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Preparation of PDMS/SiO$_2$ nanocomposites via ultrasonical modification and miniemulsion polymerization

Lei Yang · Shouji Qiu · Ya Zhang · Yongshen Xu

Abstract In this paper, the ultrasonic dispersion process was utilized to modify the silica sol nanoparticles by a certain amount of hydroxyl silicone oil (HSO), then in the presence of the modified silica sol, miniemulsion polymerization of octamethylcyclotetrasiloxane (D$_4$) was conducted with dodecylbenzene sulfonic acid (DBSA) as the emulsifier and catalyst, and finally polydimethylsiloxane (PDMS)/silica (SiO$_2$) nanocomposite latex was obtained. The modified silica sol particles, diameter and morphology of the composite latex particles, mechanical properties and thermal stabilities of the composite films were characterized and discussed, respectively. The results showed that the ultrasonic dispersion was an effective method to modify the silica sol particles, the grafted degree of HSO onto silica surface was about 5 %. The morphology of composite latex particles was shown core-shell structure with grafted SiO$_2$ particles encapsulated by PDMS, the introduction of SiO$_2$ improved the mechanical properties and thermal stabilities of polysiloxane composite films.

Keywords Silica sol · Polysiloxane · Ultrasonic dispersion · Miniemulsion polymerization · Nanocomposites

Introduction

Polydimethylsiloxane (PDMS), with a repeat unit chain [−Si (CH$_3$)$_2$O−] is the most commonly used member in the class of polysiloxanes. Because of the special chain structure, PDMS has advantages of excellent temperature resistance, weather resistance, hydrophobicity, lubricity and biocompatibility et al., and has been widely used in areas such as coatings, adhensines, textile, and biomaterials et al. [1]. However, due to its drawbacks of poor mechanical properties and high costs, researchers usually introduce silica (SiO$_2$) or other inorganic powders into the polymeric matrix to achieve the reinforcement of PDMS elastomer [2], thus obtain the PDMS/SiO$_2$ composites. In recent years, PDMS/SiO$_2$ composites have been widely studied, and the effects of silica on the properties of the composites depend on the preparation route. Typically, silica is mechanically blended into the polymeric matrix before crosslinking [3]. However, this process is always time-consuming, energy-intensive, and the aggregation of silica particles is serious. For these reasons, Mark et al. [4–10] applied the in situ sol–gel process by which silica particles were in situ generated in PDMS networks under a certain condition, and the PDMS/SiO$_2$ nanocomposites were obtained. The major advantage of this method is the avoidance of the problems associated with mechanical blending, and some properties of the resulted materials are greatly improved, as compared to those obtained by classical methods. However, for this in situ approach, the control of crosslink density of PDMS macromolecules and size of silica microdomain is still harsh, the excessive cross-linking will lead to embrittlement of PDMS elastomer.

Miniemulsion polymerization in which the monomer droplets are the main nucleation places was firstly proposed by Ugelstad et al. [11] in 1973, and it has unique advantages in the preparation of nanocomposites. Most researchers selected vinyl monomers as the organic components to prepare organic/inorganic nanocomposites [12–17] via miniemulsion polymerization in the presence of inorganic nanoparticles or inorganic precursor. However, the in situ miniemulsion polymerization of octamethylcyclotetrasiloxane (D$_4$) was rarely reported. In the meantime, compared to the conventional emulsion polymerization [18, 19] and microemulsion polymerization [20, 21] of D$_4$, miniemulsion polymerization [22, 23] has advantages of using small amounts of emulsifier to obtain stable emulsion. Therefore, we approached to prepare PDMS/SiO$_2$

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nanocomposites via in situ miniemulsion polymerization. Firstly, the ultrasonic dispersion process was utilized to modify the silica sol nanoparticles by a certain amount of hydroxyl silicone oil (HSO), then the miniemulsion polymerization of D_4 was conducted in the presence of modified silica sol, and finally PDMS/SiO$_2$ nanocomposites latex was obtained. Because the modified SiO$_2$ nanoparticles can be well dispersed in monomer droplets, the aggregation of SiO$_2$ particles can be avoided. Besides, compared to the in situ sol–gel process, the crosslink density of PDMS macromolecules can be controlled by the surface area of the pre-prepared nano-silica, which can maintain the flexibility of PDMS elastomer.

Experimental

Materials

Silica sol (average diameter=25 nm, SiO$_2$ content=30 wt%) was produced by Beijing aeronautical materials institute (Beijing, P.R. China). Octamethylcyclotetrasiloxane (D_4) and hydroxyl silicone oil (HSO, hydroxyl group content was about 6 wt%) was supplied by Bluestar new chemical materials Co.,Ltd (Jiangxi, P.R. China). Dodecyl benzene-sulfonic acid (DBSA) and γ-(2,3-epoxypropoxy)propytri-methoxysilane were purchased from Tianjin Shengbin Chemicals Co.,Ltd(Tianjin, P.R. China). Sodium bicarbonate (NaHCO$_3$) and cyclohexane were obtained from Tianjin Guangfu Fine Chemical Institute (Tianjin, P.R. China)

Surface grafted modifiaction of silica sol particles

A certain amount of HSO and silica sol were mixed in a 100 ml beaker flask, and the mixture was ultrasonicated at 80w for 3 min, then the dispersion was agitated at room temperature for 12 h, and finally the HSO-modified silica sol was obtained. Here, the mass ratio of HSO to SiO$_2$ was 15 %.

Miniemulsion polymerization of D_4 prepared in the presence of modified silica sol

In a typital experiment, 0.5 g of DBSA was firstly dissolved in 35 ml water, then 10 g of D_4 and a certain amount of HSO-modified silica sol were added to the soluton, and the mixture was ultrasonicated at 200w for 15 min. The resultant monomer miniemulsion was then transferred into a 250 ml four-necked flask with a mechanical stirrer, thermometer and refux condenser, and the polymerization was carried out at 80°C for 3.5 h. After cooling, a certain amount of NaHCO$_3$ was added to adjust the system to netural, and finally the PDMS/SiO$_2$ nanocomposite emulsion latex was obtained. The resultant emulsion latex was used to obtain composite films by mixing with a certain amount of γ-(2,3-epoxypropoxy)propytrimethoxysilane (curing agent, 3 wt% based PDMS) and then pouring on a Teflon substrate with curing at room temperature for 3 days.

Characterization

Fourier-transform infrared spectra (FTIR) were measured in the wavenumber range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} using a Nicoet Avatar 360FTIR spectrophotometer. The grafted degree of modified silica and the thermal stabilities of polysiloxane composite films were determined by Thermogravimetric analysis (TGA) using a Mettler Toledo TGA-SDTA851e derivatograph, in nitrogen atmosphere, in the temperature range from room temperature to 800°C, respectively, and a heating rate of 10°C/min. Before the FTIR and TGA measurement, both pure silica and HSO-modified silica samples were extracted exhaustively with cyclohexane for 4 days using Soxhlet appratus, respectively. The conversion rate of monomers was measured by gravimetric method with the samples neutralized and vacuum drying at 130°C for 1 h. The morphologies of grafted silica and composite latex particles were investigated by transmission electron microscopy (TEM) using a JEOL JEM 2010. The diameter and size distribution of grafted silica and composite latex particles were determined by a Zetasizer 3000 HSA analyzer (MALVERN) and TEM images. The mechanical properties of polysiloxane composite films were characterized by tensile test (DXLL1000-2000) at a stretching speed of 50 mm/min. For each datum point, at least five samples were tested, and the average value was recorded.

Results and discussion

Characterization of modified silica sol particles

FTIR

Figure 1 showed the FTIR spectra of pure SiO$_2$ particles and 15 wt% HSO-modified SiO$_2$ particles. As shown in the figure, in the spectra of pure SiO$_2$ particles, the absorption bands at 3400 cm^{-1} and 958 cm^{-1} were the characteristic peaks of Si-OH, the absorption band at 1600 cm^{-1} was the characteristic peak of bonding water, and the absorption bands at 1100 cm^{-1},800 cm^{-1}and 471 cm^{-1} were the characteristic
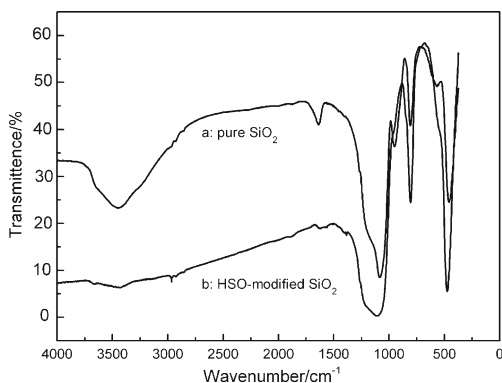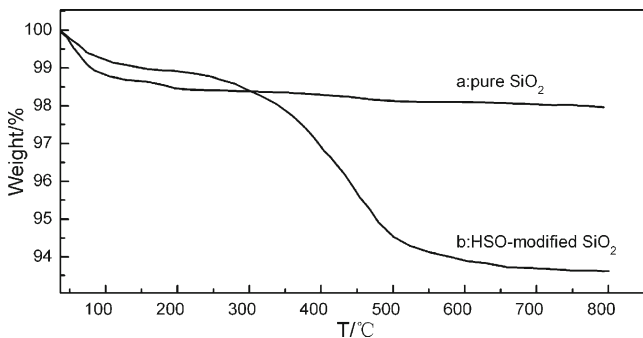
Fig. 1 FTIR spectra of: **a** pure SiO$_2$ and **b** HSO-modified SiO$_2$
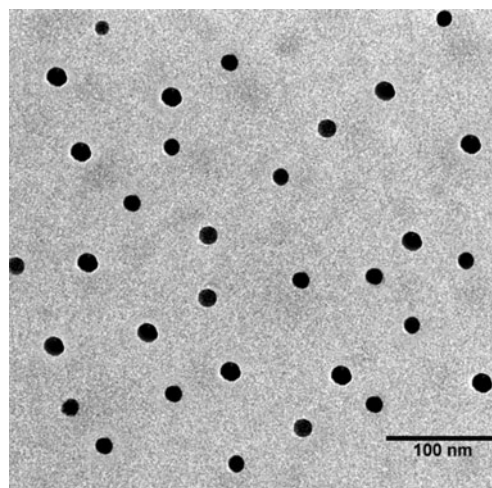
peaks of Si-O-Si. In the spectra of modified SiO$_2$ particles, there were two weak absorption bands at 2987 cm^{-1} and 1320 cm^{-1}, attributed, respectively, to the stretching vibration of Si-CH$_3$ and Si-C, which indicated that HSO was covalently bonded to SiO$_2$ particles. Besides, the absorptions of Si-OH at 3400 cm^{-1} and 958 cm^{-1} were obviously weakened compared to the pure SiO$_2$, this was because the hydroxyl content of SiO$_2$ surface decreased when HSO was covalently linked to SiO$_2$ surface through Si-O-Si by dehydration between the two hydroxyl groups.

TGA

The grafted degree of hydroxyl silicone oil onto SiO$_2$ surface can be determined by TGA. Figure 2 showed the TGA curves of pure SiO$_2$ and 15 wt% HSO-modified SiO$_2$. As shown in the figure, both pure SiO$_2$ and modified SiO$_2$ had a certain weight loss below 200°C, which was mainly due to the evaporation of the absorbed water onto SiO$_2$ surface. As the hydrophobicity of the modified SiO$_2$ particles had improved, the content of absorbed water on modified SiO$_2$ surface was less than pure SiO$_2$ particles, obviously the weight loss of modified SiO$_2$ particles below 200°C was less than pure SiO$_2$ particles. However, at 200~800°C range, the weight loss of the pure SiO$_2$ particles was only


Fig. 3 TEM image of HSO-modified silica particles

0.39 %, and the weight loss of the modified SiO$_2$ particles was about 5.42 %. This was due to the thermal degradation of the organic component which was grafted onto silica surface under high temperature. According to the above results, the grafted degree of HSO onto SiO$_2$ surface was about 5 % with the ultrasonical dispersion method.

TEM and Zetasizer analyzer

Figure 3 showed the TEM image of the 15 wt% HSO-modified SiO$_2$ particles with an average diameter of 27 nm, and the measurement results of Zetasizer analyzer showed the polydispersity of the modified SiO$_2$ particles was 2.17 %. According to the results, we found the changes between SiO$_2$ and modified SiO$_2$ particles in size and size distribution were not obvious, which confirmed that the

Fig. 2 TGA curves of: **a** pure SiO$_2$ and **b** HSO-modified SiO$_2$
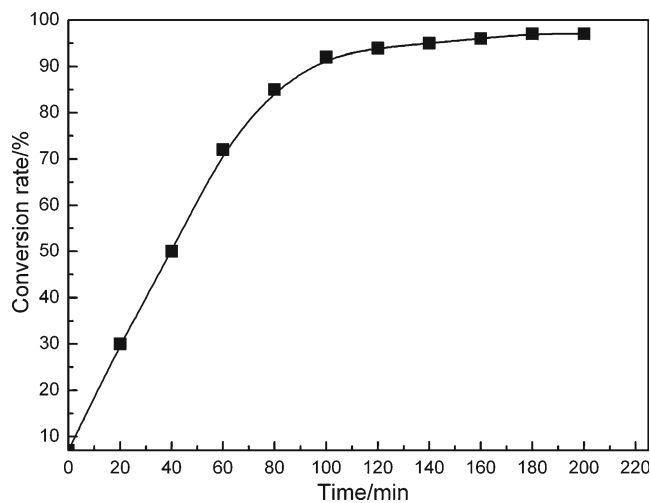
Fig. 4 The kinetics of monomer miniemulsion polymerization (SiO$_2$ content 15 wt%)

aggregation of SiO_2 particles did not happen in the process of modification by HSO.

Mechanism of miniemulsion polymerization

Figure 4 showed the kinetics of monomer miniemulsion polymerization, as seen from the figure, the miniemulsion polymerization rate was very fast, and the conversion rate of monomer could reach 90 % with only 1.5 h. Meanwhile, we found the changes between monomer droplets (after ultrasonicating 15 min) and composite latex particles in size were not obvious, which were about 81 and 78 nm, respectively. Thus, according to the above results, we can identify that the mechanism of the emulsion polymerization was the typical miniemulsion polymerization.

Characterization of composite latex particles

Figure 5 showed the diameter and size distribution of composite latex particles with different SiO_2 contents. As can be seen from the figure, the diameter and size distribution of the composite latex particles was not obviously influenced by different SiO_2 contents, the diameters were all about 80 nm with a narrow distribution. This indicated that the introduction of SiO_2 did not change the homogeneity and dispersion stability of monomer droplets, the polymer latex particles were well composited with SiO_2 particles.

Figure 6 showed the TEM photogragraphs of the composite latex particles with 15 wt% SiO_2. As shown in the figure, the morphology of composite latex particles was shown core-shell structure. PDMS shells coat
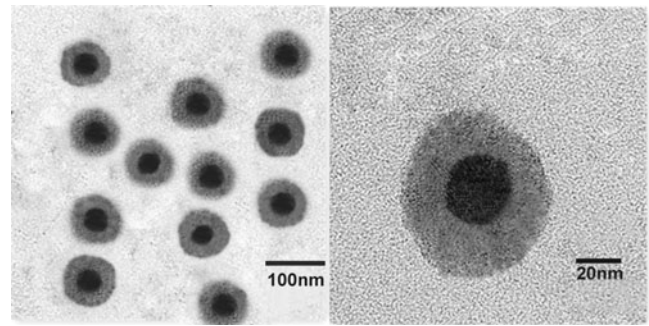
**Fig. 6** TEM images of composite latex particles

the grafted SiO_2 cores, and the average diameter of the core-shell particles was 78 nm which was closed to the data measured by Nano particle analyzer. From the TEM image, the thickness of light PDMS shells and the size of dark SiO_2 cores was about 25 and 28 nm, respectively. In addition, most of the composite particles had only one single core, the free SiO_2 particles could not be found outside the composite particles, which confirmed that most SiO_2 particles had been encapsulated by polymer during the miniemulsion polymerization.

### Characterization of composite films

Mechanical properties

The effects of SiO_2 content on the mechanical properties of the composite films were investigated. Typical tensile stress–strain curves of the composite films with different SiO_2 contents were shown in Fig. 7. With the

Fig. 5 The particle size and polydispersity index of the composite latex particles with different SiO_2 contents
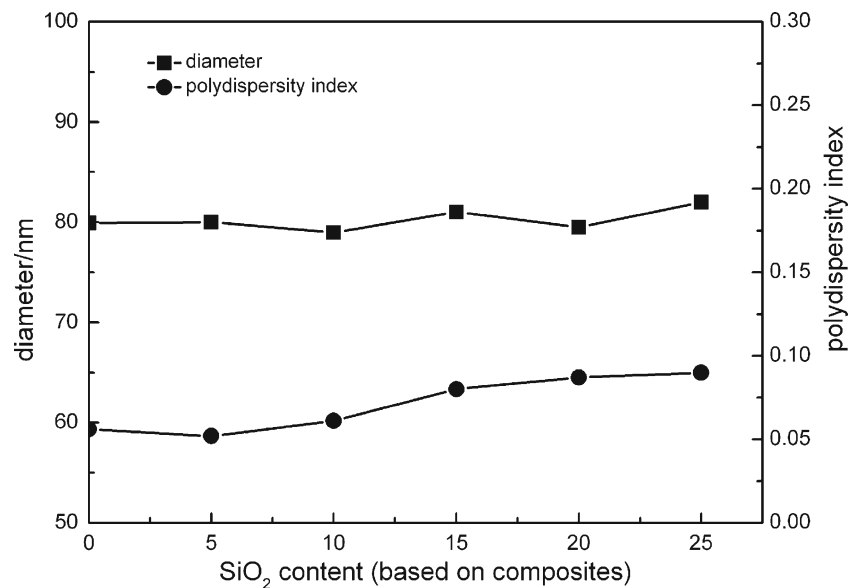
Fig. 7 The stress–strain curves of composite films with different SiO_2 contents: **a** 25 wt%, **b** 20 wt%, **c** 15 wt%, **d** 10 wt%
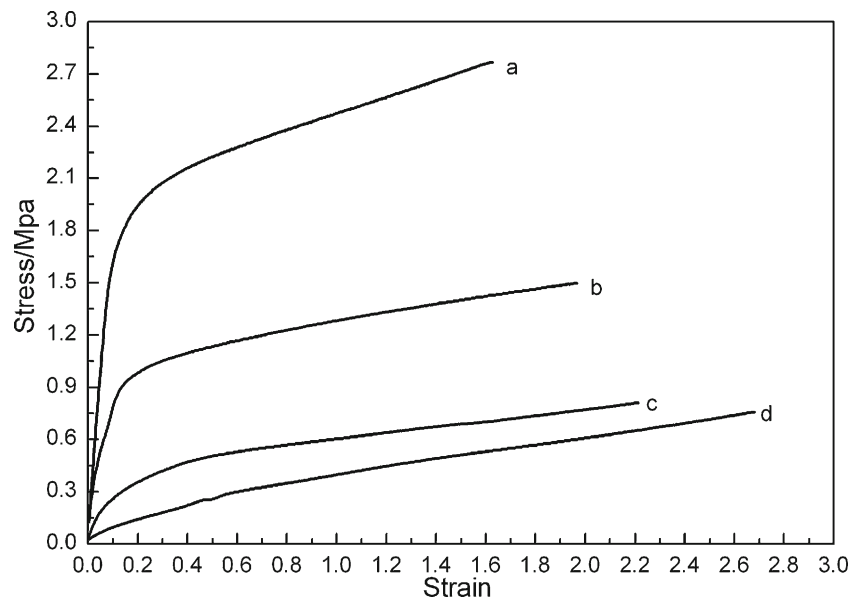
increase of SiO_2 content, the composite films exhibited increased tensile strength and decreased elongations at break, which indicated that both reinforcing and toughening effects of the SiO_2 particles on the polymer matrix were fully brought into play.

Thermal stabilities

The thermal stabilities of the prepared materials were investigated by thermogravimetric analyses (TGA). Fig. 8 showed the TGA curves of cured films of PDMS latex and PDMS/SiO_2 composite latex. From Fig. 7, it could be seen that the degradation temperature of composite film with 25 wt% SiO_2 and pure cured PDMS film was 401 and 350°C, respectively, which indicated that the
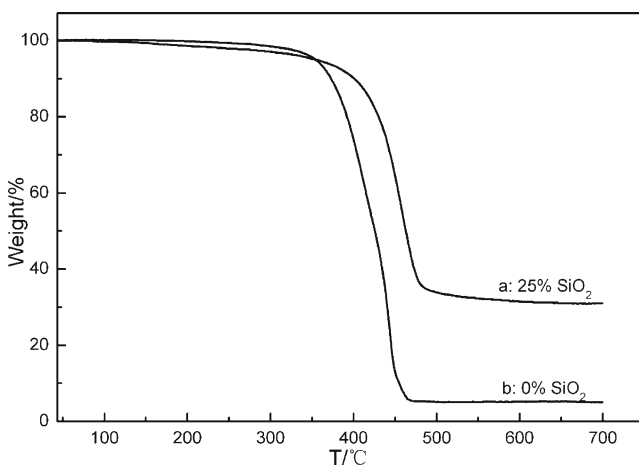
incorporation of SiO_2 particles into the PDMS matrix could enhance the thermal stability of the material by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. Meanwhile, the final residue amounts of the two samples were slightly higher than the theoretical SiO_2 content, and it was because that the thermal degradation temperature of a small part of highly cross-linked silicone was higher than 700°C, thus, in additon to SiO_2, there was also little amount of highly cross-linked silicone in the final residue.

Conclusions

PDMS/SiO_2 nanocomposites were successfully prepared by miniemulsion polymerization. The ultrasonic dispersion process was utilized to modify the silica sol nanoparticles by a certain amount of HSO, the FTIR and TGA results showed that it was an effective way to modify the silica sol particles, the grafted degree of HSO onto SiO_2 surface was about 5 %. During the polymerization of D_4, the introduction of silica did not change the homogeneity and dispersion stability of monomer droplets, the diameter and size distribution of the composite latex particles were not obviously influenced by different SiO_2 contents, and the morphology of the composite latex particles was shown core-shell structure with grafted SiO_2 particles encapsulated by PDMS. In the meantime, the introduction of SiO_2 improved the mechanical properties and thermal stabilities of polysiloxane films, and it is possible to use the composites as high temperature coatings.

Fig. 8 TGA curves of cured films of PDMS latex and PDMS/SiO_2 composite latex

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