with the reaction temperature in the two kinds of grafting polymerization systems respectively. It is indicated clearly that at the beginning, the grafting degree increases rapidly with the rising of the temperature because of the fast grafting reaction caused by the acceleration of the decomposing reaction of the initiator. When the temperatures are over a certain value (80°C in the radical polymerization initiated by peroxide groups and 70°C in that by double bond groups), further rising of the temperature leads to the decrease of the grafting degree. The reason for this is the grafting reaction occurs too rapidly, so that in a very short time the dense overlapping and enwinding polymer layer will form on the Al$_2$O$_3$ surface. In addition, as the temperatures are too high, the chain transfer reaction to the monomers and the macromolecules in solution will speed up, leading to chain rupture of the grafted polymer, and these are all disadvantageous to the increase of grafting degree. Analogously, in Figure 4, it is also shown that at the same temperature and in the same period of time, the grafting degree for the radical polymerization initiated by peroxide groups is much higher than that by double bond groups because of the greater probability of graft polymerization on Al$_2$O$_3$ surface in the former system.

Effect of time

Fixed other reaction conditions are: (1) Amount of peroxide and double bond groups on Al$_2$O$_3$ surfaces:

0.87 mmol/g; 2) Temperature: 80 °C; 3) Concentration of monomer: 20% 4) Amount of initiator: 0.16 g), the grafting reactions were performed. Figure 5 shows the varying curves of the grafting degree with reaction time by adopting two kinds of methods of grafting polymerization, using different initiating types respectively. First, it is seen that whatever anyone of the two methods is adopted, at the initial stage of polymerization the grafting degree increases with time; when the polymerizations are performed to about 10 h, the grafting degrees no longer change with time; and under the same reaction conditions, the grafting degree in the radical polymerization initiated by peroxide groups is much higher than that by double bond groups, which should be attributed to the following reasons. Though anyone of two methods is taken, the grafting reaction may be separated into two steps. At first, growing chains or monomer molecules have to diffuse to the Al$_2$O$_3$ surface to react with the radical decomposed by the peroxide groups and the double bond groups. After this, the new attached chain continues to grow by adding further monomer molecules, and grafted polymer is formed. On the beginning, the monomers continue to be polymerized at the active sites on Al$_2$O$_3$ surface, so the grafting degree increases. However, a kinetic barrier will be built up as soon as the density of the attached macromolecules reaches a value at which the polymer coils start to overlap. The mechanism of kinetic barrier formation by grafted polymer is shown in Figure 6. Further molecules of monomers or growing chains that will be attached to the surface have to diffuse through this layer, and the diffusion process becomes more and more unfavorable, which will result in the following actions: firstly, the primary
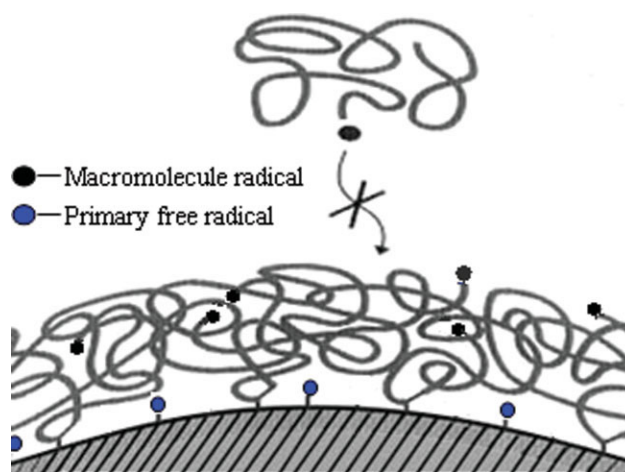

Figure 6 Schematic representation of the kinetic barrier attached polymers for polymer radicals to reach the immobilized peroxide groups. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
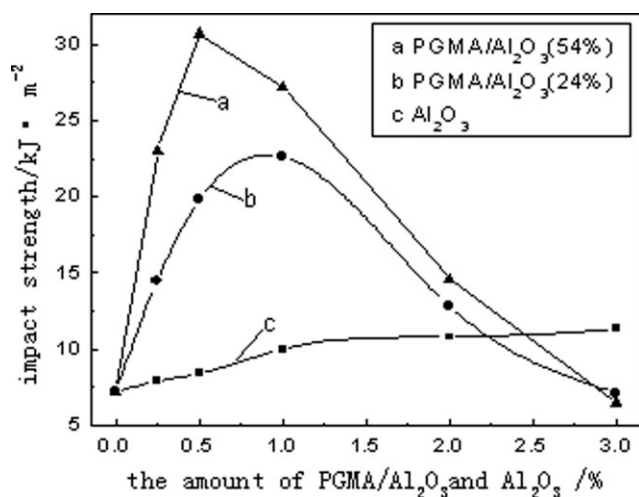
Figure 7 Varying of the impact strength of composites with the additive amount of PGMA/Al$_2$O$_3$ and Al$_2$O$_3$.

free radicals on Al$_2$O$_3$ surfaces, a little of which still exist on Al$_2$O$_3$ surfaces at 80°C after 10 h (the half-life of the *tert*-butyl hydroperoxide is 10 h at 164°C),[17] would not produce the new polymer chains; secondly, the polymer chains couldn't grow at all; finally, the grafting degree becomes constant at the middle and last stages of the polymerization reaction. Besides, according to the conclusion educed in Effect of Monomer Concentration section that the primary free radicals on the Al$_2$O$_3$ surface in the radical polymerization initiated by peroxide groups are more than that by double bond groups, and the rate of the grafting reaction in the first graft polymerization system is faster than that in the second graft polymerization system, so the former has higher grafting degree than the latter under the same reaction conditions.

Effect of the PGMA/Al$_2$O$_3$ on toughness of epoxy composites

Figure 7 gives the varying curves of the impact strength of composites with the quantity of poly-GMA-grafted Al$_2$O$_3$ and virgin Al$_2$O$_3$ particles. It can be observed that the impact strength of composites increases distinctly with the additive amount of Al$_2$O$_3$ particles, at the same time, the higher the grafting degree of the PGMA/Al$_2$O$_3$, the larger the impact strength of composites is.

According to the relational research, for the composites of polymer/inorganic particles, the impact strength of them refers to two factors: the dispersing effect and the absorbency of polymer on the impact energy. To this research, the virgin Al$_2$O$_3$ is very different from epoxy resin on chemical structure and physical modality, which may lead to a friable structure in composites and can hardly provide properties improvement at all as a result of disintegration and crumbling of the particle agglomerates under impactive conditions. However, grafted particles PGMA/Al$_2$O$_3$ are uniformly dispersed in resin because of an increased hydrophobicity resulting from the grafting polymers, and thus the specific characteristics of inorganic particles are utilized more effectively. But significantly the PGMA on the Al$_2$O$_3$ surface could react with the epoxy resin under the curing agents to form steady and three-dimensional networks throughout the composites (Fig. 8), which could transfer and separate the stress better. Besides, with the higher grafting degree of PGMA/Al$_2$O$_3$, the affinity and dispersion of PGMA/Al$_2$O$_3$ particles in resin are better, PGMA/Al$_2$O$_3$ particles in three-dimensional networks are more and will have stronger adsorption against energy, so the
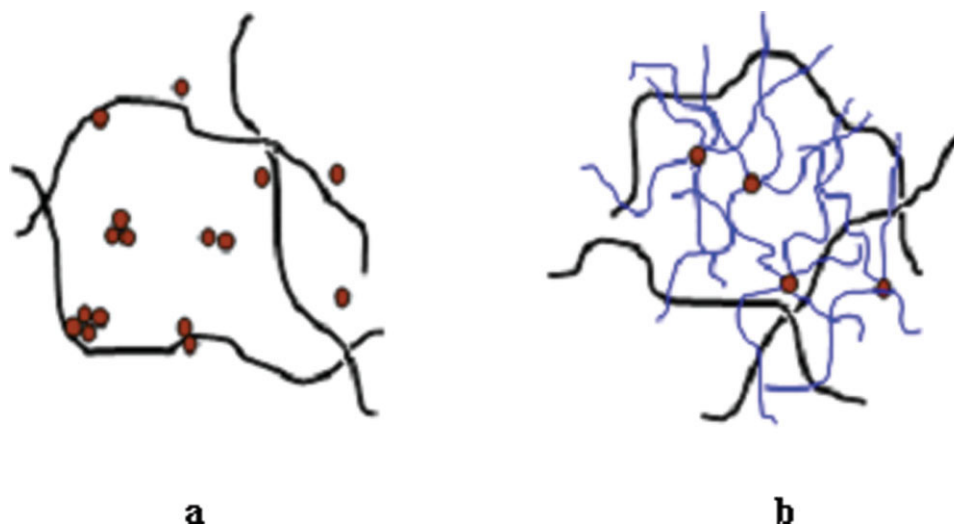

Figure 8 Schematic representation of the structures of composites containing (a)Al$_2$O$_3$ and (b) PGMA/Al$_2$O$_3$, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

impact strength of the composites will be heightened more remarkably.

CONCLUSIONS

In this article, the grafted particles PGMA/Al$_2$O$_3$, which had the higher grafting degree, was prepared successfully by the surface grafting of polyglycidyl methacrylate (PGMA) onto Al$_2$O$_3$ surface by the radical polymerization initiated by peroxide groups, i.e., by modification of alumina with SOCl$_2$, followed by TBHP, then grafting PGMA in their presence. And about the effects of other factors on the grafting degree, such as concentrations of the monomer, polymerization temperature and time, all of them have the positive influence on the grafting degree only to a certain extent because of the forming of the kinetic barrier. Moreover, the impact strength of epoxy composites containing the grafted particles PGMA/Al$_2$O$_3$ compared with that containing the virgin Al$_2$O$_3$ particles, was improved largely, and the higher the grafting degree of the PGMA/Al$_2$O$_3$, the larger the impact strength of composites is.

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