

STUDIES ON POLYSILOXANE-POLYSTYRENE COMPOSITE LATEXES*

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ABSTRACT

Polysiloxane-polystyrene composite latexes were prepared by two-stage emulsion polymerization. Polymerization of styrene in swollen polysiloxane latex particles were studied. Formation of simple polystyrene particle in the 2nd-stage polymerization depends on the particle size of the 1st-stage latex and the polymerization temperature. Polystyrene domains in the vulcanizates reinforce the silicone rubbers effectively.

INTRODUCTION

It is of great interest to carry over the properties of polysiloxanes, such as surface releasing property, low dependency of mechanical properties on temperature and excellent dielectrical properties, to organic polymers, or, on the other hand, to improve mechanical properties of polysiloxanes by incorporation with organic polymers. A number of techniques have been developed for the preparation of polysiloxanes-organic polymer systems. Vinyl monomers were grafted onto polysiloxanes by radiation polymerization^[1]. Acicular thermoplastic particles were formed in α, ω -dihydroxy polydimethylsiloxanes by precipitating polymerization which reinforced the vulcanizates tremendously^[2]. Interpenetrating networks were prepared by simultaneous cross-linking^[3,4]. Through reaction of functionalized prepolymers, polysiloxane blocks were introduced into epoxy resins^[5], polyimides^[6], polyesters^[7], polyurethanes and polyamides^[8].

For the morphology control of multicomponent polymer materials the emulsion polymerization provides an interesting technique^[9]. In this article emulsion polymerization of styrene in the presence of a polysiloxane is reported, and the resulted polystyrene - polysiloxane composite latices are described.

EXPERIMENTAL

1. Materials

The monomer for the preparation of α, ω -dihydroxyl polydimethyl-

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siloxanes was a mixed cyclopolydimethylsiloxane designated as D_n supplied by Jiling Chemical Industry Company. Dodecylbenzenesulfonic acid (DBSA) was an industrial chemical from Nanking Alkylbenzene Products Factory. Fumed silica # 2 was from Senyang Chemical Factory. Triethanolamine, styrene, azo-bis-isobutyronitrile (AIBN), ethyl orthosilicate, dibutyl tin dilaurate and sodium dodecylsulfate (SDS) are chemical reagents.

2. Preparation of polysiloxane latexes

Emulsion polymerization of D_n was carried out according to the reference [10]. The composition (D_n 25parts, DBSA 0.2 part, SDS 0.285 part and distilled water 74.5 parts) was emulsified through a homogenizer at pressure 30 to 40 MPa. The molecular weight of α , ω -dihydroxy polydimethylsiloxanes was regulated by controlling the polymerization temperature. After completion of the polymerization, the catalyst was neutralized with triethanolamine. The properties of the latexes are given in Table 1.

Table 1 Properties of the 1st-stage latex

Code	A	B	C	D
Conditions of polymerization ($^{\circ}\text{C}/\text{d}$)	80/1 20/30	80/1 20/10	80/1 20/2	80/1 20/30 35/1
Molecular weight of polymer(10^3)	196	239	197	158
Average diameter of latex particles (nm)	295	266	229	314
Polysiloxane content (%)	25	25	25	25
Surface tension (mN/m)	40.2	43.5	47.3	38.9

3. Preparation of composite latexes

In a reactor charged with the 1st-stage polysiloxane latex, a solution of AIBN in styrene was introduced. The reactor was purged with nitrogen, the mixture was stirred at room temperature for 2 h, let the monomer and initiator diffuse into the latex particles. After that the reactor was heated in a thermostat. The compositions of the polymerization and the resulted composite latexes are listed in Table 2.

4. Characterization

The average particle size of latexes was determined using a Coulter

Nanosizer. The molecular weight of the polymerizates was characterized by GPC, using a Sorbax PSM Bimodel SEC column and a RI detector, and toluene as solvent.

The morphology of the composite latex was studied using a Hitachi S-530 SEM. The coagulation of polystyrene particles in polysiloxane-polystyrene two phase materials was studied using a Torsion Braid Analyzer XHS-1.

5. Mechanical properties of the vulcanizates

The latexes were coagulated with isopropanol. The polymers were washed with ethanol repeatedly to remove the emulsifier, and dried in vacuo at 50 °C. To prepare vulcanizates the polymers were mixed with ethyl orthosilicate, dibutyl tin dilaurate and optionally fumed silica. The compounds were molded at room temperature for 18 h and 40–50 °C for 6 h under 5 MPa pressure. The tensile strength, elongation at break and permanent set were measured according to ASTM D412.

RESULTS AND DISCUSSION

1. Preparation of composite latexes

Two stage emulsion polymerization was carried out to prepare composite latexes. First a latex of α,ω -dihydroxy polydimethylsiloxane was prepared through cationic polymerization of cyclopolydimethylsiloxanes^[10], then styrene was polymerized in the presence of the 1st-stage latex using a free radical initiator. Preliminary experiments showed that the formation of composite latex was not favorable when a water soluble initiator, such as potassium persulfate, was used, even in the cases where the monomer was swollen into the polysiloxane particle first and the coverage of the latex particles by emulsifier was not saturated.

Better results were obtained when an oil-soluble initiator was used. Thus, AIBN was dissolved into

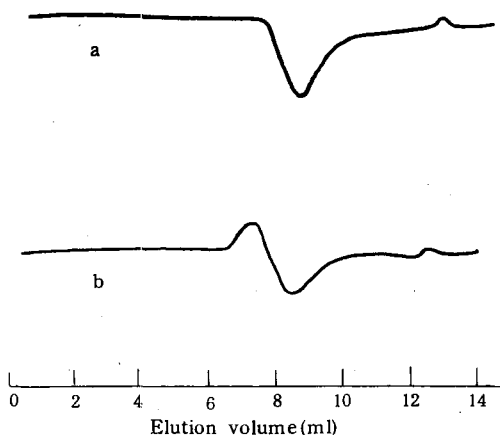


Fig. 1 GPC diagram of (a) polysiloxane A and (b) polymer 7-3-1.

styrene, the solution was added to the 1st-stage latex, and the mixture was stirred at room temperature until the organic layer was absorbed completely. The polysiloxane latexes swollen with styrene up to 50 wt% was stable, no layer formed on standing for long time. The polymerization was then effected by heating the swollen latexes.

From the data of average particle size and composition of the composite latexes, particle population per milliliter water phase can be roughly estimated. The difference in particle population of the 1st-stage latex and the 2nd-stage latex indicates the formation of new simple polystyrene particle in the 2nd-stage polymerization, which depends on experiment conditions as shown in Table 2. The particle size of the 1st-stage latex, the temperature of the polymerization and the monomer proportion are the main factors affecting the formation of new particle.

Table 2 Preparation of composite latexes

Code	7-3-1	7-6-1	7-6-2	4-3-4	7-3-1	7-3-2
1st-stage polysiloxane latex	A	B	C	A	D	A
Particle size (nm)	295	266	229	295	314	295
Particle population (10^{13} /ml water phase)	2.5	3.5	5.5	2.5	2.1	2.5
2nd-stage polymerization						
Composition styrene	50	50	50	50	50	25
polysiloxane	100	100	100	100	100	100
water	300	300	300	300	300	300
AIBN	0.5	0.5	0.5	0.5	0.5	0.5
Temperature (°C)	50	50	50	60	50	50
Time (h)	72	72	72	36	72	72
Conversion (%)	91	100	100	97	97	82
Composite latex						
Particle size (nm)	326	260	214	303	332	310
Particle population (10^{13} /ml water phase)	2.8	5.5	9.7	3.5	2.6	2.7
Simple particle number (10^{13} /ml water phase)	0.3	2.0	4.2	1.0	0.5	0.2

Since the polymerization was initiated in latex particles, the formation of simple polystyrene particle might be closely related to the desorption of growing chain from the latex particles. This process was intensified as the temperature enhanced and the boundary area enlarged. Therefore, more new particles would be formed in the 2nd-stage polymerization when the 1st-stage latex had a small average particle size and the temperature of the 2nd-

stage polymerization was high.

Since the polysiloxane particles of the 1st-stage latex were not fully covered by emulsifier as shown by surface tension of the latexes (39-50 mN/m, see Table 1), no free emulsifier micelles would be present in the water phase. The simple polystyrene particles formed in the 2nd-stage polymerization must have very strong affinity to emulsifier, so that they were able to grasp emulsifier molecules from the surface of polysiloxane particles to make themselves stable.

The proportion of styrene was limited by the stability of the swollen latex. Creaming was observed at a ratio of polysiloxane to styrene 1 : 1 by wt. Polysiloxane-polystyrene composite latexes having a polymer ratio 100:50 have been prepared without much difficulty.

Large 1st-stage latex particle and low temperature of the 2nd-stage polymerization are preferable for depressing the formation of simple particle. When the polysiloxane of the 1st-stage latex has a molecular weight 2×10^5 , and the latex has an average diameter 300nm, good composite latex can be obtained at the polymerization temperature 50°C.

2. Characterization of the composite latex 7-3-1.

Polymerization in a styrene-swollen polysiloxane latex particle initiated by AIBN can be considered as a precipitating polymerization in a microscopic reactor. It is supposed that polysiloxane makes the shell of the composite latex particles, as it is the major component (composition ratio 100:50). This supposition is supported by the fact that polysiloxane forms continuous phase when the water phase is evaporated or the latex is coagulated by adding isopropanol.

Polystyrene has a quite high molecular weight as shown in the GPC diagram (Fig. 1), which is characteristic of heterogeneous polymerization. Polysiloxane is shown by the negative peak in the diagram, corresponding to a molecular weight 2×10^5 . No graft can be recognized in the GPC diagram.

The dispersion of polystyrene particles in polysiloxane is stable at room temperature. However, as the temperature increases to the T_g of polystyrene, coagulation of particles will take place. The particle coagulation was demonstrated by TBA. Thus, glass fiber braid was soaked in the latex and dried at room temperature, relative rigidity vs. temperature diagram (Fig. 2) was recorded on a Torsion Braid Analyzer. The step-up of the relative rigidity of the braid after a temperature cycling indicates the coagulation of polystyrene particles.

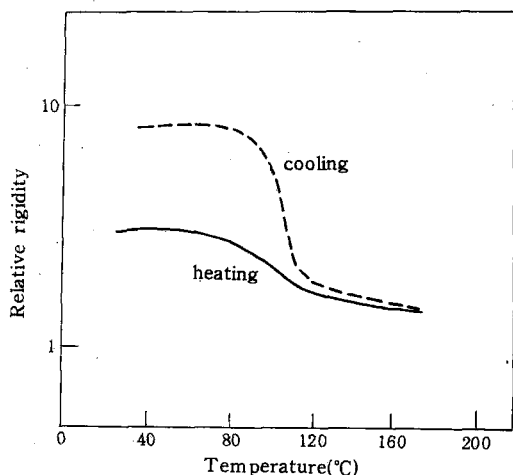


Fig. 2 The change of relative rigidity of the polymer 7-3-1 with temperature

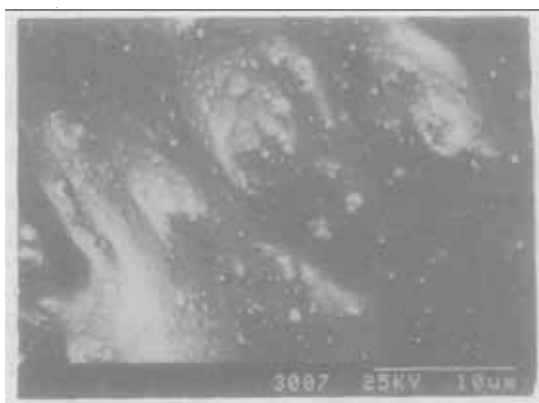


Fig. 3 SEM micrograph of the polymer 7-3-1

3. Vulcanizates from the composite latex 7-3-1

The latex was coagulated by isopropanol. The emulsifier was removed by washing with ethanol, and the polymer were dried in vacuo. Polystyrene-reinforced silicone vulcanizates were prepared using ethyl orthosilicate-dibutyl tin dilaurate curing system. The SEM micrograph (Fig. 3) of the fracture surface of the vulcanizates shows that polystyrene domains are evenly dispersed in polysiloxane matrix. For comparison, α, ω -dihydroxy polydimethylsiloxane from the 1st-stage latex was vulcanized in the same way except that fumed silica was used as reinforcement.

Mechanical properties of RTV silicone rubbers are given in Table 3. It is seen that the vulcanizates are reinforced by polystyrene greatly. Polystyrene particles are as effective as fumed silica, a most commonly used reinforcement in silicone rubber technology.

Table 3 Mechanical properties of RTV silicone rubbers

No. of experiment	1	2	3
Composition (pbw)			
Polysiloxane	65.8	81.1	90.9
Polystyrene	34.2	18.9	—
Fumed silica	—	—	9.1
Ethyl orthosilicate	2.6	3.2	3.6
DBTDL ^{a)}	0.6	0.8	0.9
Mechanical properties			
Tensile strength (MPa)	2.28	1.54	1.44
Elongation to break (%)	950	850	720
Permanent set (%)	14	10	10

a) Dibutyl tin dilaurate

Keywords:

Polysiloxane; Composite latex; Polystyrene; Emulsion polymerization

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