Surface-Modified Silica Nanoparticles for Reinforcement of PMMA

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ABSTRACT: Polymethyl methacrylate (PMMA) was introduced onto the surface of silica nanoparticles by particle pretreatment using silane coupling agent (γ-methacryloxypropyl trimethoxy silane, KH570) followed by solution polymerization. The modified silica nanoparticles were characterized by Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Sedimentation tests and lipophilic degree (LD) measurements were also performed to observe the compatibility between the modified silica nanoparticles and organic solvents. Thereafter, the PMMA slices reinforced by silica-nanoparticle were prepared by *in situ* bulk polymerization using modified silica nanoparticles accompanied with an initiator. The resultant polymers were characterized by UV–vis, Sclerometer, differential scanning calorimetry (DSC). The mechanical properties of the hybrid materials were measured. The results showed that the glass transition temperature, surface hardness, flexural strength as well as impact strength of the silica-nanoparticle reinforced PMMA slices were improved. Moreover, the tensile properties of PMMA films doped with silica nanoparticles via solution blending were enhanced. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2176–2184, 2007

Key words: nanoparticles; surface modification; nanocomposite; mechanical property

INTRODUCTION

In recent years, the synthesis, modification, and application of nanosized materials have attracted much attention.[1–33] Surface modification techniques for preventing nanoparticles[1] from aggregation become increasingly important in the applications of nanoparticles.[2–4] As a functional-filling material, nanosized silica is widely used in many fields.[5–8] However, the specific surface area of nanoparticles is enormous, the surface energy of particle is high, and the chemical properties of particle surface are very active, nanoparticles are prone to aggregation. Moreover, the surface of bare silica nanoparticles is hydrophilic, while the polymer matrix is hydrophobic. As a result, the coupling between nanosized silica and polymer matrix is not strong when these nanoparticles are employed as fillers. Above all, it is necessary to modify the surface of silica nanoparticles.[9]

Published work in reference revealed some surface modification methods for nanoparticles, such as physical coating using detergents[10] or chemical coating using coupling agents.[11,12] The surface chemical reactions can be classified as surface grafting[13,14] or esterification,[15,16] wherein, surface grafting reaction becomes the hot topic because the resultant nanoparticles showed strong covalent bond between particle surface and polymer matrix, and are well-consistent with organic medium.

Composite polymers with high performance are used increasingly in various demanding conditions. The polymer must withstand high mechanical loads, and is usually reinforced with fillers. The fillers, which have dimensions in micrometers or even in nano-

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meters, though generally strengthen the polymers, sometimes might have detrimental effects on material properties, for example, the polymer's resistance against impact.[17] To overcome the basic problem, a new approach is to use nanosized fillers.[18–20] P. Rosso et al.[21] added 5 vol % of silica nanoparticles into an Araldite-F epoxy and found that the addition of silica-nanoparticles could improve both the stiffness and the toughness of epoxy resin. Mulhaupt et al.[22] pointed out that the application of nanosized fillers demonstrated the potential to improve the general performance of thermosetting and thermoplastic polymers fundamentally. It has been shown that considerable improvement of mechanical properties can be achieved at very low volume content of nanosized filler, in the range of 1–5 vol %.[23–27] This is very important because of the high cost of nanosized fillers.

However, the unique effects of nanocomposites can be effective only when the nanoparticles are well dispersed in the surrounding polymer matrix. By modifying silica nanoparticles with stearic acid and dispersing the nanoparticles into PEN using solution blending, Kim and Lee[28] found that the nanoparticle-reinforced PEN exhibited higher tensile modulus comparing with that using unmodified silica. Yang and Nelson[9] successfully prepared PMMA/silica nanocomposites by solution polymerization, and found that the nanoparticle-doped materials exhibited better mechanical properties when the nanoparticles size decreased or the nanoparticles surface was modified. Karayannidis and coworkers[29] prepared isotactic polypropylene/silica nanocomposites by melt blending. The silica nanoparticles were first treated with dimethyldichlorosilane so that silica nanoparticles could be more compatible with iPP polymer matrix. Rong et al.[30] presented experimental results for epoxy/TiO_2 nanocomposites, indicating that the wear performance significantly depends on the dispersion state. The compatibility between nanoparticles and polymer matrix must be considered as a very important factor to obtain polymeric materials with the desirable properties.

In the present investigation, nanosized silica was first pretreated with silane coupling agent (KH570) and then introduced polymer chains onto the particle surface. The results showed that the surface of silica nanoparticles have been successfully covered by poly-methyl methacrylate (PMMA) chains. To study the influence of nanoparticles on the performance of PMMA slices, the bare and modified silica nanoparticles were dispersed in methyl methacrylate (MMA) respectively, followed by bulk polymerization. Afterwards, the resultant polymers were characterized to see the difference in mechanical properties. And also, the tensile properties of PMMA films reinforced by silica nanoparticles via solution blending were investigated.

EXPERIMENTAL

Materials

Surface-unmodified silica nanoparticles (M-5) was obtained from Deutschland Cabot. MMA of chemical grade (at a purity of 99.9%) was distilled under reduced pressure prior to use. Azo-bisisobutyronitrile (AIBN) was used as an initiator, which was recrystallized in ethanol. The $(CH_3O)_3SiCH_2CH_2CH_2O$-$C(O)C(CH_3)=CH_2$ (γ-methacryloxypropyl trimethoxy silane, KH570) was employed to introduce the reactive double bonds onto the surface of silica nanoparticles. The PMMA, which was used to prepare thin films, was obtained from Anli Chemical Works, Suzhou, China. Ethanol, methanol, acetone, tetrahydrofuran (THF), dimethylbenzene and other materials were all analytical grade.

Surface modification of silica nanoparticles

Silica nanoparticles were dispersed in dimethylbenzene in a flask by ultrasonic vibration for 1 h. Then certain amount of coupling agent (KH570) was added. The reaction was carried out at 80°C under the atmosphere of Ar for 3 h. When the system was cooled, the suspension of KH570 grafted nanoparticles in dimethylbenzene was available.

The KH570 grafted nanoparticles in the above suspension were separated by high-speed centrifugation, and washed with ethanol several times, then dried in vacuum for 12 h at room temperature. Thus, the reactive double bonds were introduced onto the silica nanoparticles, and the resultant sample is called KH570-grafted silica nanoparticles.

Some initiator (AIBN, 0.1% weight of monomer) was added into the above suspension, then MMA was added into the suspension dropwise using a tundish. After being kept at 80°C under Ar protection for 3 h, the suspension was cooled, the precipitate was washed by acetone several times and then dried in vacuum for 12 h at room temperature. The resultant sample is called PMMA-grafted silica nanoparticles.

Preparation of silica-reinforced PMMA

Preparation of PMMA slices

The typical procedure for preparing PMMA slices was described as follows: (1) Prepolymerization: Some silica nanoparticles (2 wt % of monomer) if necessary were dispersed into MMA monomer under ultrasonic vibration for 2 h, then the initiator (AIBN, 0.1% of monomer) was added. The polymerization reaction was performed at (80 ± 2)°C under magnetic stirring for about 20 min. until the MMA conversion was

about 12%–15%. The suspension with satisfactory viscosity should be cooled down quickly before the gel-point. (2) Mold preparation: The molds with parallel plats made of stainless steel were washed and dried carefully, and then was coated with a thin film of stearic acid. (3) Mold filling: Some more initiator was added into the prepolymer. The suspension was poured into the molds. The aperture at the top of the mold should be wrapped with a plastic foil, although there is still a small hole in the foil. (4) Low-temperature solidification: The suspension of MMA and silica nanoparticles was kept at 40°C for 24 h, and the solidification process took place. (5) High-temperature treatment: The temperature was adjusted to 100°C and kept for 1 h to increase the molecular weight. Then the molds with PMMA slices were cooled to room temperature. Finally, different kinds of PMMA slices were obtained by disassembling the molds.

For the samples used in the UV–vis measurements, similar procedures were used as listed above except that the glass molds were adopted instead of the stainless steel ones.

Preparation of PMMA films

The PMMA films reinforced by silica nanoparticles were obtained as following: PMMA was first dissolved in tetrahydrofuran (THF) at room temperature and an appropriate amount (2 wt % of the PMMA) of respective silica nanoparticles was added into the solution and dispersed using a high-performance ball mill operating at 40 rpm for 2 h. Finally the suspension was spread onto a glass plate using a wet film applicator (SZQ-100, XD Env. Eng. Tech., Shanghai, China). The wet film applicator was driven by an automatic film dauber (AFA-II, XD Env. Eng. Tech, Shanghai, China) to improve the precision of film thickness. Afterwards, the wet films were left for drying at room temperature for 1 day. Finally, the dried films were taken off from the glass plates and different PMMA films were prepared. The thickness of the dried films measured using a thickness gauge (No. 7327, Mitutoyo Corp., Japan) is about 15 μm.

Characterization

Particle characterization

Fourier-transform infrared spectroscopy (FTIR) was performed using Avatar 360 (Nicolet, USA) with KBr method. The size and shape of nanoparticles were determined using a transmission electron microscope (TEM, H-600-II, Hitachi, Japan). The UV–vis absorption of different kinds of PMMA slices was measured using a U-2810 spectrophotometer (Hitachi, Japan). The glass transition temperature (T_g) was obtained

using a differential scanning calorimetry (DSC, DSC2010, TA, America).

Sedimentation test

To investigate the modification effect on silica nanoparticles, sedimentation tests were performed in the following way: some modified silica nanoparticles were dispersed in 25 mL acetone by ultrasonic vibration for 2 h, and then introduced into a test tube (25 mL) with a scale and a cover. The suspension was kept at quiescent state for 7 days. First, the total height of suspension (H) was determined. Then the sedimentation height (h) of the nanoparticles was recorded every day. The sedimentation rate of nanoparticles was calculated using the following expression:

$$R = \frac{H - h}{t}$$

where t is the sedimentation time.

### Measurement of lipophilic degree

The dispersibility of silica nanoparticles in organic solvents can be evaluated in some extent by the so-called lipophilic degree (LD) measurement. The hydrophilic and hydrophobic characteristics of the modified nanoparticles can be obtained. The LD of nanoparticles was characterized by dispersing the nanoparticles of 0.5 g in 50 mL water with the addition of organic solvent (methanol). When silica nanoparticles were put into distilled water, the unmodified silica nanoparticles precipitated in water, while the modified silica nanoparticles which grafted with KH570 or PMMA chains, floated on the water surface. When methanol was dropped into the water slowly and continually with stirring, the modified silica nanoparticles were wetted and hence precipitated gradually. The volume of the methanol (V) used was recorded and the LD was calculated according to the following equation[2]:

$$\text{LD} = \frac{V}{V + 50} \times 100\%$$

Mechanical properties of PMMA slices

PMMA, being used as a polymeric engineering material, should possess necessary mechanical properties. Therefore, several tests were conducted to obtain an overview about the mechanical performance of the silica-reinforced PMMA.

Hardness test was conducted according to the China National Standards GB/T 1039-79 using a plastic hardness tester (LX-D, Qianzhou testing Instruments Co., Wuxi, China) at room temperature.
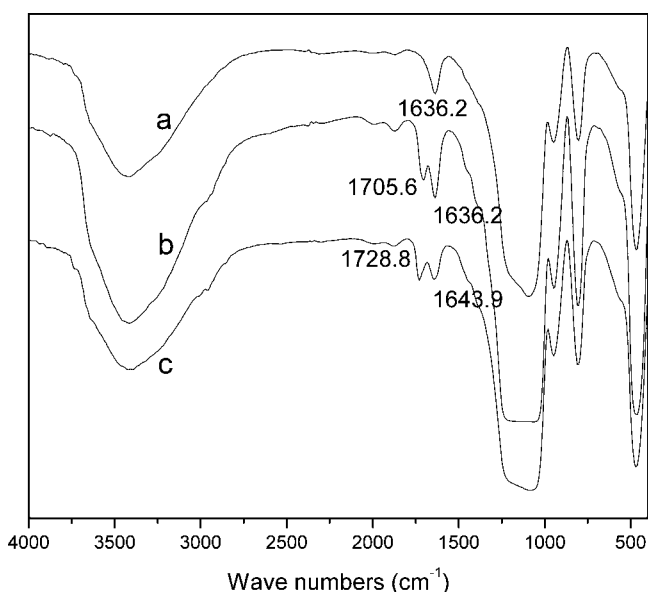
Figure 1 FTIR spectra of silica before and after modification. (a) bare SiO_2, (b) KH570-grafted SiO_2, (c) PMMA-grafted SiO_2.

Measurements were performed 5 times for each sample, and the mean value was calculated.

To obtain the impact strength of different kinds of PMMA slices, an Izod impact machine tester with digital display (JBL-22, Shenzhen KQL Testing Instruments Co.) was used according to the China National Standards, GB/T 1843-1996.[34] Unnotched specimens with rectangular dimensions of $80 \times 10 \times 4$ mm^3 were fractured by the impact energy of 5.5 J with an impact speed of 3.5 m/s at room temperature. The distance between the impact point and fixed point was set to 22 mm.

Flexural tests for PMMA slices were performed according to the China National Standards, GB/T 9341-2000[35] using a universal testing machine (WDT20, Shenzhen KQL Testing Instruments Co.) in a three-point bending configuration at room temperature. A PC was connected to the testing machine, and the crosshead speed was set to be 2 mm/min. The force transducer with a precision of $\pm 0.02‰$ was made by Transcell Tech. (USA).

The tensile experiments of PMMA films were carried out according to the China National Standards, GB/T 14,452-93 using the above universal testing machine at room temperature.

The GB standards were established according to the ISO ones.

RESULTS AND DISCUSSION

FTIR spectra

Three FTIR spectra of different kinds of silica nanoparticles are shown in Figure 1. It can be found that

there is an adsorption peak around 1640 cm^{-1} for the three spectra, which is assigned to the bending mode of physically absorbed water molecules. For the spectrum of the silica modified with KH570 in Figure 1 (spectrum b), the adsorption peak at 1705.6 cm^{-1} is due to the C=O functional groups, which is not found in the spectrum of the unmodified silica (spectrum a). The reason is that the C=O functional groups in KH570 have a hydrogen bonding with surface hydroxyl groups of silica, so the adsorption peak transfers to 1705.6 cm^{-1} from 1728.8 cm^{-1}.[36] Therefore, the surface modification is performed via chemical reaction between KH570 and silica. In spectrum c, the adsorption peak at 1728.8 cm^{-1} is assigned to the C=O functional groups in PMMA which have been fixed on the surface of silica nanoparticles by solution polymerization. The fact confirmed that there existed strong chemical bonds between PMMA chains and silica, and polymer chains had been successfully grafted on the surface of silica nanoparticles.

Transmission electron microscopy

The transmission electron microscopy (TEM) photographs of unmodified and modified silica nanoparticles are shown in Figure 2. From Figure 2(a), we can see that the particle size of unmodified nanoparticles is about 5–30 nm, and some nanoparticles aggregated due to the large specific surface area and high surface energy. After modification with KH570, nanoparticles were prevented from aggregation, and also the surface property of nanoparticles change from hydrophilic to hydrophobic. So the size of aggregates in Figure 2(b) gets smaller compared with that in Figure 2(a). On the other hand, the surface of silica has been modified with KH570, the grafting percentage is not very high, and there are some un-reacted hydroxyls on the surface of silica, and still exist a few aggregates. Therefore, it might be necessary to modify silica nanoparticles further by MMA. By compared Figure 2(c) with Figure 2(a,b), we can see that the size of silica nanoparticles is the smallest after modified with MMA. The edge of the particles is not very clearly. That is because the surface of modified nanoparticles was wrapped with polymer chains, which linked neighboring nanoparticles together. It is considered that the structure and surface characteristic of the nanoparticles have been changed.

Thermogravimetric analysis

The thermogravimetric (TG) curves of silica nanoparticles modified by various quantity of MMA were shown in Figure 3. It can be found from the curves that there existed an obvious weight loss around 400°C. That is evident that the polymer chains had been grafted on the surface of silica nanoparticles. The
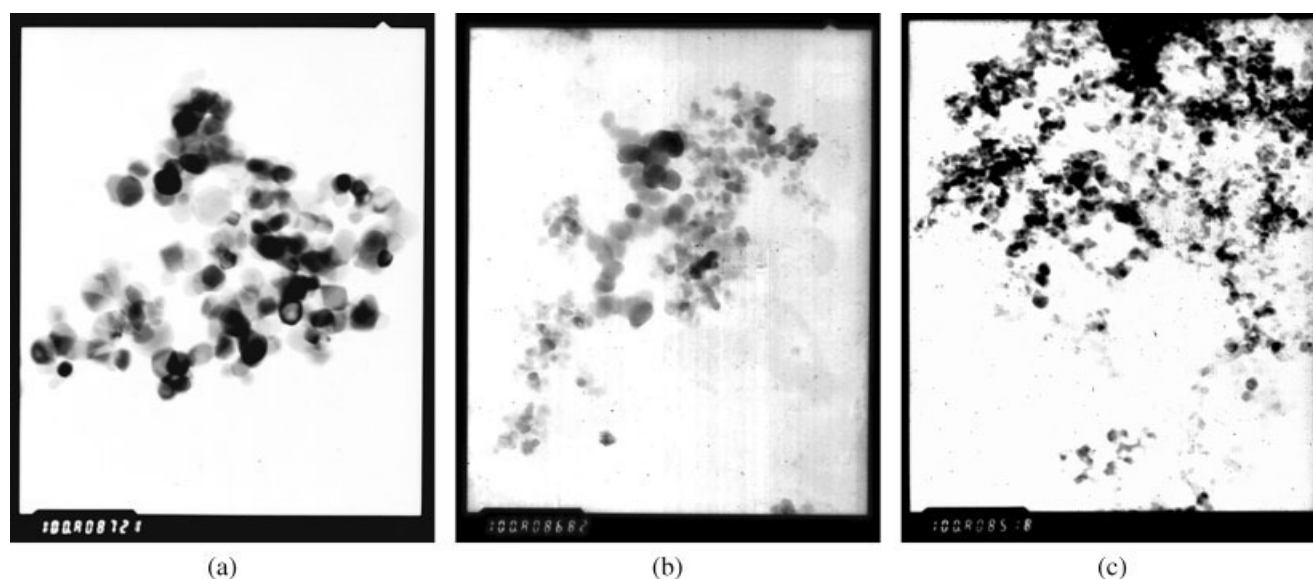
Figure 2 TEM micrographs of silica before and after modification (magnification 100,000). (a) bare SiO_2, (b) KH570-grafted SiO_2, (c) PMMA-grafted SiO_2.

weight loss of modified nanoparticles are 4.25%, 7.31% ,and 9.4%, reacted with 2, 6, and 10 mL monomer, respectively. That is to say, as the amount of modifier (monomer) increased, the grafting percentage also enhanced, but the extent is not very large. This can be explained that there exist two competition reactions in the system: one is the self-polymerization of MMA monomer, the other is the propagation of polymer chains on the silica nanoparticles surface. As the amount of modifier increased, it is easier for self-polymerization to take place and consume the monomer in the system. Therefore, it is necessary to slowly drip the modifier into the reaction system to control the rate of self-polymerization.

### Surface property of silica nanoparticles

Determination of LD

To determine the surface properties of silica nanoparticles before and after modification, and also observe the influence of grafting percentage on lipophilic degree (LD), the LD values of different silica samples were measured. The results are shown in Table I. From experiments, we noticed when unmodified particles were mixed with water with stirring, the particles dispersed in water, indicating the particle surface was hydrophilic. While modified particles floated on water surface, indicating the particle surface was hydrophobic.

By titration of methanol into water with stirring, the silica nanoparticles floating on water was wetted by methanol and settled down. The outcome suggested the surface property of silica after modification changed from hydrophilic to hydrophobic, and as the

grafting percentage of PMMA-grafted silica nanoparticles increased, the value of LD also enhanced.

Sedimentation test

The sedimentation curves are shown in Figure 4. It is found that the suspension of unmodified silica in water is unstable and most of the nanoparticles settled down within 24 h. On the other hand, after modification with different amount of MMA, the nanoparticles could suspend in organic solvent (acetone), and form a stable suspension. As time went on, the modified
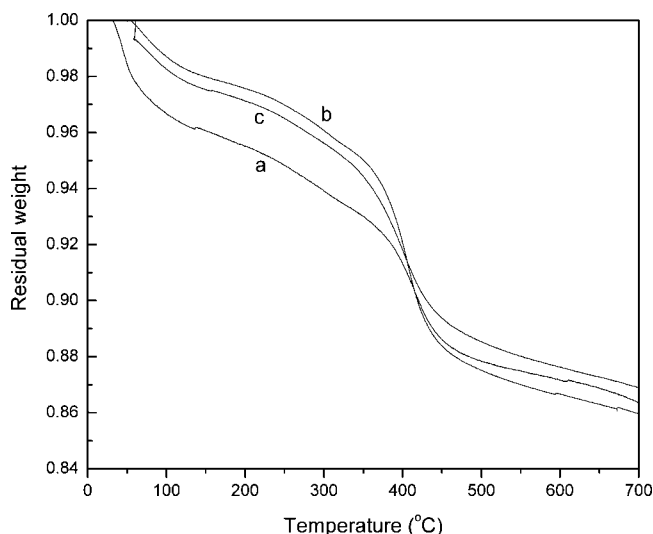
Figure 3 TGA of PMMA-grafted silica nanoparticles (a) bare SiO_2 modified with MMA (2 mL), (b) bare SiO_2 modified with MMA (6 mL), (c) bare SiO_2 modified with MMA (10 mL).

TABLE I
**Lipophilic Degree of Modified Silica Nanoparticles**

Samples	Methanol (mL)	Lipophilic degree (%)
KH570-grafted silica	0.65	1.28
KH570-grafted silica nanoparticles + MMA (2 mL)	0.9	1.77
KH570-grafted silica nanoparticles + MMA (6 mL)	1.2	2.53
KH570-grafted silica nanoparticles + MMA (10 mL)	1.6	3.1

particles precipitated very slowly. Moreover, as the grafting percentage enhanced, the average sedimentation rates of powders decreased. The rates are 0.2278 mm/h, 0.2176 mm/h, and 0.1964 mm/h, respectively. It can be concluded that the surface characteristic of silica nanoparticles after coating by polymer chains was hydrophobic, which displayed well compatibility with organic solvents.

DSC analysis of silica-reinforced PMMA

As already discussed earlier, different kinds of PMMA slices were obtained via bulk polymerization. The DSC behaviors of neat and silica-reinforced PMMA slices are shown in Figure 5. It was observed that the additive silica had changed the thermal behavior of PMMA slices and the glass transition temperature (T_g) of silica-reinforced PMMA increased. The T_g of neat PMMA (a) is 120.5°C, while the T_g is 126.5°C, 126.9°C, and 131.8°C, respectively, after doped with unmodified silica (b), PMMA-grafted silica (c) and KH570-grafted silica (d).

The reason for the increase of T_g can be explained as follows: as bare silica nanoparticles added during
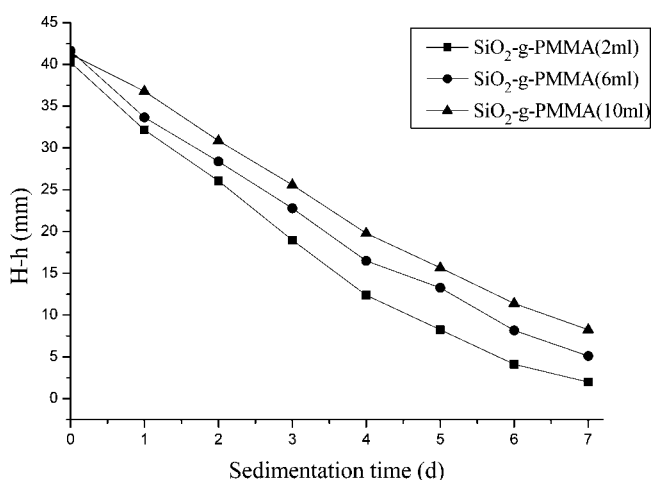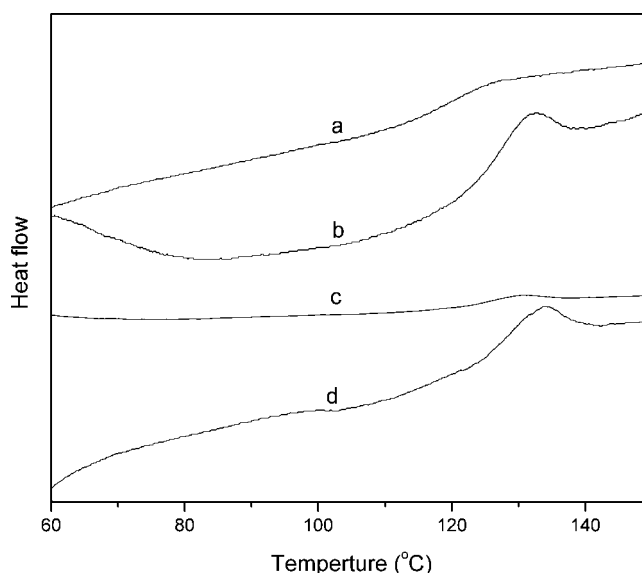
the *in situ* polymerization, strong physical bond between silica nanoparticles and macromolecule meshwork formed, and restrained the movement of polymer chains at high temperature. Comparing with bare silica, PMMA-grafted silica nanoparticles has a stronger coalescent force with PMMA, since the compatibility between the polymer matrix and nanoparticles improved. So the thermal stability had been enhanced and the T_g increased. For KH570-grafted silica nanoparticles, the value of T_g increased the most. It was considered that the functional groups C=C on KH570-grafted silica surface copolymerized with MMA. Therefore, a covalent bonding between KH570-grafted silica nanoparticles and PMMA matrix were formed. The movement of macromolecule chains was restrained due to the interaction of the PMMA network.

Mechanical properties of silica-reinforced PMMA

Hardness

The results of hardness measurement for silica-reinforced PMMA slices were listed in Table II. After modified with bare silica nanoparticles, the hardness of PMMA slices enhanced by 1.2 (HD). While doped with KH570-grafted silica or PMMA-grafted silica other than bare silica nanoparticles during the *in situ* polymerization, the hardness of doped PMMA slices enhanced more. This maybe due to the following reason: as bare silica nanoparticles owned large surface area and high surface energy, the silica nanoparticles might be adsorbed in the PMMA chains via physical force. Due to the higher LD value, PMMA-grafted silica nanoparticles could disperse more effectively in

Figure 4 Sedimentation of PMMA-grafted silica nanoparticles in acetone. ■: bare SiO₂ modified with MMA (2 mL), ●: bare SiO₂ modified with MMA (6 mL), ▲: bare SiO₂ modified with MMA (10 mL).

Figure 5 DSC of different kinds of PMMA slices. (a) neat PMMA, (b) unmodified silica + PMMA, (c) KH570-grafted silica + PMMA, (d) PMMA-grafted silica + PMMA.

TABLE II
Hardness of PMMA Reinforced with Unmodified and Modified Silica Nanoparticles

Samples	Measurements (HD)					Average hardness (HD)
	1	2	3	4	5	
Neat PMMA	86.0	86.2	87.2	88.0	86.2	86.7
Unmodified silica nanoparticles + PMMA	88.0	87.3	88.0	88.2	88.0	87.9
KH570-grafted silica nanoparticles + PMMA	87.0	89.0	89.2	90.0	90.2	89.1
PMMA-grafted silica nanoparticles + PMMA	88.4	88.2	88.8	89.2	89.8	88.9

PMMA matrix than bare silica nanoparticles. For the KH570-grafted silica, there is functional groups C=C bonding on the KH570-grafted silica nanoparticles surface, the PMMA chains in the bulk polymer could easily be fixed onto the silica nanoparticles by covalent bond via copolymerization with functional groups C=C, and silica nanoparticles acted as chemical junction in the network of PMMA. This will be confirmed in following sections.

Flexural stress

The effect of particulate fillers on the stress-strain behavior of polymeric materials is influenced by the incorporation of filler with polymer matrix because the interaction between the particles and polymer could be much different. The reinforcement mechanism of polymer by nanoparticles can be explained as this: as the active surface of filling particles coupled with some long molecular chain and formed a coupling structure, the flexural stress can be transferred through the linking point to other molecular chains. While one chain ruptured under external stress, the other can act as the same role. So the whole specimen

Figure 6 Mechanical properties of different kinds of PMMA slices. 1: neat PMMA, 2: unmodified silica + PMMA, 3: KH570-grafted silica + PMMA, 4: PMMA-grafted silica + PMMA.

is not threatened by the stress and the mechanical property is strengthened. With the knowledge mentioned above, KH570 was used to modify the surface of silica nanoparticles so that the interaction between the filling particles and polymer can be enhanced, and the effect of modification to the polymer can be strengthened. The experimental results of flexural strength measured for the PMMA composites are illustrated in Figure 6. KH570-grafted silica nanoparticles ensure good filler-matrix coupling, consume the cracking energy and distort the slit. The flexural strength is slightly lowered after modified by PMMA-grafted silica nanoparticles, but is still higher than that of the neat PMMA. It can be seen that surface treatment of silica nanoparticles could improve the compatibility between silica and polymer matrix, and enhance the mechanic property of polymer.

Impact property

The impact strength of different kinds of PMMA slices is illustrated in Figure 6. It can be seen that the doping with silica nanoparticles offers an obvious improvement of impact strength, while keeps the basic properties of neat PMMA. Compared with KH570-grafted silica nanoparticles, a sudden drop of impact strength is observed after modified with PMMA-grafted silica nanoparticles. It is possibly due to the stress concentration effect.[31] Compared with modified silica nanoparticles, the bare silica nanoparticles dispersed in MMA less effectively and were inclined to aggregate. Therefore, the sample was brittle and suffered from detrimental failure. Considering again the strong increase in impact strength, it is obvious that some energy was eliminated during the rupture of the sample if the polymer was doped with nanoparticles.
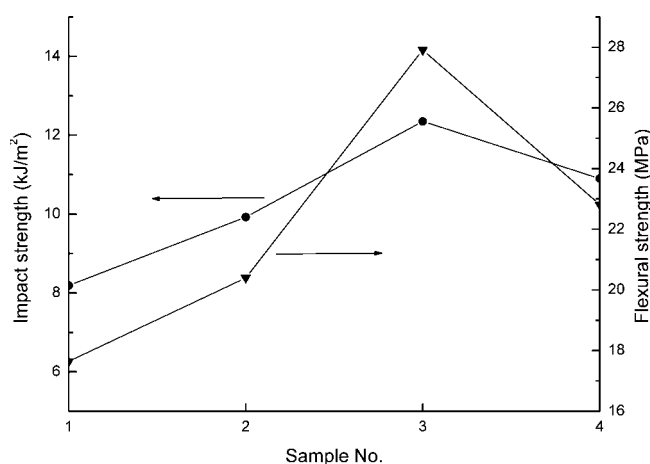
UV–vis analysis

The UV–vis spectra of modified PMMA slices are shown in Figure 7. The peak around 540 nm was due to the absorption of glass of the mold. Compared with neat PMMA, it can be concluded that the transparence of modified PMMA was decreased slightly. The

reason is that: first, the wavelength of the incidence ray is at the same magnitude of the modified silica, and the silica nanoparticles have strong reflectivity against the incidence ray. Second, silica nanoparticles have high surface energy and easy to aggregate in polymeric materials, that is also a reason for the fall of transparence. Compared with bare silica nanoparticles, PMMA reinforced with KH570-grafted silica nanoparticles have higher transparence. That is because after modification with MMA, silica nanoparticles have better compatibility with organic matrix. Moreover, it can be seen in Figure 7 that there are strong absorptivity at the range of UV (around 390 nm). It is due to the absorbability to the UV ray by the silica nanoparticles. It is considered that PMMA has superior performance of antiaging after modified with silica nanoparticles.
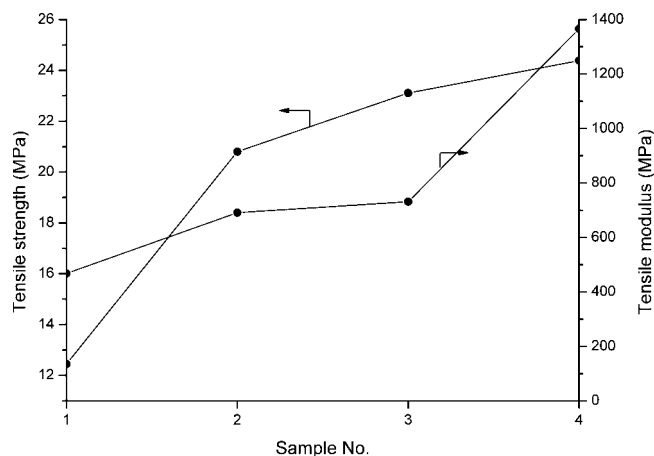
Tensile properties of PMMA films

The dispersion of nanoparticles in the polymer matrix is reported to have significant impact on the mechanical properties of nanocomposites.[32] Since the nanoparticles have a strong tendency to aggregate, homogeneous dispersion of nanoparticles in polymer matrix has been considered as a difficult task. A good dispersion may be achieved by surface modification of nanoparticles under an appropriate processing condition.[33] In the present investigation, we prepared two kinds of modified silica nanoparticles, and also studied the influence of modified silica nanoparticles on the tensile behaviors of PMMA films.

Figure 8 illustrates the tensile strengths and tensile modulus of various silica-reinforced PMMA films. These films were prepared by solution blending, as described under ''Preparation of PMMA films.'' The tensile strength and tensile modulus of the films
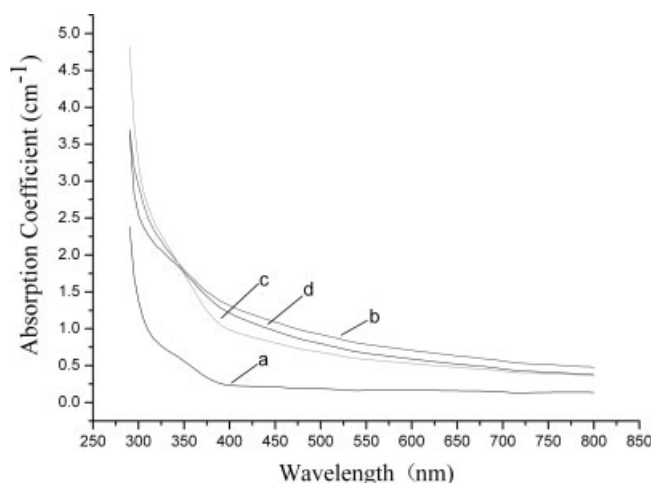
Figure 8 Effects of silica nanoparticles on the properties of PMMA films. 1: neat PMMA, 2: unmodified silica + PMMA, 3: KH570-grafted silica + PMMA, 4: PMMA-grafted silica + PMMA.

increased after doped with silica nanoparticles. The testing results indicated that the mechanical properties of PMMA films with a uniform dispersion of silica nanoparticles are greatly improved. The tensile strength and tensile modulus of PMMA films doped with PMMA-grafted silica nanoparticles increased up to 95.83% and 193.16% respectively, in comparison with neat PMMA films. In contrast, the bare silica nanoparticles have poor compatibility with PMMA solution and exhibit little improvement in its mechanical properties. The result confirms the reported observations.[32]

CONCLUSIONS

The following conclusions can be drawn in the present investigation: (1) PMMA was successfully grafted onto silica nanoparticles via solution polymerization. The surface property of silica was turned from hydrophilic to hydrophobic after modification.(2) The weight loss of modified silica nanoparticles increased with the increasing amount of modifier.(3) The glass transition temperature (T_g) of PMMA slices was increased while doped with different kinds of silica nanoparticles.(4) Silica-reinforced PMMA exhibited strong UV absorptivity, while very low absorptivity at visual light.(5) By adding silica nanoparticles into PMMA, the hardness, impact energy and flexural property of PMMA slices could be simultaneously improved.(6) The tensile strength and tensile modulus of silica reinforced PMMA films were increased.

Figure 7 UV–vis of different kinds of PMMA slices. (a) neat PMMA, (b) unmodified silica+PMMA, (c) KH570-grafted silica+PMMA, (d) PMMA-grafted silica+PMMA.

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