

# A Novel Method for Preparing Composites of PDMS/PS Core–Shell Emulsion and Polystyrene

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**ABSTRACT:** A novel and simple method for preparing composites of PDMS/PS core–shell emulsion and polystyrene was reported. This method was based on emulsion and suspension *in situ* polymerization. The relationship between the process of core–shell emulsion breaking and electrolyte concentration was studied by spectrophotometry. The results of transmission electron microscopy showed that polydimethylsiloxane soft particles were dispersed uniformly in the composites. Diameters of the composite beads ranged from 0.5 to 4.0  $\mu\text{m}$ , which could be controlled by adjusting the amount of hydroxyapatite. At last, the properties of the latex film including water absorption ratio, con-

tact angle, pendulum hardness and transparency were tested. The results showed that the content of emulsion obvious affected the properties. During the process of emulsion and suspension *in situ* polymerization, the contact angle of the latex films ascended to  $106.06^\circ$  and the transmission ratio at 500 nm decreased to 0.3 with the increasing of core–shell emulsion. Whereas, the absorption and pendulum hardness fell to 0.37% and 322 S, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2571–2576, 2007

**Key words:** emulsion polymerization; suspension polymerization; synthesis; composites; films

## INTRODUCTION

Techniques for preparing composite particles of organic and inorganic substances have attracted more attention because composite particles offer potential applications in adhesives, electrical, optical, magnetic, catalytic, and enhanced mechanical properties.<sup>1–7</sup> For synthesis of the composite particles with different structures and sizes, various methods such as a sol–gel method, homogeneous precipitation, atom transfer radical polymerization, disperse polymerization, suspension and emulsion polymerization have been reported.<sup>8–12</sup> In general, the preparation of composites needs a complex process, such as emulsion breaking, washing, and drying. It is likely to lead to coagulation and deformation of particles during the handling process from emulsion to dry particles, and it is difficult to remove the impurities absorbed on partial surfaces. In our previous work, emulsion and suspension *in situ* polymerization has been designed for preparing a composite of polystyrene containing core–shell emulsion particles.<sup>13</sup> This method is very convenient and easy compared with others, in which emulsion polymerization and suspension polymerization are combined to synthesize

composites. During this process, composites are obtained directly by emulsion solution, without further handling of the emulsion particles. Moreover, nanoparticles disperse in the composites and do not coagulate. Polydimethylsiloxane (PDMS) is usually used as a silicone polymer and has many peculiar characteristics including a low glass transition temperature and surface tension, high flexibility, high hydrophobicity, high thermal and chemical resistances. These features make PDMS useful in many fields.<sup>14–20</sup>

In this work, composites of PDMS/PS core–shell emulsion and polystyrene were successfully synthesized by emulsion and suspension *in situ* polymerization. First, monodisperse PDMS/PS core–shell microspheres were prepared via surface grafting and seeded emulsion polymerization. Then, the lattices were broken with electrolyte dripping, and the emulsion particles became swollen and were transformed into the monomer in the suspension polymerization system. The process of emulsion breaking and swelling was further confirmed by spectrophotometry. The microtome section of the composites was observed by using transmission electron microscopy (TEM), and the diameter of composite beads increased from 0.5 to 4.0  $\mu\text{m}$  with the decrease of hydroxyapatite (HAP). The effects of emulsion content on water absorption ratio, contact angle, pendulum hardness, and transparency of latex film were also investigated.

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## EXPERIMENTAL

### Materials

Octamethyl cyclotetrasiloxane (D4) was fractionated under reduced pressure before used. Methacryloxypropyl trimethoxysilane (MATS) and styrene were distilled under reduced pressure before used. Sodium dodecylbenzen sulfonate (SDBS) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%) were used as received. Potassium persulfate (KPS) was refined by methanol and dried in a vacuum oven. Benzoyl peroxide (BPO) was recrystallized twice in chloroform and methanol. Hydroxyapatite (HAP) was synthesized as reported.<sup>21</sup> Polyvinylalcohol (PVA) and other reagents were analytical grade and used without further purification. Deionized water was used for polymerization and treatment process.

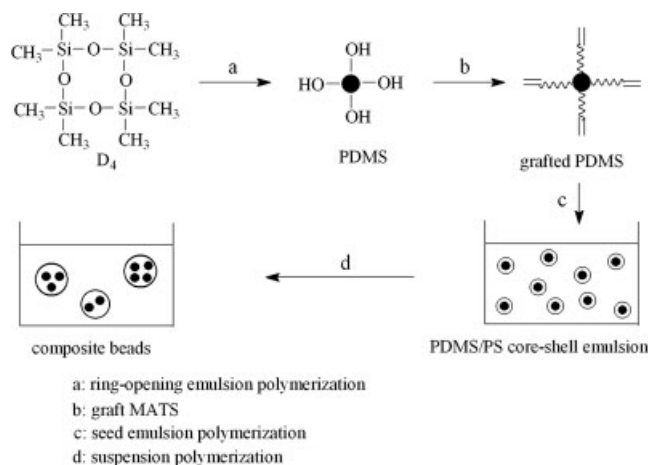
### Synthesis of PDMS/PS core-shell nanoparticles by seeded emulsion polymerization

PDMS lattices were prepared by ring-opening emulsion polymerization of D4 50 g deionized water, SDBS, 1.5 mL  $\text{H}_2\text{SO}_4$ , and 5 mL D4 were added into a four-neck flask, and the temperature was increased to 70°C for 24 h. pH of PDMS lattices was adjusted to about 4.5 and a solution of MATS in methanol was dripped into the PDMS lattices within 10 h. After 38 h, the grafted PDMS lattices were obtained.

Monodisperse PDMS/PS core-shell microspheres were synthesized by seed emulsion polymerization. A certain amount of grafted PDMS lattices and water were added to a four-neck flask with a machine stirring. 0.03 g SDBS, 0.15 g KPS, and 10 mL styrene were dripped into the solution. Then, the polymerization was carried out in an atmosphere of nitrogen for 10 h at 80°C. At last, PDMS/PS core-shell microspheres were obtained.

### Synthesis of the composites of PDMS/PS core-shell emulsion and polystyrene through emulsion and suspension *in situ* polymerization

Composites of PDMS/PS core-shell emulsion and polystyrene were obtained by emulsion and suspension *in situ* polymerization. The procedure was given as follows: the suspension agent (PVA), 30 mL PDMS/PS core-shell emulsion and 15 mL styrene were added into 100 mL deionized water. Then 25 mL electrolyte, 2 wt % calcium chloride was dripped into the suspension system within about 2 h. The emulsion was broken and the swollen core-shell nanoparticles diffused into the monomer phase. The initiator, 0.15 g BPO was dissolved in 5 mL styrene and 30 mL HAP was added to the solution. The mixture was heated to 82°C for 12 h. After that, the reaction system was treated with high-pressure steam to



**Figure 1** Scheme for emulsion and suspension *in situ* polymerization.

remove the unreacted monomer. The composites were washed with hydrochloric acid and dried under vacuum. At last, the composite beads of PDMS/PS core-shell emulsion and polystyrene were synthesized through emulsion and suspension *in situ* polymerization. All steps of the whole reaction process are shown in Figure 1.

### Characterization

#### The morphology of core-shell emulsion

The core-shell emulsion was diluted by distilled water and some of them were placed on a copper grid. The morphology of PDMS/PS core-shell microspheres was examined with a JEOL JEM 2010 TEM at an acceleration voltage of 200 kV. An aqueous solution of phosphotungstic acid was used to increase the contrast in the TEM pictures.

#### Measurement of solid content of emulsion

10 mL sample of PDMS/PS core-shell emulsion of PDMS/PS was precipitated by adding 4 wt % hydrochloric acid aqueous. The precipitate product was washed with water to pH 7 and dried in a vacuum oven at 45°C. Then, the product was weighed and the solid content of emulsion was calculated.

#### Transmittancy measurements

For the process of incomplete breaking and break-swell of PDMS/PS core-shell emulsion, the transmittancy of emulsion was studied by spectrophotometry. 30 mL emulsion was charged to a conical flask and maintained at 30°C under constant stirring, then it was titrated by 1.0 wt % of electrolyte aqueous at a rate of 0.1 mL/min. Every 5 min, 0.2 mL of the mixed solution was accurately transferred

**TABLE I**  
**The Properties of the Latex Films**

| PDMS/PS emulsion volume (mL) | Water absorption (%) | Contact angle (°) | Transmittancy at 500 nm | Pendulum hardness (S) |
|------------------------------|----------------------|-------------------|-------------------------|-----------------------|
| 10                           | 0.61                 | 100.03            | 18.4                    | 399                   |
| 20                           | 0.56                 | 102.39            | 12.6                    | 374                   |
| 30                           | 0.50                 | 103.88            | 5.80                    | 363                   |
| 40                           | 0.46                 | 104.51            | 5.40                    | 351                   |
| 50                           | 0.37                 | 106.06            | 0.30                    | 322                   |

from the conical flask into 2 mL of the comparison vessel with a pipette. The comparison vessel was filled with deionized water, shaken uniformly, and used for spectrophotometry measurements.

#### Measurement of molecular weight and molecular weight distribution

The composite beads were placed in chloroform, and the soluble polystyrene was precipitated by methanol and dried in vacuum. Molecular weight and molecular weight distribution were measured at 35°C by using a Waters 410 GPC instrument (Waters, Milford, MA), THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were calibrated with polystyrene standards.

#### The microtome section of composites of PDMS/PS and polystyrene

The composites of PDMS/PS core-shell emulsion and polystyrene were solidified by ethylene oxide, and microtome section with width of 80 nm was prepared by Leica Ultracut Uct microtome. The morphologies of microtome section were investigated by TEM using a JEOL JEM 2010 at an acceleration voltage of 80 kV.

#### The properties of latex films

The measurement of film's water absorption ratio was taken as follows: an amount of latex film ( $W_1$ ) was added into water at 50°C for 24 h; then, the surface of latex film was sipped up rapidly and quantified ( $W_2$ ). The water absorption ratio was determined by the follow equation:

$$[(W_2 - W_1)/W_1] \times 100\%$$

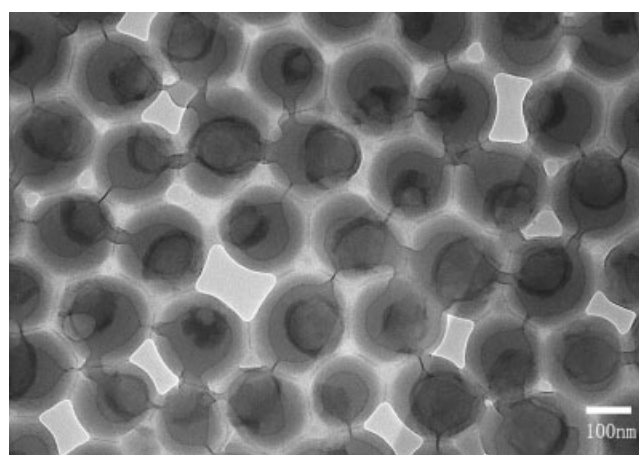
Pendulum hardness was measured by QBY-pendulum hardness apparatus made by TianJin, China. Water-contact angles were determined by using a JCR-10 goniometer, employing deionized water on thin films cast on a glass substrate. Contact angles were measured after 60 s by using the sessile drop technique. The volume of each water droplet was about 20  $\mu$ L, with each contact angle value given in

Table I representing an average of five readings. The transparency of each film was characterized as the 500 nm visible light and 1 mm thickness of film. This was calculated by using the equation  $TR = 10^{-A/d}$ , where  $A$  was the absorbance at 500 nm of the latex film, as measured by a UV-1100 photometer (Beijing RuiLi Company, China), and  $d$  (mm) was the thickness.

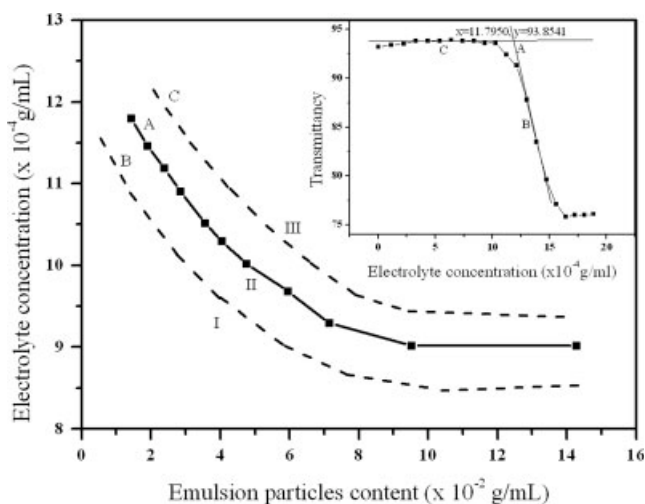
## RESULTS AND DISCUSSION

### Preparation of PDMS/PS core-shell emulsion

PDMS/PS microspheres were obtained through emulsion polymerization of styrene and grafted PDMS particles. Morphologies of core-shell emulsion were determined by TEM with PTA as the staining agent. The morphology of the particle showed a quite uniform fine structure, as shown in Figure 2 (where the dark areas represent the PDMS component as core and the light ones represent the PS as shell). To ensure that the experiment of emulsion and suspension *in situ* polymerization could carry through smoothly, it was important to control the amount of electrolyte. Therefore, effect on electrolyte concentration on the process of core-shell emulsion breaking was carefully investigated. According to the different amount of core-shell emulsion in the process of emulsion and suspension *in situ* transformation, we obtained a set of parallel curves between transmittancy and electrolyte concentration. All of these curves were treated mathematically like the one as shown in the inset in Figure 3. (point A was the intersection of tangential point coordinates B and C, respectively) These curves showed that the core-shell emulsion was stable in a certain electrolyte concentration. With the increasing in electrolyte concentration, the hydrated electrical double layer became thin or was destroyed. This made the core-shell emulsion collide with each other and aggregate.



**Figure 2** TEM image of the monodisperse PDMS/PS core-shell particles.



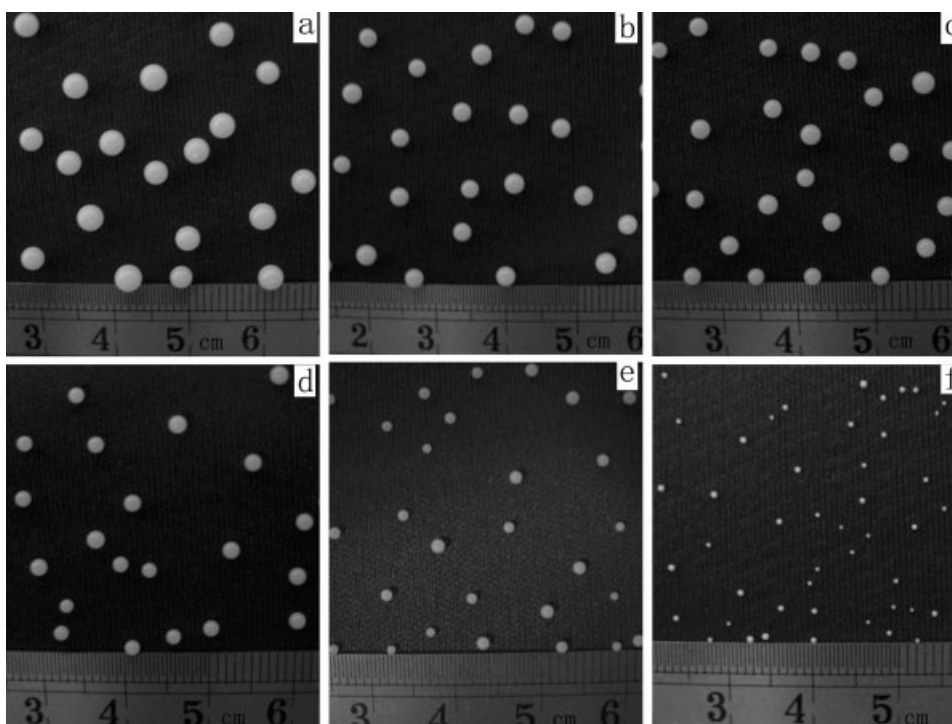
**Figure 3** Plot of electrolyte concentration against core-shell emulsion particles content in the process of emulsion breaking under constant stirring at 30°C. I: The stable state of core-shell emulsion; II: the incomplete-breaking state of emulsion, that is, a transitional region between the stable state and the unstable state of core-shell emulsion; III: the formed unit of stable flocks after the core-shell emulsion was broken completely.

Thus, the transmittancy of the emulsion decreased obviously and appeared the first sharp inflection in the curves. In the end, the core-shell particles collided to form the flocks and the second sharp inflection appeared in the curves with the addition of the electrolyte. Therefore, these parallel curves were

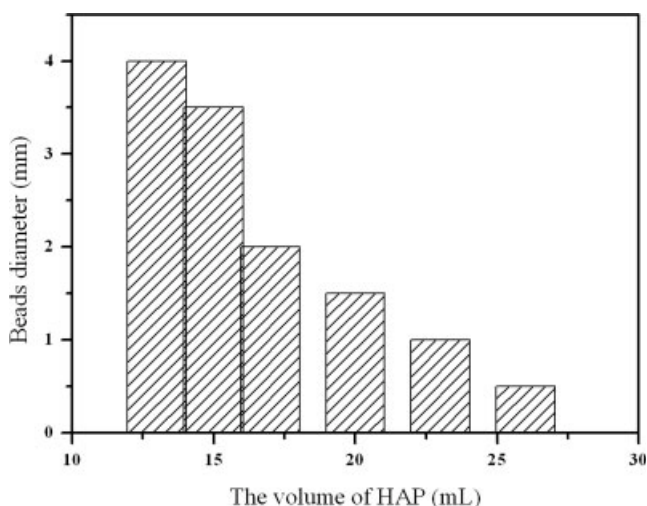
mathematically treated, respectively. These intersection points and tangential points were drawn in the inset of Figure 3. The inflection points were connected to construct an emulsion breaking curve and the tangential points on each side of the emulsion breaking curve were also connected to obtain two theoretical deduction incomplete-breaking curve and complete-breaking curve. Three curves divided the region of the right-angled coordinates system into three regions. Region I represented the stable state of core-shell emulsion; region II represented the incomplete-breaking state of emulsion, that is, a transitional region between the stable state and the unstable state of core-shell emulsion; and region III represented the formed unit of stable flocks after the core-shell emulsion was broken completely. By determining this transitional region in the process of incomplete-breaking emulsion, the content of the electrolyte must be controlled to make the emulsion and suspension *in situ* polymerization occur steadily and not aggregate, so emulsion particles can be smoothly transferred from the emulsion phase to the oil phase. Therefore, the process of emulsion and suspension *in situ* polymerization was confirmed further.

#### Preparation of composite beads of PDMS/PS emulsion and polystyrene

In the process of emulsion and suspension polymerization for preparation of composite beads of PDMS/PS emulsion and polystyrene (Fig. 4), the di-



**Figure 4** Morphology of the final products of emulsion and suspension *in situ* polymerization with (a) 13, (b) 15, (c) 17, (d) 20, (e) 23, and (f) 26 mL HAP.



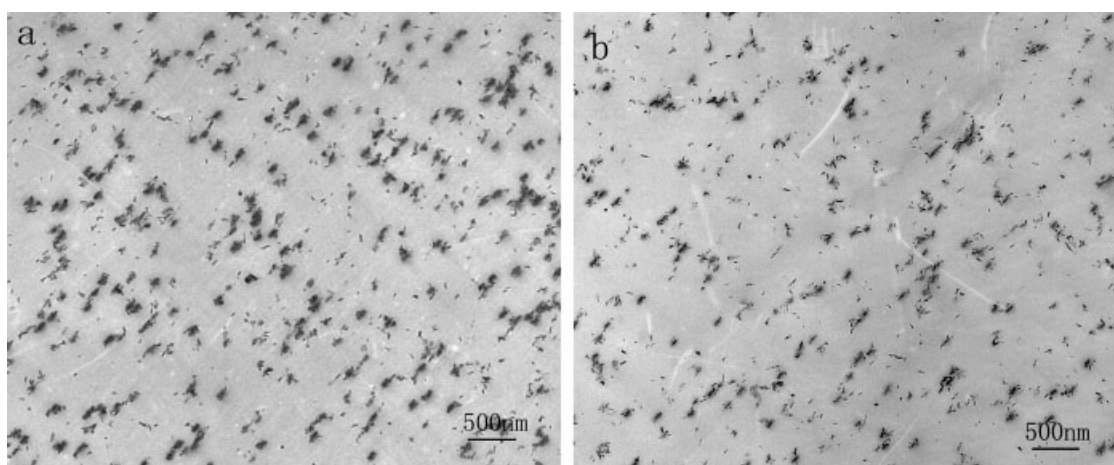
**Figure 5** Relationship of volume of HAP versus the composite beads diameter.

iameter of beads was influenced by many factors such as the ratio of oil and monomer, speed of stirring, reaction temperature, and so on.<sup>22</sup> When HAP and SDBS were used in the suspension polymerization, the polymerization system became more stable. We found that the inorganic dispersion agent, HAP played an important role in the process of emulsion and suspension *in situ* polymerization. The amount of HAP largely influenced the size of composite beads in the transformation process. As shown in Figure 5, the diameter of composite beads increased from 0.5 to 4.00 mm with the decrease of HAP. The largest size of composite beads was 4.00 mm obtained in the suspension polymerization. When the diameter of composite beads was larger than 4.00 mm, the beads could be conglomerated. Thus the size of composite beads in the process of emulsion and suspension *in situ* transformation could be controlled by the amount of HAP.

When the suspension polymerization was ended, white composite beads and clear water were observed in the system. The images of composite beads were obtained from the microtome method by TEM. As shown in Figure 6, the PDMS latex particles dispersed uniformly in the polystyrene composites without aggregating (where the dark parts represent PDMS and the light parts represent PS composites). Figure 6(a,b) corresponds to the composite beads obtained from 40 and 30 mL emulsion which added into the suspension system, respectively. These particles still were uniformly dispersed in the polystyrene composites even though more emulsion could be added into the suspension polymerization. Therefore, PDMS as a soft core were dispersed in the polystyrene composites successfully.

### The properties of the latex films

The properties such as water absorption ratio, contact angle, transparency and hardness pendulum of the latex films were also studied to further extent their potential applications. The water absorption ratio and water contact angles of the latex films are two important parameters for characterizing the hydrophobicity. As shown in Table I, the absorption ratio was influenced by the content of PDMS/PS core-shell emulsion. With an increase in the latter, the water absorption ratio of the latex films decreased from 0.61 to 0.37%, which could be attributed to the excellent hydrophobicity of PDMS. Moreover, the content of emulsion also affected the contact angle of the films. Because the PDMS tended to migrate to the air surface of the latex films for its low surface energy, the contact angle increased when the content of core-shell emulsion was enhanced from 10 to 50 mL. But the largest contact angle of the latex films was lower than that of the



**Figure 6** The microtome section of PDMS/PS composites obtained from emulsion and suspension *in situ* polymerization from (a) 40 and (b) 30 mL emulsion.

pure PDMS because of the influence of the surfactant used in the emulsion polymerization.

Because of PDMS and polystyrene were not compatible completely and phase separation was unavoidable, transparency of the composite films was usually unsatisfactory in this latex films. The transmission ratio at 500 nm decreased to 0.3 with the increase in content of PDMS/PS emulsion. The pendulum hardness of the latex films decreased from 399 to 322 S with increasing PDMS proportion and it was attributed to the fact that molecular chain of PDMS was very pliant.

### CONCLUSIONS

Composites of PDMS/PS and styrene were achieved by emulsion and suspension *in situ* polymerization. The soft particles of PDMS were dispersed uniformly in the composites. Different diameter of composites beads was synthesized through changing the amount of HAP. Finally, the film properties were investigated and they could be changed by the content of PDMS/PS core-shell emulsion. Moreover, this method is easy and convenient when compared with others and can be applied for other composites.

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