

Formation Mechanism of Silicone Rubber Particles with Core–Shell Structure by Seeded Emulsion Polymerization

WEI-DONG HE, CHUN-TAO CAO, and CAI-YUAN PAN*

Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China

SYNOPSIS

Silicone rubber particles with core–shell structure were prepared by polymerization of vinyl monomers in the presence of crosslinked and linear poly(dimethyl siloxane–methyl vinyl siloxane) latex. The monomers were added with either continuous or swelled-continuous addition mode. The core–shell morphology of silicone rubber/polystyrene [PST] and silicone rubber/poly(methyl methacrylate–divinyl benzene) [P(MMA–DVB)] composite particles were obtained. The effects of monomer addition mode, the compatibilities of the monomers or their homopolymer with silicone rubber, and the reactivity of polysiloxane with vinyl monomers on the formation of the core–shell structure were discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Since core–shell particles have plenty of applications, such as the toughening and strengthening of plastics,^{1–3} preparation of core–shell particles by seeded emulsion polymerization has been attracting great interest among researchers. Thus, a tremendous progress in this field has been achieved.

The factors influencing the formation of core–shell particles have been extensively studied. The crucial factor is thermodynamics, which determines the formation of the core–shell or inverted core–shell structure.⁴ Kinetic factors, such as diffusion restriction,⁵ seeded emulsion polymerization rate⁶ and addition mode of monomers,⁷ are very important in the morphology formation of the obtained particles. However, most of the researches concentrated on the poly(meth)acrylate systems.

In our previous work, we reported the preparation of the core–shell particles of silicone rubber/PMMA and silicone rubber/PGMA using one-stage method.⁸ The compatibility of vinyl monomer with silicone rubber and the reaction rate between vinyl monomers and Si–H of silicone oils affected greatly the morphology and the content of vinyl polymers in the surface layer of the obtained particles.

In this paper, we will study the preparation and formation mechanism of the core–shell particles by staged polymerization of vinyl monomers in the presence of linear and crosslinked polysiloxane latices.

EXPERIMENTAL

Materials

Octamethyl cyclotetrasiloxane (Me–D4) and tetramethyl tetravinyl cyclotetrasiloxane (Vi–D4) were purchased from BengBu Organic Silicone Factory. Styrene (ST) and methyl methacrylate (MMA) were analytical reagents and purified before using. Glycidyl methacrylate (GMA) was synthesized according to the method described in Tong et al.⁹ Sodium dodecyl benzene sulfonate (Na–DBSA) was used as received.

Preparation of Seed Latex

Distilled water (500 mL), Na–DBSA (2 g) and 98% sulfuric acid (1 mL) were added into a three-necked flask equipped with a mechanic stirrer, a thermometer and a reflux condenser. When the temperature of the reaction solution rose to 80°C, the mixture of Me–D4 (75 g) and Vi–D4 (75 g) was added while strongly stirring. After the reaction was carried out for 6 h, the reaction mixture was neutralized with saturated Na₂CO₃ solution. The unreacted monomer

* To whom all correspondence should be addressed.

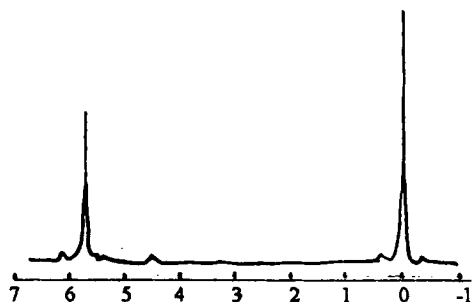


Figure 1 Proton NMR spectra of polysiloxane resulted from emulsion polymerization of Me-D4 and Vi-D4.

and polymer floated on the surface of the latex were removed, the linear polysiloxane latex (Y3) was obtained, the yield of polysiloxane was 30%. Y3 latex was kept at 80°C for 24 h and $K_2S_2O_8$ (0.10 g) was added every 6 h. Thus, the crosslinked silicone rubber latex (X3) was obtained. The solid content of the seed latex was measured,¹⁰ and it was 8 wt %.

Seeded Emulsion Polymerization

Continuous Addition of Monomers

Monomer (3 g) and $K_2S_2O_8$ (0.053 g) were added into silicone rubber or linear polysiloxane latex (50 mL) while stirring. The obtained mixture was dropwise added into a solution of Na-DBSA (0.080 g) and $NaHSO_3$ (0.080 g) in distilled water (50 mL) which was purged with high purity of nitrogen at 80°C. After the addition was completed for 4 h, the reaction continued for additional 4 h. The precipitates were obtained by adding anhydrous Na_2SO_4 while stirring and heating, then filtrated and washed

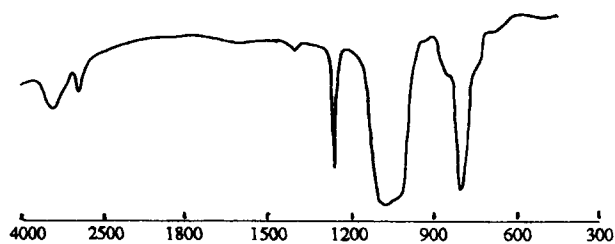


Figure 2 IR spectra of silicone rubber particles.

with warm distilled water. After drying in vacuum oven at 60°C, white powder particles were obtained.

Swelled-Continuous Addition of Monomers

Monomer (3 g) was added into silicone rubber or linear polysiloxane latex (50 mL) while stirring magnetically, then stood for 2 days. $K_2S_2O_8$ (0.053 g) was added into the latex. The next procedures of seeded emulsion polymerization were the same as those described above.

Compatibility of Vinyl Monomers with Silicone Rubber

A piece of silicone rubber with smooth surface was prepared by heating the mixture of linear polysiloxane (5 g) and benzyl peroxide (1 wt %) at 80°C for 12 h. The films of vinyl polymers were obtained by pouring the polymer solution on the surface of glass, then vaporizing the solvent. The contact angles of silicone rubber and vinyl polymers with water were measured on the T-Y-82 Contact Angle Apparatus. From the microscope, the shape of water droplet on the polymer surface could be observed. The interfacial tensions of them against water and the inter-

Table I The Receipt of Seeded Emulsion Polymerization

Sample ^a	Seed Latex ^b (mL)		Monomer (g)				Yield ^c (%)
	X3	Y3	ST	MMA	GMA	DVB	
X3-S(1)	50.0	—	3.00	—	—	—	76.0
X3-S(2)	50.0	—	3.00	—	—	—	77.3
Y3-S(2)	0	50.0	3.00	—	—	—	87.2
X3-M(1)	50.0	—	—	3.00	—	—	97.5
X3-M(2)	50.0	—	—	3.00	—	—	94.7
X3-G(2)	50.0	—	—	—	3.00	—	69.3
X3-MD(1)	50.0	—	—	—	2.80	0.20	83.4

Polymerization condition: temp.: 80°C; silicone rubber latex: 50 mL; distilled water: 50 mL; $K_2S_2O_8$: 0.053 g; $NaHSO_3$: 0.080 g; Na-DBSA: 0.080 g.

^a (1) and (2) mean continuous and swelled-continuous addition of the monomers, respectively.

^b The solid contents of the seed latices X3 and Y3 were 8.0 wt %.

^c Yield is the weight of the vinyl polymer obtained divided by the weight of the monomer added.

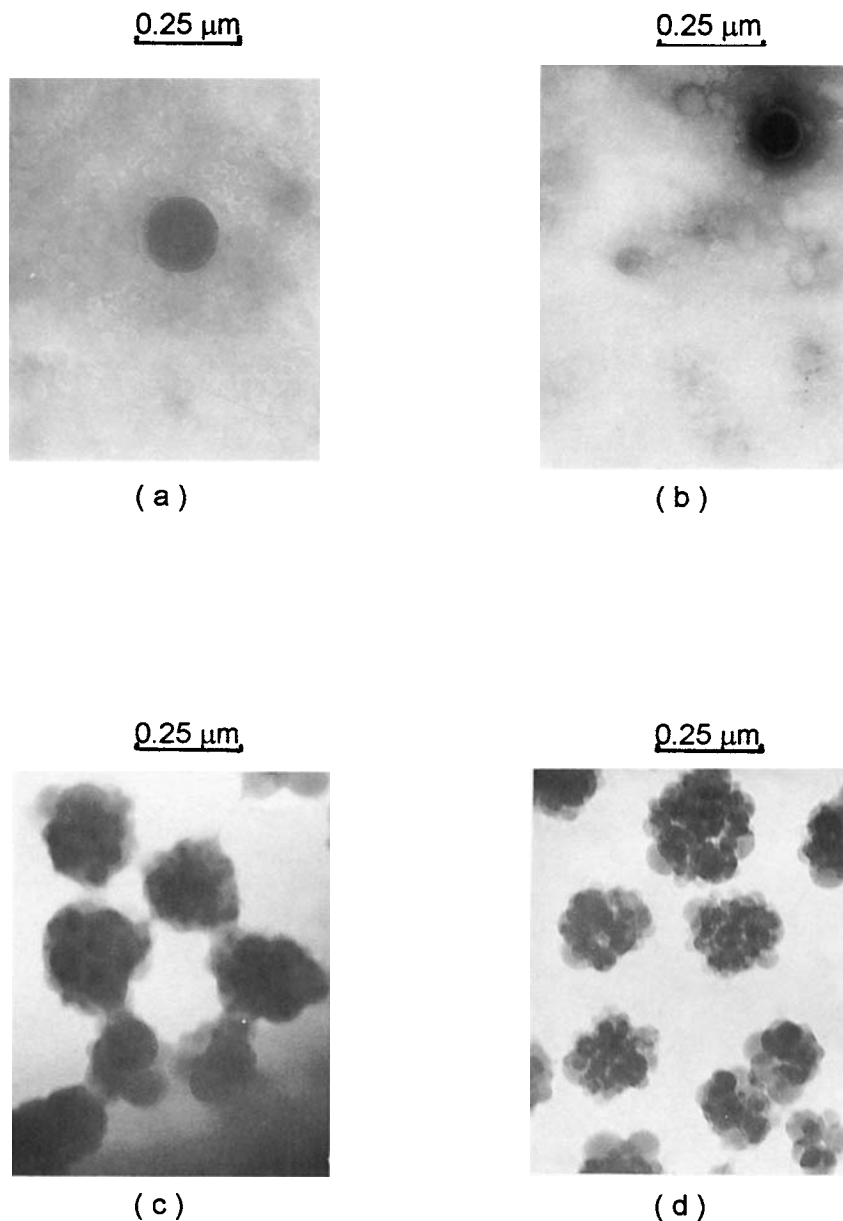


Figure 3 TEM photos of latex particles: (a) X3-S(1), (b) X3-S(2), (c) X3-M(1), (d) X3-M(2), (e) X3-G(2), (f) Y3-S(2), (g) X3-MD(1).

facial tensions between silicone rubber and vinyl polymers were calculated according to the methods described in He et al.⁸ and Wu.¹¹

Swelling Degree of Silicone Rubber in Monomers

Silicone rubber was immersed in the different monomers containing an inhibitor of *p*-hydroxyphenol at 30°C for 48 h. The swelling degrees of silicone rubber in various monomers were calculated.

Distribution of Monomers in the Silicone Rubber Latex

Monomer (1.2 g) was added into silicone rubber latex (20 mL) while stirring, then stood for 2 days. The serum and silicone rubber were separated using a ultracentrifugation instrument and the amount of monomers in water was measured using bromine titration.¹⁰ The concentrations of monomers in the seed particles and water were calculated, respectively.

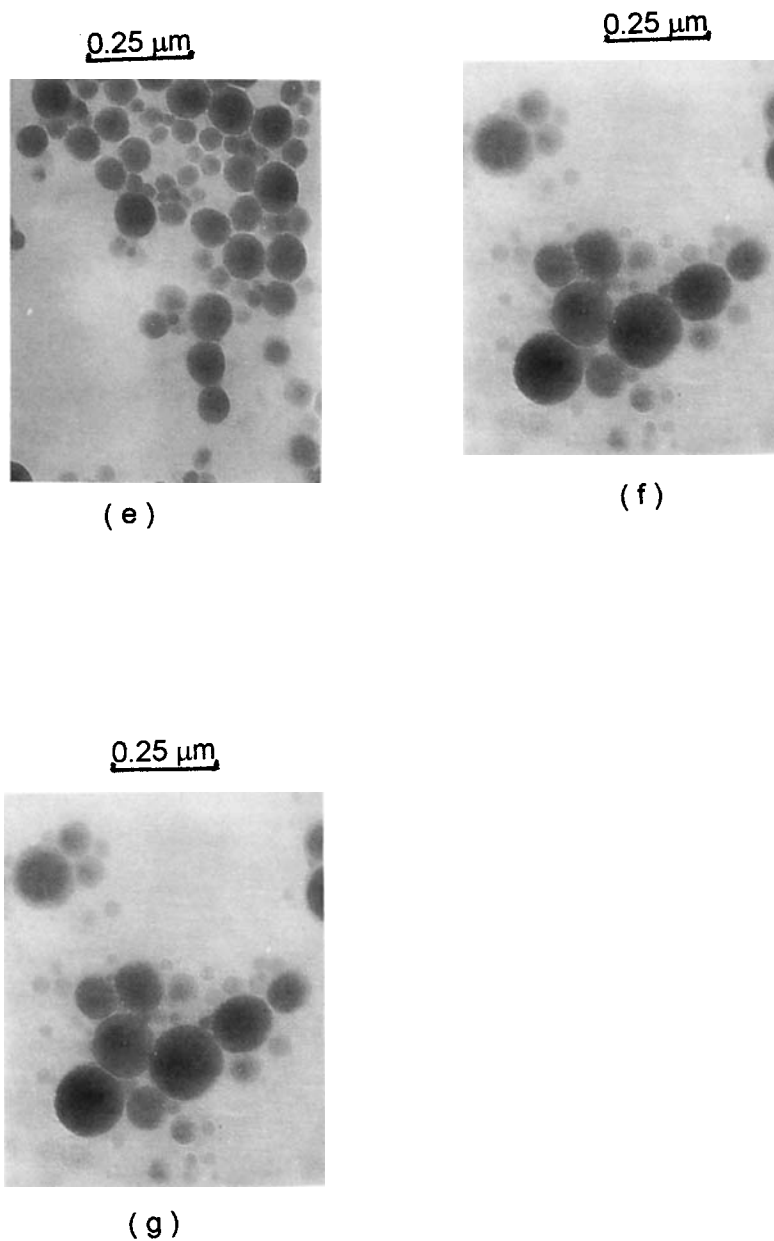


Figure 3 (Continued from the previous page)

Characterization of Composite Particles

The latex were diluted with distilled water and treated with a ultrasonic instrument. Two or three drops of the diluted latex were put onto copper grid and then the morphology of latex particles was observed using Hitachi H-800 Transparent Electron Microscopy (TEM).

RESULTS AND DISCUSSION

Synthesis of Seed Latices

The preparation of silicone rubber latex particles included two steps: (1) the preparation of linear poly-

siloxane latex by cationic ring-opening polymerization of Me-D4 and Vi-D4; (2) the crosslinking reaction of the vinyl groups in the polysiloxane latex particles using $K_2S_2O_8$ initiator at 80°C. The solid

Table II The Weight of the Absorbed Monomers per Weight of Silicone Rubber

Monomer	ST	MMA	GMA	DVB
W_a^a (g)	0.890	0.647	0.322	0.854

^a The weight of vinyl monomers absorbed by a gram silicone rubber.

content of the latex was 8.0 wt %. The yield of polysiloxane obtained in the latex was not high (30%) because a large amount of the latex particles became instable during polymerization, and it was observed that the mixture of the polymer partly produced and unpolymerized monomer floated on the surface when stirring stopped after polymerization. The proton NMR spectrum of polysiloxane before crosslinking was shown in Figure 1. Based on the integral values of the peaks at $\delta = 5.80$ ppm corresponding to vinyl group and at $\delta = 0.00$ ppm indicating methyl group, the mole percentage of Vi-D4 unit in the polysiloxane could be calculated and was 39 % (mol). The IR spectrum of silicone rubber particles was shown in Figure 2. The absence of the absorption peaks at $\nu = 1690$ cm^{-1} corresponding to carbon-carbon double bond indicates complete polymerization of the vinyl group of polysiloxane.

Formation Mechanism of Core-Shell Particles

In order to study the factors influencing the formation of core-shell particles, the seeded emulsion polymerization of various monomers were carried out with two addition modes of monomers. The receipt is listed in Table I. TEM photos of the particles resulted from silicone rubber latex were shown in Figure 3. Comparing the morphology of the particles prepared from the continuous addition of monomers [X3-S(1) and X3-M(1)] with that from the swelled-continuous addition of monomers [X3-S(2) and X3-M(2)] [See Fig. 3(a-d)], it was found that the addition mode of monomers did not effectively influence the morphology of the obtained composite particles. The facts that the formation of X3-S(1, 2) core-shell particles, and no appearance of core-shell structure for the others indicate that the physical properties of the monomers and their polymers are the determining factor for the formation of core-shell structure.

In the case of swelled-continuous monomer addition, monomers had enough time to diffuse into the seed particles, but the quantity of monomers in the seed particles depends upon the compatibility of monomers with silicone rubber and the crosslinking

Table III Partition of the Monomers between the Particles and the Water Phase

Monomer ^a	ST	MMA	GMA
The quantity of monomer in the water phase ^b (g)	0.16	0.67	1.16
The quantity of monomer in the particles ^b (g)	1.04	0.33	0.04

^a The weight of monomer is 1.20 g.

^b The volume of the latex is 20.00 mL.

degree of silicone rubber particles. Thus the weights of the absorbed monomers per weight of silicone rubber (W_a) were measured by swelling silicone rubber in the monomers. The results were listed in Table II. From the data listed in Table I and II, it was found that ST was completely absorbed by the particles after swelling. Another important factor influencing the formation core-shell structure is the partition of vinyl monomer between the latex particles and the water phase should be considered. The data are listed in Table III. From the data, the content of the monomers in the seed particles decreased as the following order:

$$\text{ST} > \text{MMA} > \text{GMA}$$

From these facts, it can be deduced that styrene was initiated by the radicals produced from $\text{K}_2\text{S}_2\text{O}_8$ and polymerized mostly in both of linear polysiloxane and silicone rubber particles in the case of swelled-continuous addition.

For seeded emulsion polymerization in the presence of silicone rubber latex, considering higher $\gamma_{s\text{-water}}$ of silicone rubber than that of polystyrene and the reduction of compatibility between silicone rubber and polystyrene as the polymerization of styrene, it was reasonable that the growing chain of polystyrene would diffuse to the surface of the particles, thus the shell rich in polystyrene was formed. However, for seeded emulsion polymerization in the presence of linear polysiloxane latex, styrene could homopolymerize and copolymerize with the vinyl group of polysiloxane, crosslinking reaction occurred at the same time. The compatibility of silicone rubber with polystyrene in-

Table IV The Surface Tension and Interfacial Tension

Polymer	Silicone Rubber	PST	PMMA	PGMA
γ_{s-g} (dyn/cm)	9.17	16.45	27.35	36.37
$\gamma_{s\text{-water}}$ (dyn/cm)	29.22	19.61	10.59	6.01
γ_{s-s} (dyn/cm) ^a	0	2.89	10.17	—

^a γ_{s-s} is calculated according to the method described in Wu.⁹

creased due to the formation of polysiloxane grafted with polystyrene. Therefore, the diffusion of monomers to the surface did not happen. The obtained particles homogeneously consisted of poly(styrene-co-polysiloxane) and no core-shell structure of Y3-S(2) particles was not observed [see Fig. 3(e)].

Based on higher solubility of MMA and GMA in water (see Table III), the polymerization of monomers in water should be considered. The growing chains produced in water might precipitate onto the seed particles and some of them continued to propagate to form the shell layer or aggregate each other to produce new vinyl polymer particles. It was thought that the relative degree of two processes was controlled by the compatibility of silicone rubber particles with vinyl polymers. The surface tensions of polymers (γ_{s-g}), interfacial tensions between polymers and water ($\gamma_{s-water}$) and interfacial tensions between vinyl polymers and silicone rubber (γ_{s-s}) are listed in Table IV.

Lower interfacial tension between PST and silicone rubber than that of PMMA or PGMA with rubber (see Table IV) indicated that propagating chain of PST might easily precipitate onto the seed particles, then covered the particle. For X3-M(1, 2) particles, the propagating polymer chain of PMMA was difficult to precipitate to the particles surface because of the higher interfacial tension between PMMA and the particles, thus PMMA propagating chains made silicone rubber particles adhere each other [see Fig. 3(c,d)] TEM photo of X3-G(2) particles prepared from the polymerization of GMA in the silicone rubber latex [see Fig. 3(f)] shows smaller particles of PGMA. The propagating chains produced in water would aggregate each other to form new particles due to high interfacial tension between PGMA and silicone rubber.

In order to confirm the presumption, the mixture of divinylbenzene (DVB) and MMA was used in the seeded polymerization for reducing the interfacial tension between silicone rubber and vinyl polymer. The TEM photo of the particles obtained [see Fig. 3(g)] shows the core-shell structure. The fact demonstrates that the addition of DVB helped precipitation of the propagating chain onto the seed particles probably because the polymerization of DVB in the surface layer of the rubber particles improved the interfacial tension.

CONCLUSION

The core-shell particles of silicone rubber/PST and silicone rubber/P(MMA-DVB) were successfully prepared by the seeded emulsion polymerization in the presence of silicone rubber latex. Monomer addition mode did not influence the morphology of the composite particles. The compatibility of vinyl monomers and polymers with silicone rubber and the reactivity of the latex particles and vinyl monomers affected the formation of core-shell particles. For styrene monomer, the core-shell particles were formed from the crosslinked polysiloxane latex. However, the contrary result was obtained when the seeded polymerization performed in the presence of linear polysiloxane latex. Lower interfacial tension between silicone rubber and vinyl polymers is favorable to form the core-shell particles, especially for the case which the initiation and propagation of vinyl monomers occurred mainly in the water phase.

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Received January 19, 1996

Accepted February 8, 1996