

Preparation and Properties of Polydimethylsiloxane/Polyacrylate Composite Latex Initiated by ^{60}Co γ -Ray Irradiation

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ABSTRACT: In this study, polydimethylsiloxane (PDMS)/polyacrylate composite polymer latex was synthesized via polymerization of the acrylate monomer in the presence of vinyl-containing PDMS seeded latex. The polymerization was initiated by ^{60}Co γ -ray irradiation. The morphology of the PDMS/polyacrylate composite polymer latex was a core-shell structure with PDMS as the core and polyacrylate as the shell. There was an interpenetration layer between the PDMS core and the polyacrylate shell. The composition of the vinyl-containing PDMS and the PDMS/polyacrylate composite latex were investigated with NMR and Fourier

transform infrared spectroscopy, respectively. The effect of irradiation dose on the seeded emulsion polymerization conversion is discussed. Finally, the mechanical properties of latex film, such as water-absorption ratio, tensile strength, pendulum hardness, and heat-decomposed temperature, were tested. The results showed that the mechanical properties of the PDMS/polyacrylate film were remarkably improved when compared to the polyacrylate film. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2732–2736, 2003

Key words: emulsion polymerization; irradiation; films

INTRODUCTION

Polydimethylsiloxane (PDMS) has many well-known, peculiar characteristics such as very high thermal and chemical resistances, a low transition temperature, a low surface tension, a high hydrophobicity, and an excellent stability against different types of radiation.¹ At the same time, it is well known that polyacrylate materials have many merits including good oxidation-resistance and weather-resistance properties.² However, its water-resistance and cold-resistance properties are very poor due to its hydrophilicity. So in recent years, interest has increased in the combination of PDMS with polyacrylate materials to obtain the preferential properties of the two materials and to compensate for the nonadapted features of each component. However, as is well known, PDMS/polyacrylate composite materials have poor compatibility and give rise to phase separation, the extent of which depends on various parameters, including the concentration of each component, the interfacial tension between the phases, the molecular weights,³ and more generally, the thermal treatment of the samples.⁴

Chen and White⁵ pointed out that adding compatibilizing agents into the composite polymer would mitigate the phase separation. The compatibilizing agents

would lower the interfacial tension of the composite polymer and prevent phase growth or coalescence. They also pointed out that the ability of the compatibilizing agents to locate themselves at the polymer-polymer interface seems to be the important factors in the determination of how well they perform.

It was thought that the emulsion copolymerization between vinyl-containing PDMS and the acrylate monomer would improve the compatibility of the PDMS/polyacrylate polymer blends. Efforts have been made to study the reactivity ratios of vinyl monomer with the vinyl groups of PDMS,⁶ the stability in blends of PDMS and vinyl monomer copolymerization emulsion, and the effect of the pH of the PDMS/polyacrylate copolymer on the stability of the emulsion blends.⁷

Generally, irradiation emulsion polymerization has some peculiar advantages when compared to other polymerization methods, including non-temperature-dependent initiation and an extremely large G value. In addition, the irradiation emulsion polymerization process can easily lead to a higher molecular weight. However, until now, there have been no known studies on the preparation of PDMS/polyacrylate composite latex using ^{60}Co γ -ray initiation.

In this work, a PDMS/polyacrylate core-shell composite latex was prepared by seeded emulsion polymerization, which was initiated by ^{60}Co γ -rays irradiation. First, we prepared linear vinyl-containing PDMS seeded latex according to the cationic ring-

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opening polymerization of octamethyl cyclotetrasiloxane (Me-D4) with sulphuric acid as the catalyst and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane as the ends sealant. Then, acrylate monomer was added into the PDMS seeded latex to start the seeded emulsion polymerization for the preparation of the PDMS/polyacrylate composite latex.

EXPERIMENTAL

Materials

Me-D4 and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane were purchased from BengPu Organic Silicone Factory, BengPu, China. Methyl methacrylate (MMA), butyl acrylate (BA), and 98% sulphuric acid were obtained from the Shanghai Chemical Reagent Co., Ltd., Shanghai, China, and were purified before used. Dodecyl benzene sulfonic acid sodium salt (Na-DBSA) and octylphenoxypoly(ethoxyethanol) (OP-10) were used as received.

Preparation of the vinyl-containing PDMS latex

Distilled water (70.0 g), Na-DBSA (0.8 g), OP-10 (0.5 g), Me-D4 (30.0 g), and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane were added into a three-necked flask equipped with a mechanical stirrer. The flask was immersed in a water bath. When the temperature of the reaction mixture had risen to 80°C, 98% sulphuric acid (0.5 mL) was added into the flask with strongly stirring. After the reaction had been carried out for 12 h, the seeded emulsion polymerization was quenched by neutralization through the addition of Na₂CO₃ solution. The unreacted monomer and oligomer floating on the surface of the latex were removed. Finally, vinyl-containing PDMS latex was obtained.

Seeded emulsion polymerization initiated by ⁶⁰Co γ -ray irradiation

An appropriate amount of acrylate monomer (BA or MMA) was added into the vinyl-containing PDMS seeded latex (15.0 g) while it was stirred magnetically for 0.5 h. Then, the mixture stood for 48 h at room temperature. Polymerization was carried out in a sealed glass bottle after the emulsion was bubbled with nitrogen. The bottle was subjected to γ -ray irradiation with a ⁶⁰Co source. After irradiation, the polymerization product was removed from the glass bottle at room temperature.

Characterization of the composite latex morphology

The composite latex was diluted by distilled water and examined with an ultrasonic instrument; then, some of

the particles were placed on a copper grid, and the morphology of the latex particles was examined with a Hitachi H-800 transmission electron microscope (Japan).

¹H-NMR analyses

¹H-NMR spectra were recorded on a Bruker 400-MHz instrument. CDCl₃ was used as a solvent.

Fourier transform infrared spectroscopy (FTIR)

FTIR was registered with a VECTOR22 FTIR spectrometer (Switzerland).

Water-absorption 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 properties

Pendulum hardness was measured by a QBY-pendulum hardness apparatus made by TianJin Instrument Co., Ltd., TianJin, China.

Tensile strength properties

Tensile strength was measured according to ASTM D-638-52T (test speed = 100 mm/min).

Heat-decompose temperature properties

The heat-decompose temperature was measured with WRTA-3P minimum heat balance (heat speed = 20 C/min) (China).

RESULTS AND DISCUSSION

Characterization of vinyl-containing PDMS

AlCl₃ aqueous solution was used to agglomerate the vinyl-containing PDMS latex, and the PDMS was separated from water by ether extraction. After vacuum desiccation, the pure vinyl-containing PDMS was obtained.

The H-NMR spectrum of the pure vinyl-containing PDMS is shown in Figure 1. From the integral value of the peak at $\zeta = 5.80$ – 6.20 , corresponding to vinyl groups, and at $\zeta = 0.00$, corresponding to methyl groups, we could conclude that the vinyl-containing

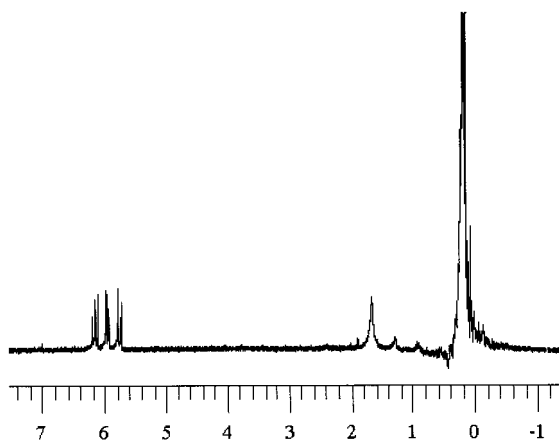


Figure 1 $^1\text{H-NMR}$ spectrum of the pure vinyl-containing PDMS.

PDMS was prepared. Additionally, the PDMS number-average molecular weight could be calculated and was about to 5700 according to the integral areas of vinyl groups and methyl groups.

Characterization of the composition of the composite latexes

The composite latex was precipitated with ethanol, and the agglomerator was extracted by toluene for 12 h to achieve a pure PDMS/polyacrylate copolymer whose composition could be confirmed with FTIR.

From the IR spectrum [Fig. 2(a)], we observed that the absorption peak at 1734.5 cm^{-1} corresponding to a carbonyl group was very strong, which indicated that the insoluble polymer after extraction must have been comprised of a polyacrylate component. Additionally, the siloxane's symmetric stretching vibration absorption peak at 1261.6 cm^{-1} and silicone's other characteristic absorption peak at 801.9 cm^{-1} were also

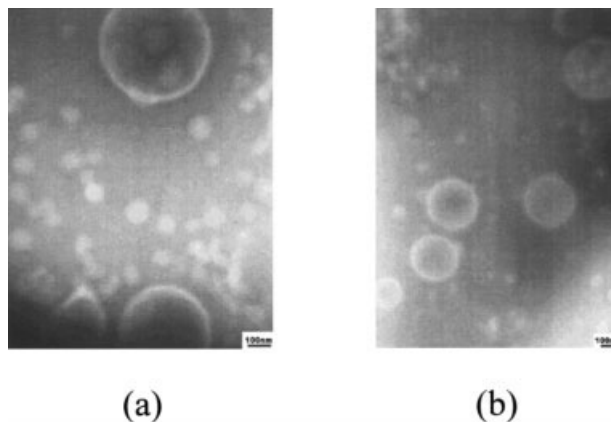


Figure 3 TEM photo of the PDMS/polyacrylate composite latex particles.

present in the IR spectrum because the extraction operation excluded the existence of pure polyacrylate. Thus, from Figure 2, we concluded that in the seeded emulsion polymerization initiated by ^{60}Co γ -ray irradiation, the reaction in essence was the radical copolymerization of carbon-carbon double bonds between vinyl-containing PDMS and acrylate monomer. In addition, the homopolymerization of BA and MMA also existed in the reaction system.

Morphology of the composite latex particles

From the transmission electron microscopy (TEM) photos of the PDMS/polyacrylate latex particles (Fig. 3), we found that the large particle had a core-shell structure with PDMS as the core and polyacrylate as the shell. Because of the higher hydrophilicity of the acrylate monomer and the poor compatibility between polyacrylate and PDMS, the acrylate monomer, which swelled in the PDMS core, was prone to move to the

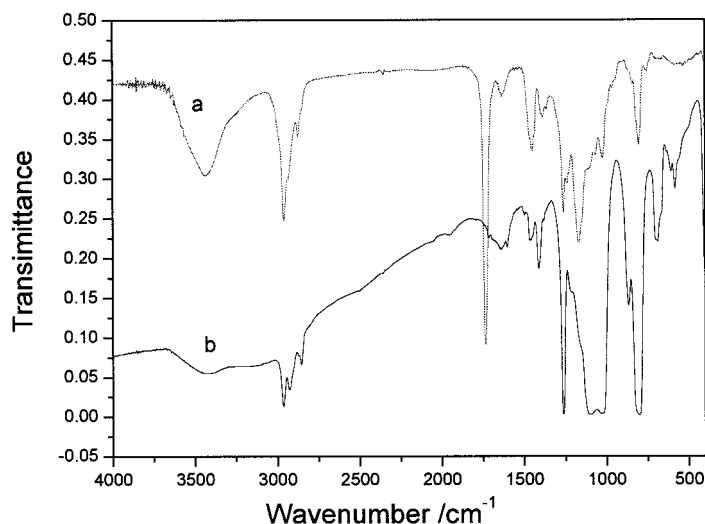


Figure 2 IR spectrum of the product.

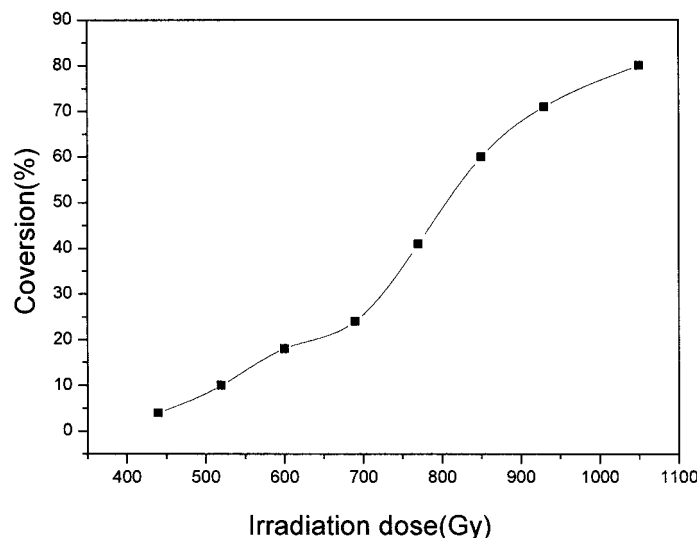


Figure 4 Effect of irradiation dose on the conversion (dose rate = 29 Gy/min).

PDMS surface. When the acrylate monomer polymerized in the presence of vinyl-containing PDMS, the copolymerization of the acrylate monomer with the vinyl groups of PDMS produced an interpenetration layer containing PDMS/polyacrylate copolymer and the physical interpenetration of the polymer chains. The behavior of the interpenetration layer was the same as the compatibilizing agent, which had the ability to decrease the interfacial tension and improve the miscibility of the PDMS/polyacrylate. Due to the improvement in the compatibility, the propagating polymer chains could be absorbed in the surface of the PDMS particles. There were the reasons for the formation of the core-shell structure in the PDMS/BA/MMA particles. Additionally, as shown in the TEM photos, there were some pure polyacrylate particles, but their size was much smaller than that of the PDMS/BA/MMA core-shell particles.

Effect of irradiation dose on the polymerization conversion

Figure 4 shows the effect of irradiation dose on the polymer conversion. The irradiation dose dependence of the conversion was represented by S-shaped

curves. When the seeded polymerization started, the reaction speed (R_p) reached a constant value in a very early stage and then remained invariable until the conversion arrived at about 20%. It was unlike the normal emulsion polymerization conditions. The reasons was that the emulsion nucleation process was not clear in the early stages, and so the polymerization was carried out mainly in the PDMS seed, which resulted in the R_p remaining invariable. Then, when the conversion was up to 25%, with increasing irradiation dose, the R_p increased abruptly, which resulted from the increasing amount of emulsion nucleation.

Studies of the mechanical properties of the latex films

The composite latex was cast onto the smooth surface of glass. After the water was evaporated completely at room temperature, the obtained films were dried in a vacuum (Table I). With the other component ratios and reaction conditions kept invariable and the ratios of the PDMS and acrylate monomer varying, the water-absorption rate decreased with increasing PDMS content, which resulted from the excellent water-resistance properties of PDMS. When PDMS content reach

TABLE I
Mechanical Properties of the Composite Latex Film

PDMS content (%)	Water absorption (%)	Tensile strength (Mpa)	Decomposition temperature (°C)	Pendulum hardness (S)
0	18.4	15.14	284.3	97
5	11.2	13.86	353.2	117
10	9.3	12.90	364.6	130
15	7.3	11.51	373.6	146
20	5.0	10.85	389.2	153
30	2.7	9.35	394.2	170

to 30 wt %, the surface of the latex films had some silicone oil; this was mainly because the PDMS had a low surface tension. Thus, the excessive PDMS molecular chain was prone to transfer to the surface of the latex films. The tensile strength and the pendulum hardness of the latex film decreased gradually with increasing PDMS proportion, because molecular chain of PDMS was very pliant. Therefore, the tensile strength and the pendulum hardness decreased with increasing PDMS content. The heat-decomposed temperature improved remarkably with increasing PDMS content, resulting from the higher heat-resistance properties of PDMS.

CONCLUSIONS

PDMS/polyacrylate core-shell particles were successfully prepared by the irradiation seeded emulsion polymerization of acrylate monomer in the presence of vinyl-containing PDMS seeded latex. The copolymer-

ization between the PDMS and the acrylate monomer produced an interpenetration layer, which was the major factor for the formation of the core-shell structure. The polymerization conversion against irradiation dose curves were S-shaped, but the R_p in the early stage was abnormal when compared to common emulsion polymerization, mainly due to the detention of the formation of emulsion nucleation. Additionally, the mechanical properties of the latex film improved rapidly with increasing PDMS ratios.

References

1. Zogoui, C.; Abadie, M. J. M.; Eur Polym J 2000, 36, 2115.
2. Naguchi, T.; Katoh, T.; Zhang, W.; Takesh, K. Presented at the International Conference on Synthesis and Properties of Polymer Emulsion, Kobe, Japan, Oct, 1993; p9.
3. Class, J. B.; Chu, S. G.; J Appl Polym Sci. 1985, 30, 805.
4. O'Connor, K. M.; Tsaur, S. L.; J Appl Polym Sci 1987, 33, 2007.
5. Chen, C. C.; White, J. L.; Polym Eng Sci 1993, 33, 923.
6. He, W. D.; Cao, C. T.; Polym Inter. 1996, 39, 31.
7. Richard, J.; Mignaud, C. Polymer, 1993, 34, 4287.